

Fullerenes

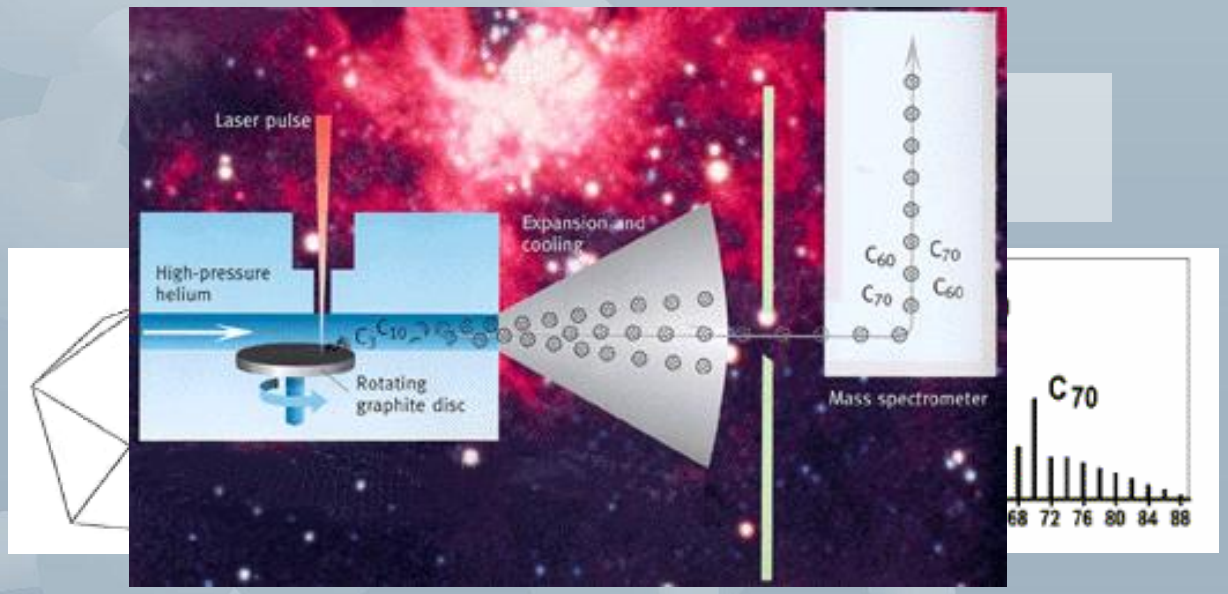
M. Riccò



Fullerenes discovery

HAROLD KROTO, ROBERT CURL E RICHARD SMALLEY (1985)

They studied the mass spectra of carbon vapors obtained from graphite crystals using high-energy lasers (Nobel Prize in Chemistry, 1996)





Fullerenes discovery

C_{60}: Buckminsterfullerene

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

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During experiments aimed at understanding the mechanisms by which long-chain carbon molecules are formed in interstellar space and circumstellar shells[1], graphite has been vaporized by laser irradiation, producing a remarkably stable cluster consisting of 60 carbon atoms. Concerning the question of what kind of 60-carbon 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 C_{60} 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.



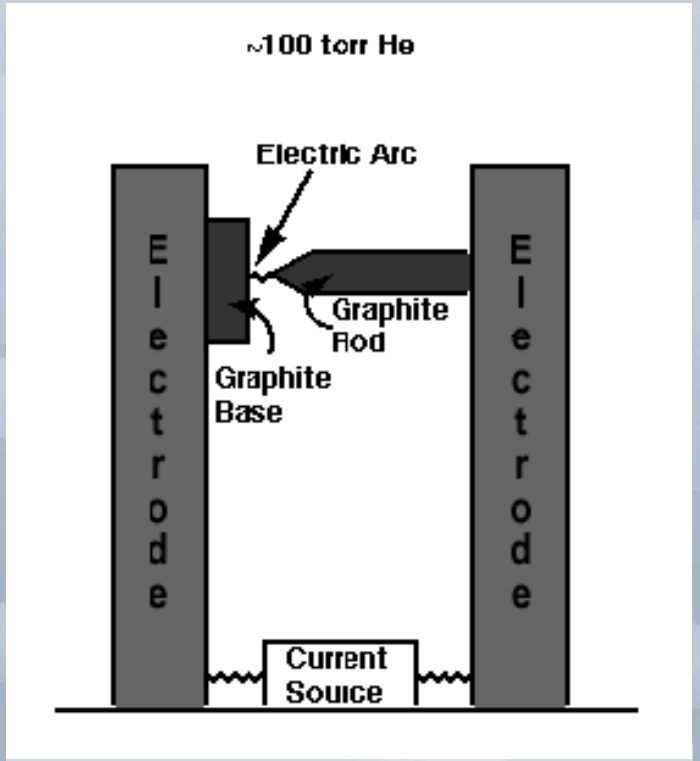
Fig. 1 A football (in the United States, a soccerball) on Texas grass. The C_{60} molecule featured in this letter is suggested to have the truncated icosahedral structure formed by replacing each vertex on the seams of such a ball by a carbon atom.

graphite fused six-membered ring structure. We believe that the distribution in Fig. 3*c* 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

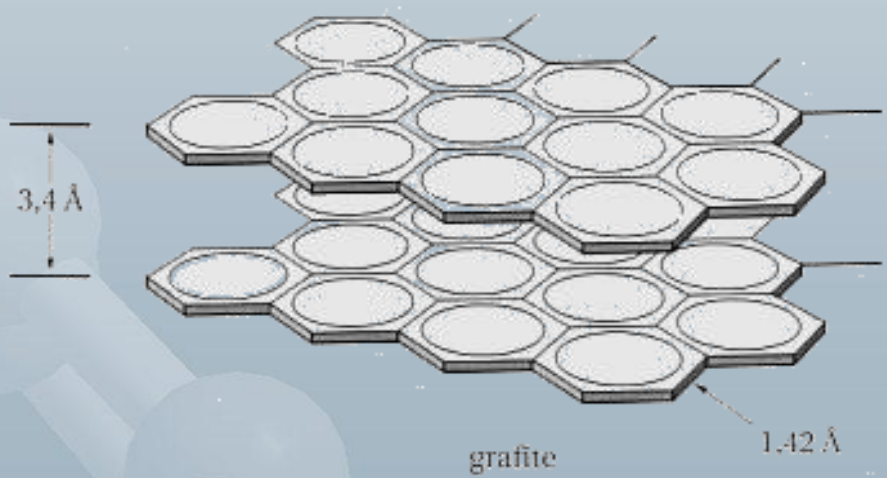


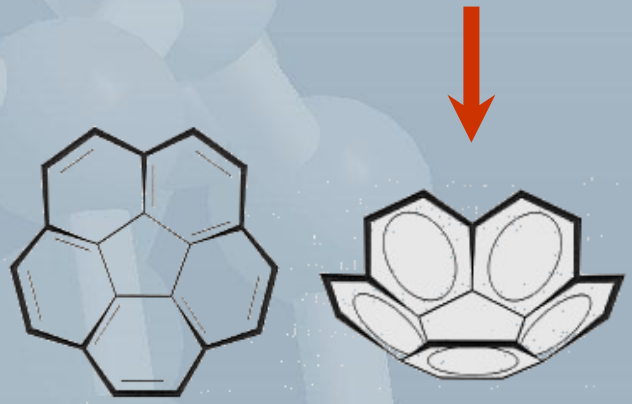
Fullerenes discovery



Kratschmer and Huffman's machine (1990) for large-scale production of fullerenes

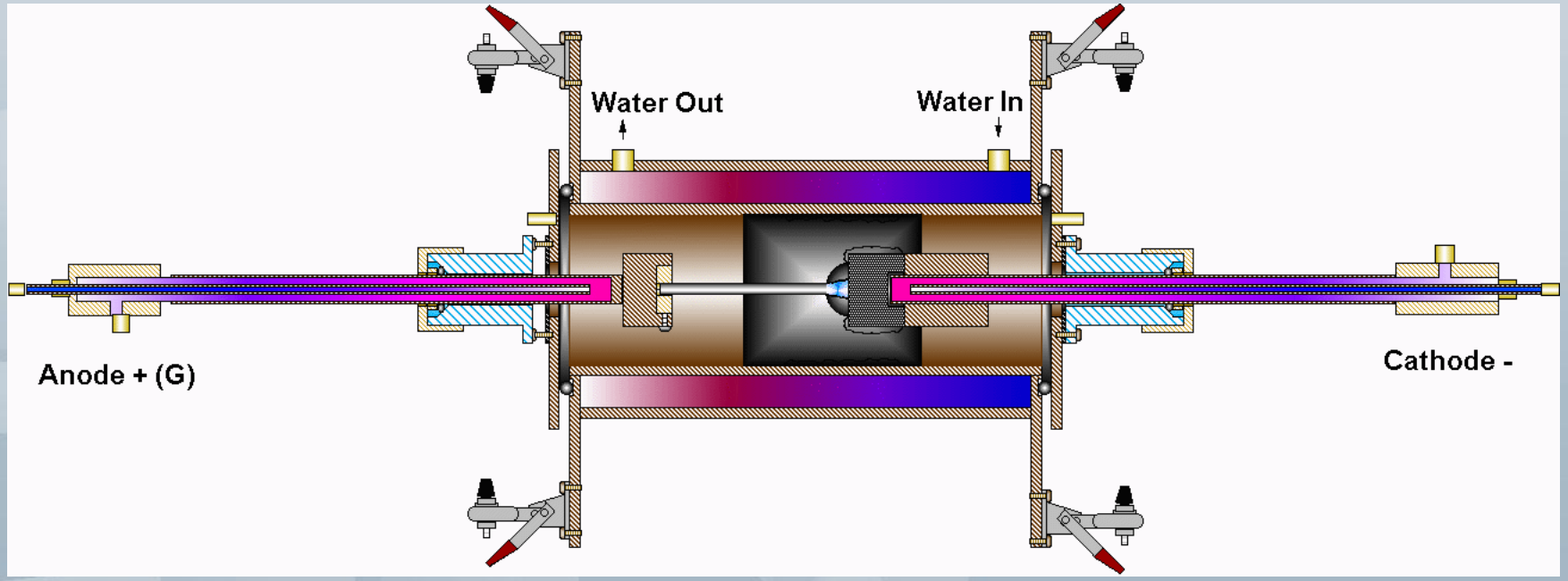
Graphite crystalline structure







Synthesis in a plasma reactor



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



Synthesis in a plasma reactor



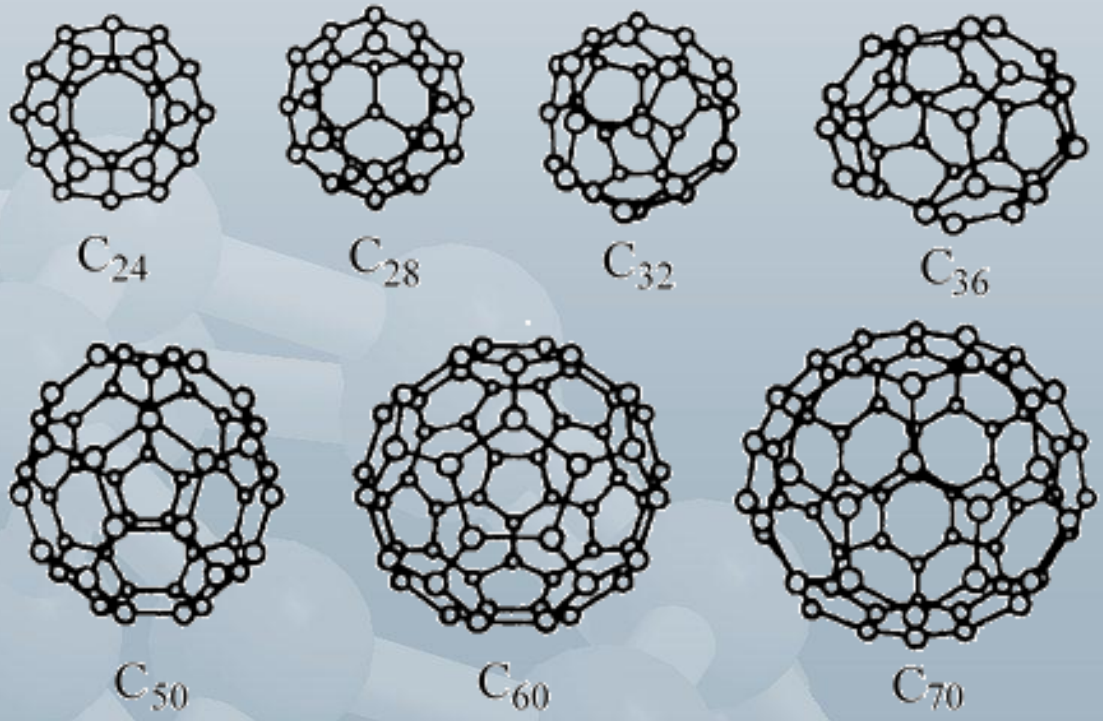
Pumping station

Arc reactor

Power, control, and cooling



Fullerenes family



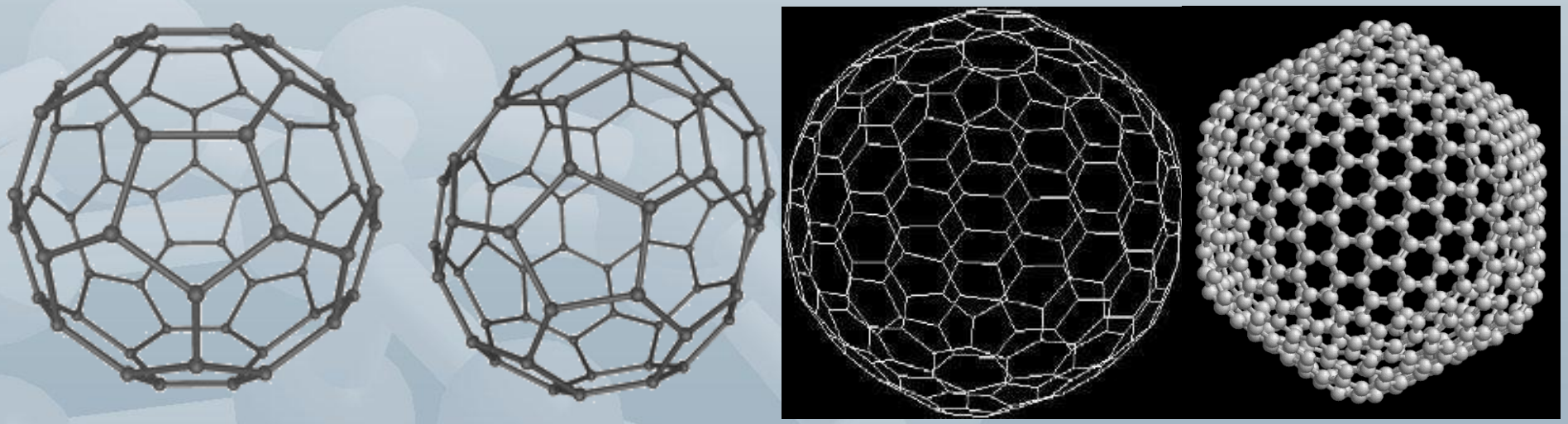
The smallest possible fullerene is C20, which contains 20 pentagons and no hexagons; however, this type of structure has strong internal stresses because the shape of each carbon molecule is highly non-planar.

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



Fullerenes discovery

C_{60} C_{80} C_{240} C_{540}

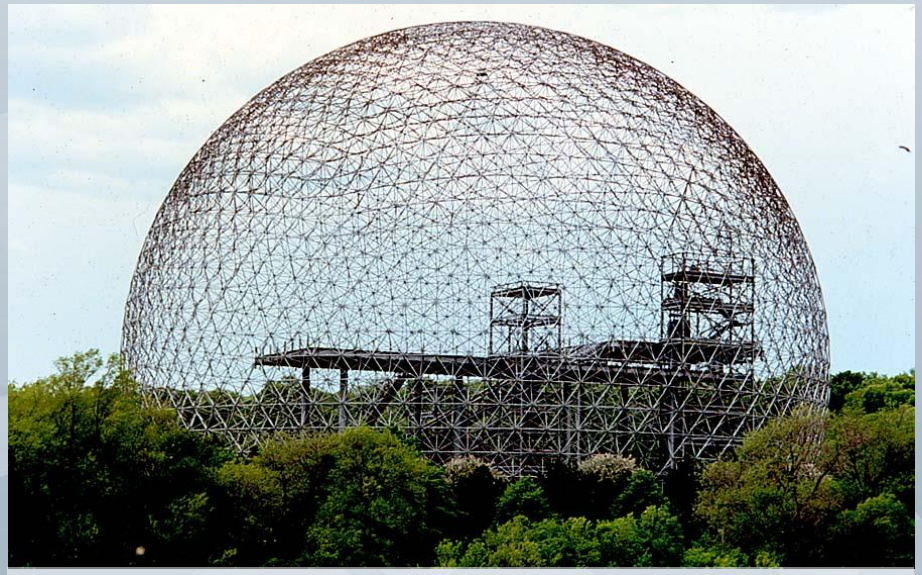


Other possible fullerenes are C_{28}, C_{32}, C_{44}, C_{50}, C_{58}, C_{70}, C_{76}, C_{84}, C_{240}, C_{540}, C_{960} And many others.

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



C_{60} Molecule



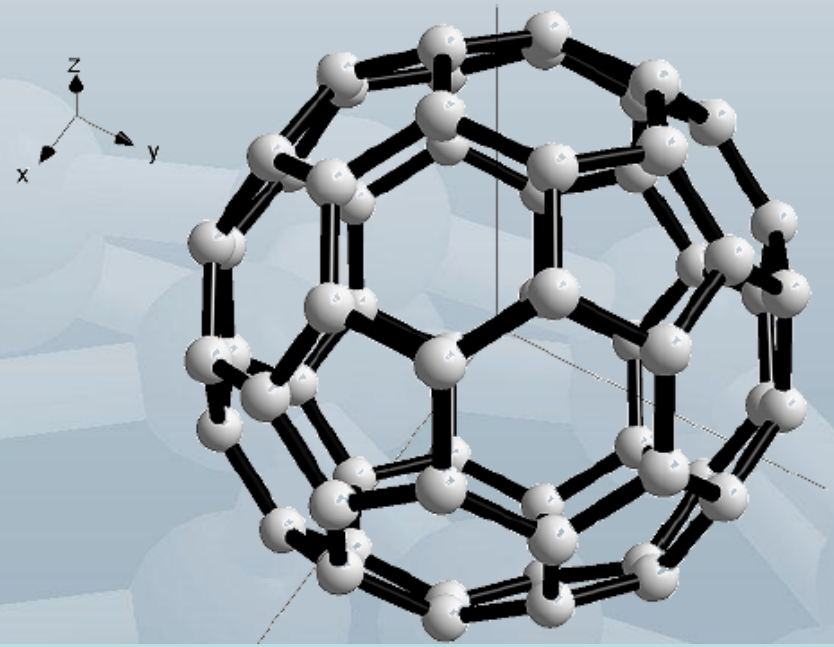
Geodesic dome designed by Buckminster Fuller

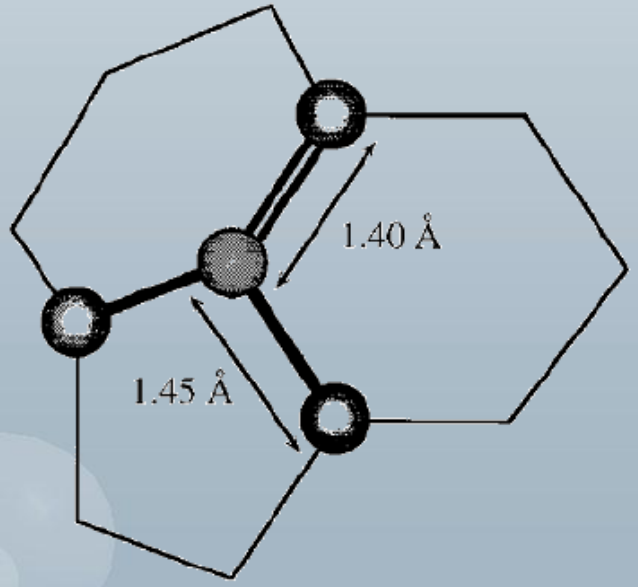


- C_{60} is the most stable molecule of the fullerene family.
- Truncated icosahedron with sp^2 hybridized carbon atoms
- Delocalized π orbitals determine electronic properties



C_{60} Molecule

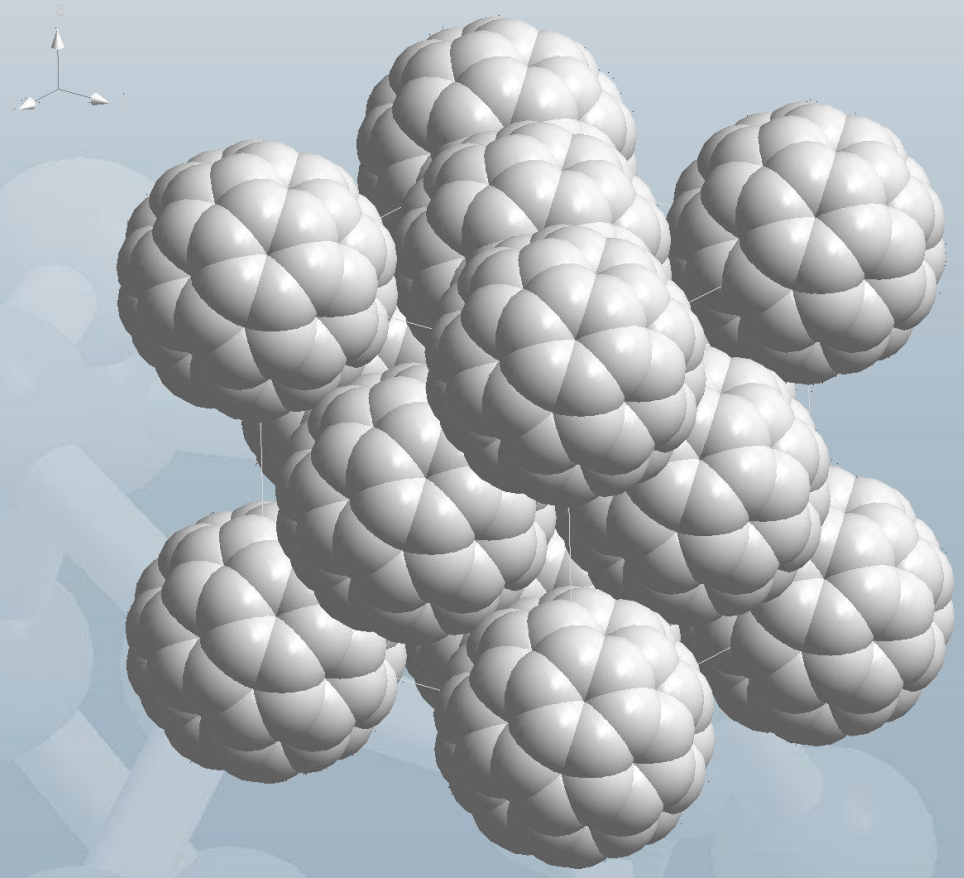




Molecule of C_{60} and representation of the bonds in which each atom participates: all carbon atoms are equivalent from the point of view of the local electronic environment. The bond angles within the hexagons are always about 120°, as in graphite, while the third angle (inside the pentagonal face) is 108°, due to the significant deviation from planar geometry. The molecular radius is 3.55 Å, but if the electron shells are also considered, it reaches 5.02 Å.



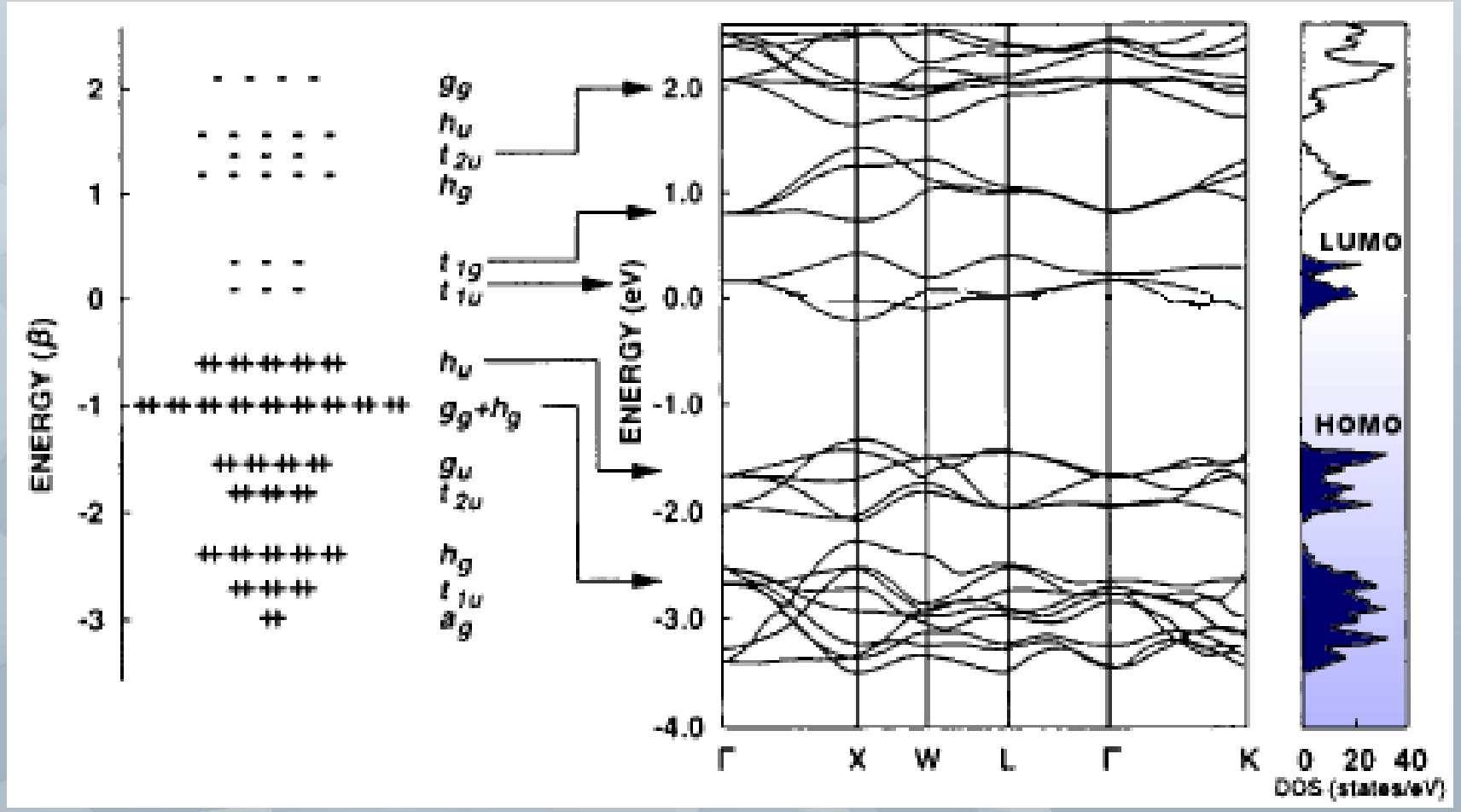
C_{60} Crystal



Plastic Crystal



Electronic structure



C_{60} A_3C_{60}



Electronic structure

- Peculiar characteristic of C_{60} : it has several stable redox states.
- In pure C_{60} the LUMO band originating from the t_{1u} orbital is empty. → insulating compound
- Compounds obtained by intercalating suitable ions into solid C_{60} are called fullerites. In fullerites, electrons transferred by intercalated atoms progressively fill the LUMO band. Effects due to the high electron correlation occur.



Fullerene derivatives

In the solid state, C_{60} molecules aggregate to form a molecular crystal with a f.c.c. structure.

Compounds obtained by intercalating suitable ions into solid C_{60} are called fullerites.

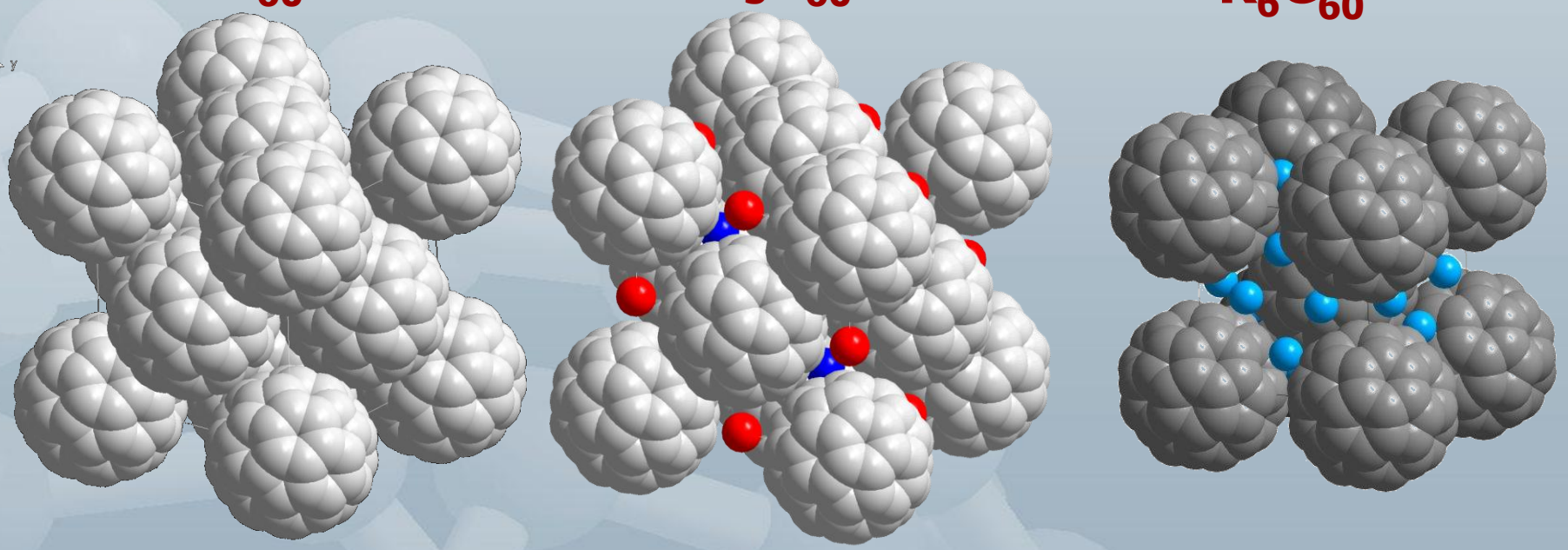
The most interesting materials derived from C_{60} are:

- Fullerites intercalated with alkali metals (K, Na, Rb) (A_3C_{60}: metallic conductors and superconductors at ~10-40K)
- High-pressure polymerized fullerenes
- Lithium fullerides (compounds with a polymeric structure, superionic conductors)
- Cationic fullerides (fullerenium salts)
- Endohedral fullerides



Fullerites

C_{60} K_3C_{60} K_6C_{60}



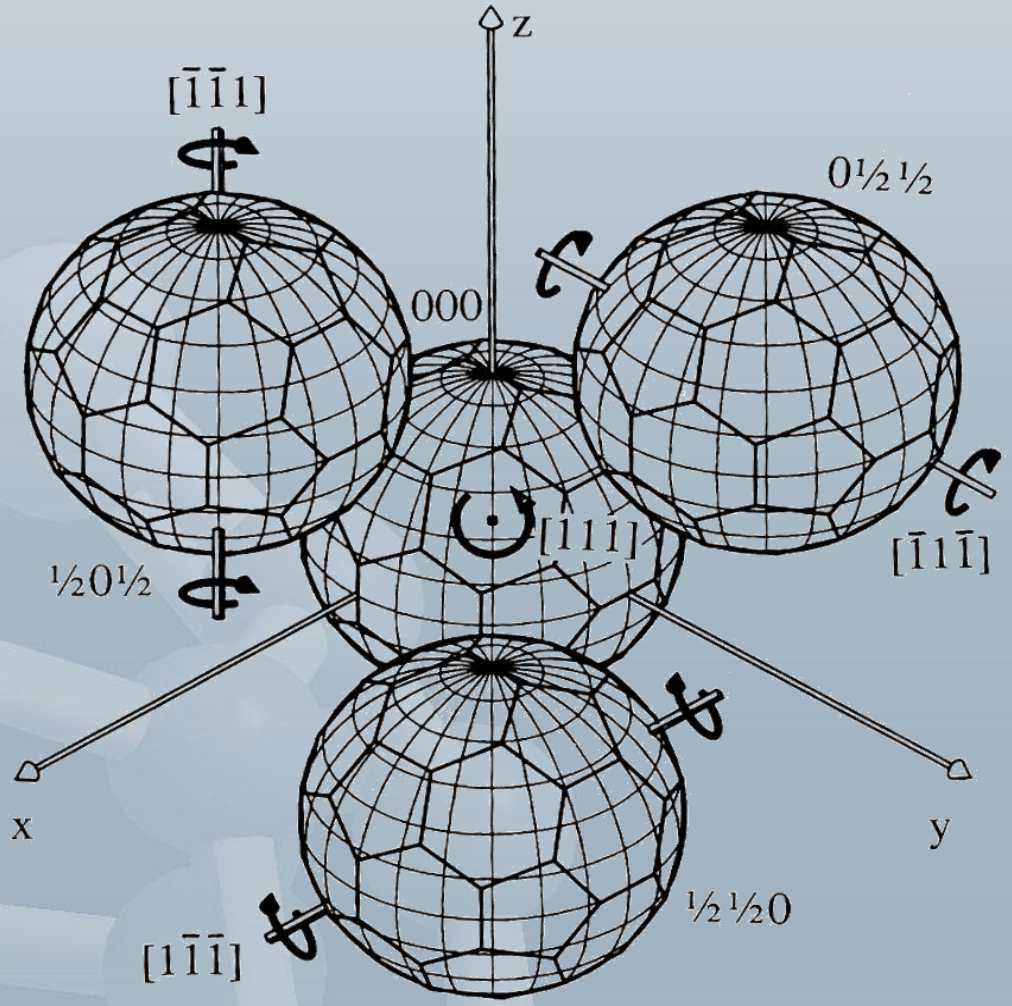
Metal at RT and superconductor at 19 K



C_{60} blocked phase: merohedral disorder

Despite its very high degree of symmetry (icosahedral space group, I_h),the structure of C_{60} is not compatible with the point symmetries of the fcc lattice; this gives rise to the intrinsic orientational disorder of the solid:

merohedral disorder





Fullerites

stoichiometric	electronic properties	structura
A_1C_{60}	insulating	structura
A_3C_{60}	metallic and superconc- T_c between 10 and 40	*fcc*
A_4C_{60}	non-metallic	*bct*
A_6C_{60}	insulating	*bcc*

Characteristics of the main fullerides. Depending on the stoichiometry of the alkali metals, completely different structures and electronic properties are observed, many of which can be interpreted based on the “conduction band” formed by the LUMO: for example, it is evident that fullerides of type A_6C_{60}, having this band completely filled, must be insulating.



Superconducting materials: characteristic BCS parameters

The first discovered superconductors can be described in terms of three main parameters:

- λ : **coupling constant:**
  indicates the strengh of the coupling force ($\lambda << 1$)
- λ_p : **penetration length.**
- ξ : **coherence length.**

$\kappa = \lambda_p / \xi =$ **Ginzburg-Landau ratio**



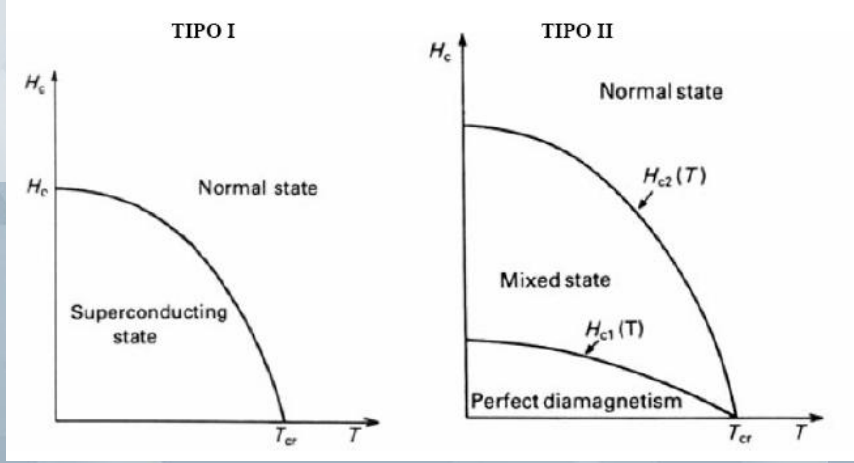
Type I and II superconductivity

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

Its importance is related to the calculation of the free energy of the superconducting state:

- $\kappa > \frac{1}{\sqrt{2}} \Longrightarrow$ the penetration of the field with fluxons is favorable, so the superconductor turns out to be type II.
- $\kappa < \frac{1}{\sqrt{2}} \Longrightarrow$ the formation of fluxons is no longer a condition for minimizing the free energy, so the material is a type I superconductor.

- **LTS**



- **HTS +MgB_2**
- **Fullerites**
- **Pnictides**



Superconducting materials: characteristic BCS parameters

The **BCS theory** (Bardeen, Cooper, and Schrieffer, 1957, Nobel Prize 1972) explains conventional superconductivity through the formation of **Cooper pairs**, consisting of two electrons bound by an attractive interaction mediated by phonons, the vibrations of the crystal lattice.

Below the **critical temperature (T_c)**, Cooper pairs form a collective, coherent quantum state.

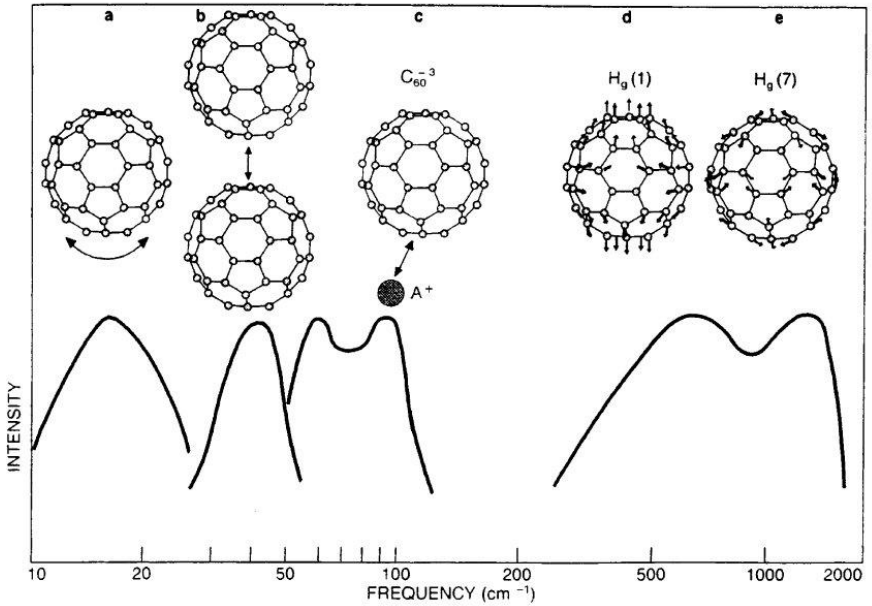
An **energy gap** opens in the electronic excitation spectrum, making it energetically costly to break Cooper pairs.

The quantum coherence of this state enables the flow of electric current **without electrical resistance**.

The theory predicts that (T_c) depends on the strength of the attractive interaction and the **electronic density of states at the Fermi level**, ($N(E_F)$).



Superconductivity in A_3C_{60} fullerides



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.

$$k_B T_c \approx \frac{\hbar \omega_D}{1.45} e^{-\frac{1}{N(E_F)V}}$$

$$N(E_F)V = \lambda$$

$N(E_F)$ = density of states at the Fermi energy

V = Coulomb pseudopotential

1 cm^{-1} = 0.124 meV



Superconducting fullerides

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
KRb_2C_{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



Superconductivity in A_3C_{60} fullerides

- conventional coupling mechanism, the electron-phonon interaction:
  - Intra-molecular phonon-mediated coupling: oscillations of the C_{60} molecule (H_g modes ~ 0.2 eV)..
  - Conduction band width ~0.5 eV => Fermi energy E_F ~ 0.25 eV

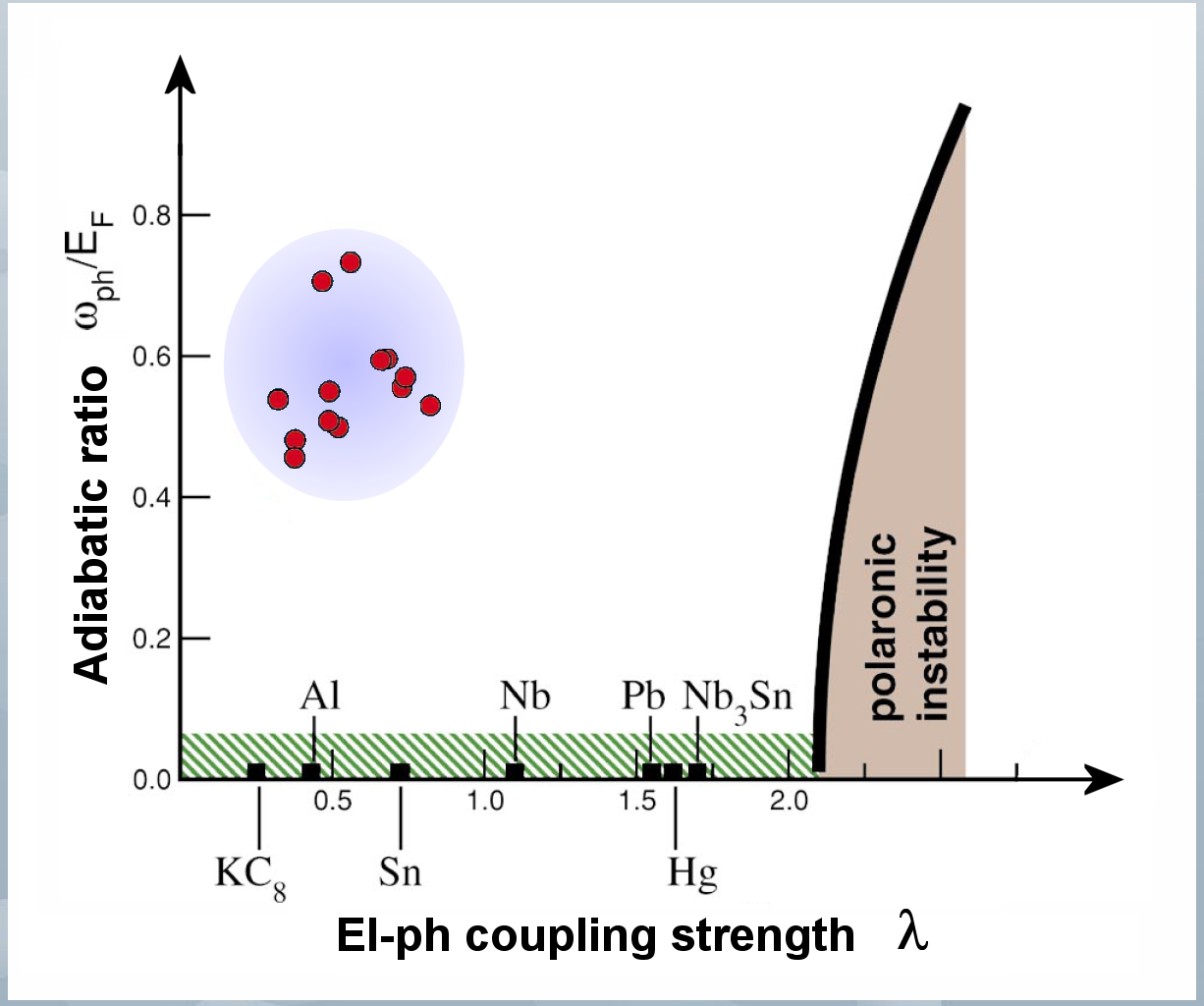
The Fall of the Adiabatic Approximation: Electronic and Lattice Dynamics No Longer Independent

- Unconventional phenomenology, high critical temperatures (up to 40K). Incorrect predictions of classical theories (BCS, M-E) on SC parameters.

E. Cappelluti, C. Grimaldi, L. Pietronero and S. Strässler; Journ. Mod. Phys. B 14, 2950 (2000)



Superconducting Fullerites





SC in Cs_3C_{60} (2008)

LETTERS

Bulk superconductivity at 38 K in a molecular system

ALEXEY Y. GANIN[1]*, YASUHIRO TAKABAYASHI[2]*, YAROSLAV Z. KHIMYAK[1], SERENA MARGADONNA[3], ANNA TAMAI[3], MATTHEW J. ROSSEINSKY[1†] AND KOSMAS PRASSIDES[2†]

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C_{60}-based solids[1] 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.) A_3C_{60} (A = alkali metal) increases monotonically with inter C_{60} 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_xC_{60} 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 Cs_3C_{60} 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 A_3C_{60} materials, two distinct cubic Cs_3C_{60} structures are accessible. Although f.c.c. Cs_3C_{60} 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 Cs_3C_{60} 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 C_{60} 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 methylamine[11–13] 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 °C followed by removal of the solvent under dynamic vacuum at room temperature and heating at 180 °C for 48 h yields a material of composition $Cs_{3.08(10)}C_{60}$ (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 $Cs_{3-x}Rb_xC_{60}$ family[14].

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 in Cs_3C_{60} (2008)



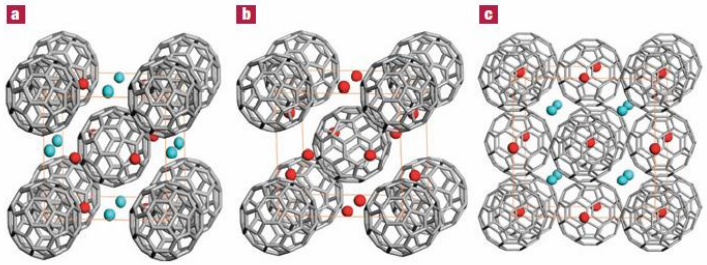
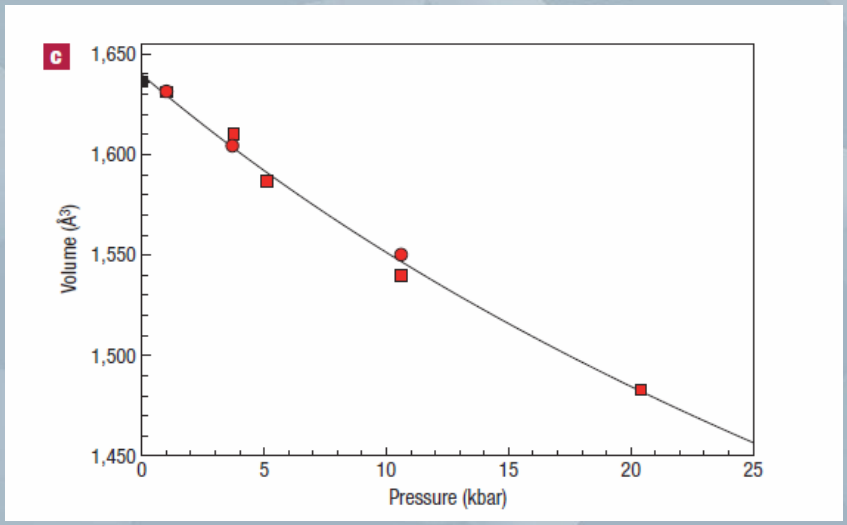
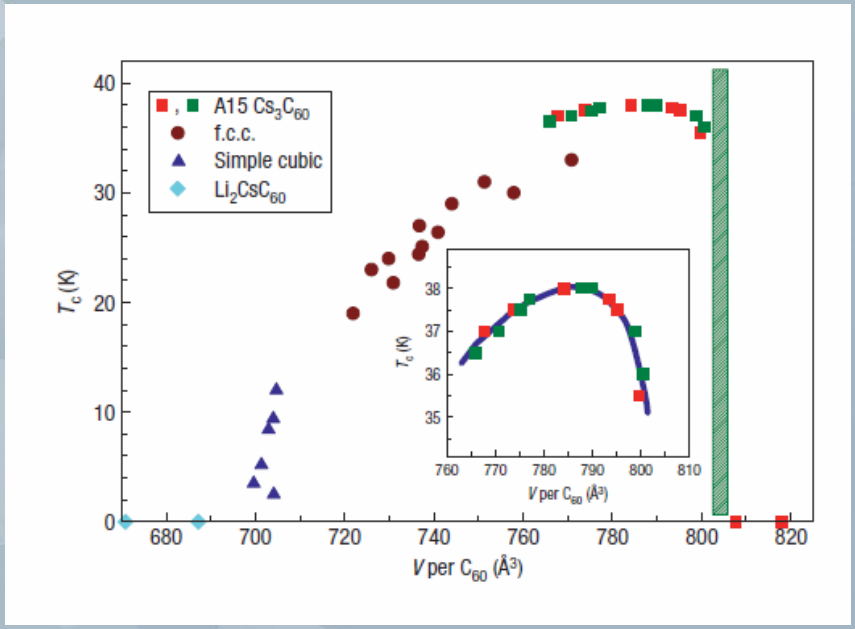


Figure 1 **Candidate crystal structures for Cs_3C_{60}.** **a**, b.c.o. unit cell with partial (75%) occupancy of the indicated cation sites (space group *Immm*). **b**, A15 unit cell (space group $Pm\bar{3}n$) based on b.c.c. anion packing. **c**, f.c.c. unit cell (space group $Fm\bar{3}m$). It is important to note that in **a** and **b** one unique orientation of the C_{60}^{3-} anions is present, whereas in **c** two orientations related by 90° rotation about [100] occur in a disordered manner. In the representation of **c** here, only one of these orientations is shown for clarity. The Cs^+ ions are shown as red and blue spheres to signify symmetry-inequivalent positions in the unit cell. In **c** the red and blue spheres correspond to octahedral and tetrahedral sites respectively, whereas in **a** the two sites differ in the anion faces presented to the cations. In **b**, one of two possible sets of cation sites is shown. The lower densities of the body-centred packings in **a** and **b** offer more spacious sites (with four fulleride neighbours) for the large Cs^+ cation.







SC ↔ AF (2009)

The Disorder-Free Non-BCS Superconductor Cs_3C_{60} 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. Rosseinsky[2]†

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 Cs_3C_{60}, 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 electron-electron correlation energies associated with inter-electron 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



SC in Cs_3C_{60} (2008)



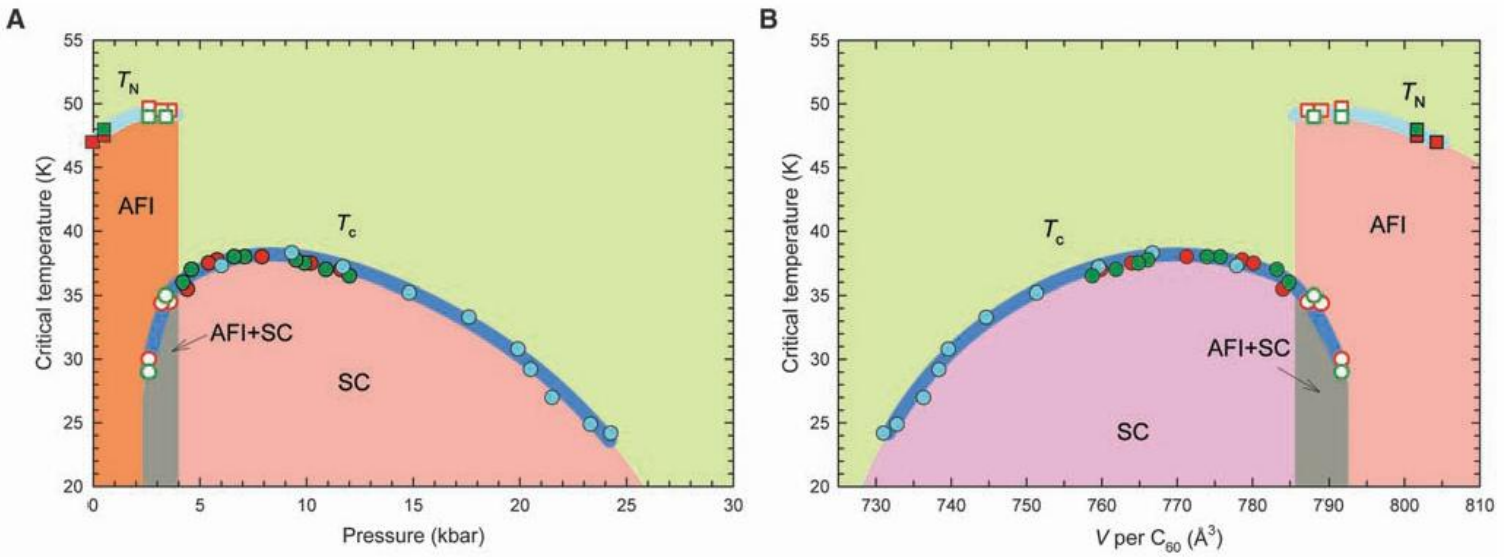
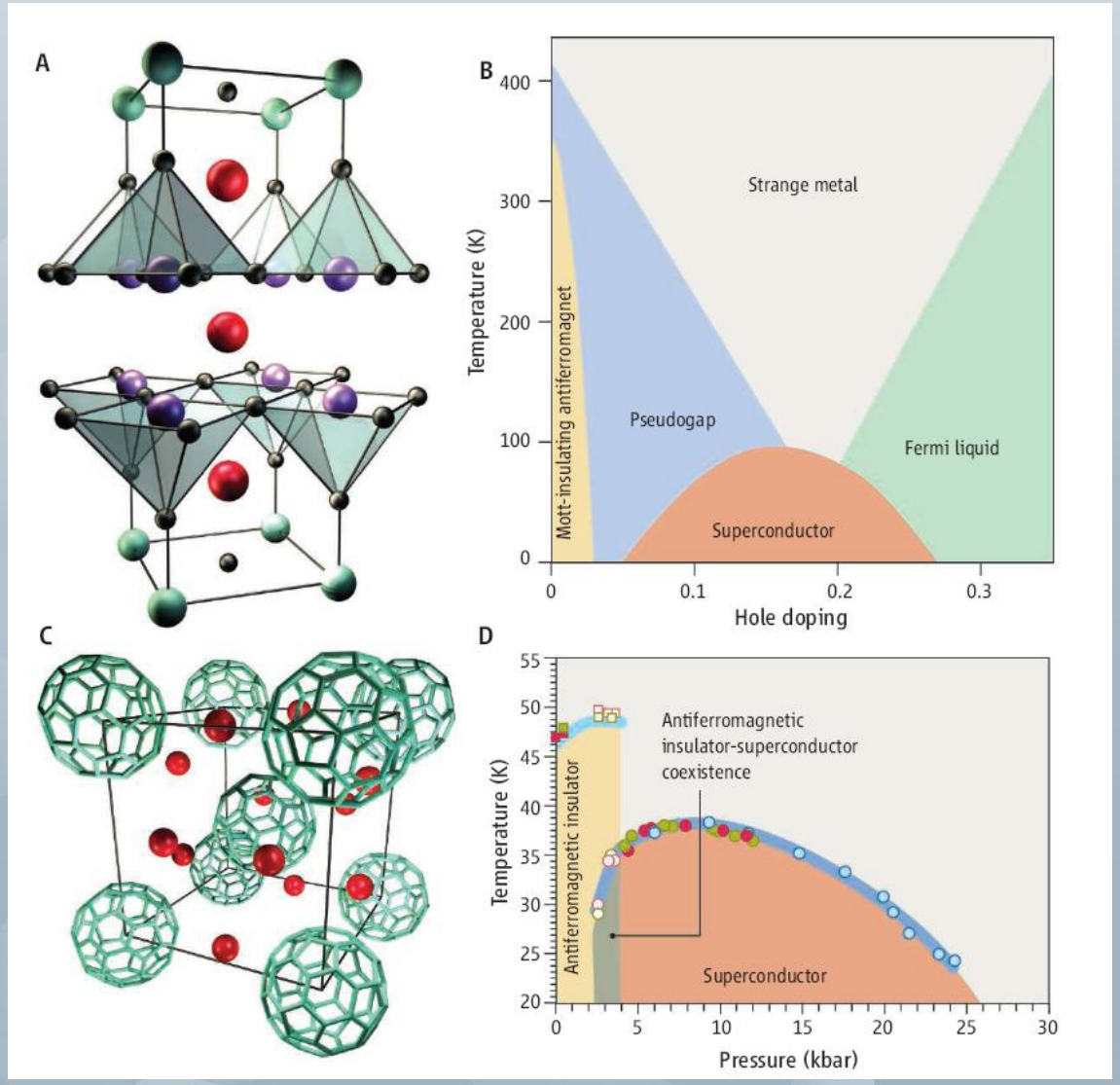


Fig. 4. Electronic phase diagram of A15 Cs_3C_{60} showing the evolution of the Néel temperature T_N (squares) and the superconducting transition temperature T_c (circles), and thus the isosymmetric transition from the ambient-pressure AFI state to the high-pressure superconducting state, (**A**) with change in pressure and (**B**) as a function of volume occupied per fulleride anion, V, at 14.6 K for A15 Cs_3C_{60}. Different symbol colors represent data obtained for different sample batches. Open symbols represent data in the AFI-superconductor coexistence regime. T_N is defined as the temperature at which the 20 Oe FC temperature-dependent magnetization M begins to increase; T_c is defined as the temperature at which the 20 Oe ZFC temperature-dependent M begins to decrease.



Cs_3C_{60} ↔ HTC


A
B
400
300
200
100
0
Temperature (K)
Strange metal
Mott-insulating antiferromagnet
Pseudogap
Fermi liquid
Superconductor
0
0.1
0.2
0.3
Hole doping
C
D
55
50
45
40
35
30
25
20
Temperature (K)
Antiferromagnetic
insulator-superconductor
coexistence
Antiferromagnetic insulator
Superconductor
0
5
10
15
20
25
30
Pressure (kbar)



K_3C_{60} ↔ light induced HTC (2016)



LETTER

doi:10.1038/nature16522

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

M. Mitrano[1], A. Cantaluppi[1,2], D. Nicoletti[1,2], S. Kaiser[1], A. Perucchi[3], S. Lupi[4], P. Di Pietro[3], D. Pontiroli[5], M. Riccò[5], 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 superconductivity[1]. 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, K_3C_{60}. By exciting metallic K_3C_{60} 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.

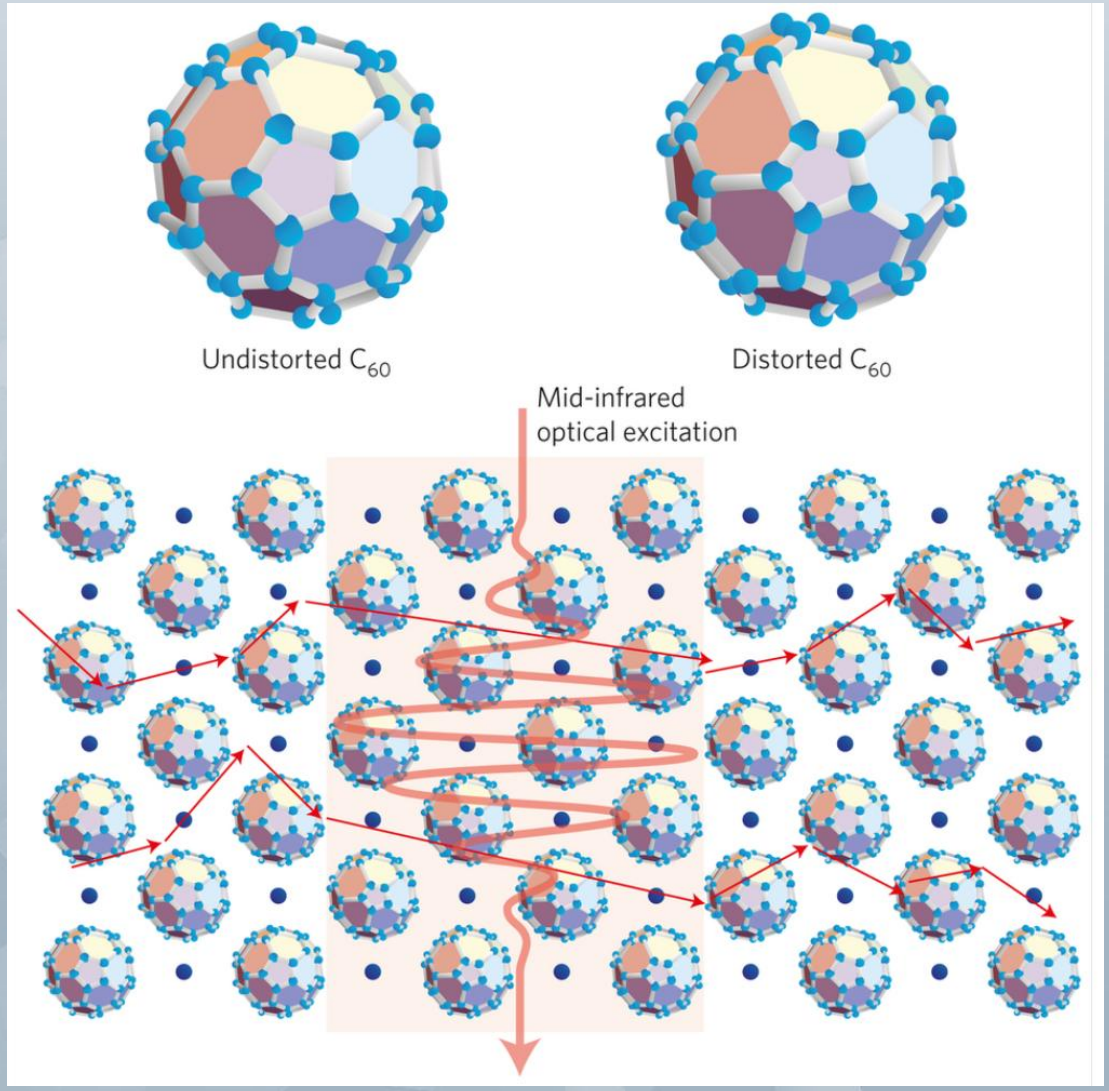
at 7 μm wavelength (180 meV photon energy), which is tuned to the $T_{1u}(4)$ vibration (see Fig. 2 for measurements at 1 ps time delay). For all temperatures between $T_c = 20$ K and $T = 100$ K, photo-excitation drove transient changes in the optical properties, which were very similar to those observed 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} ↔ light induced HTC





SC nel picene

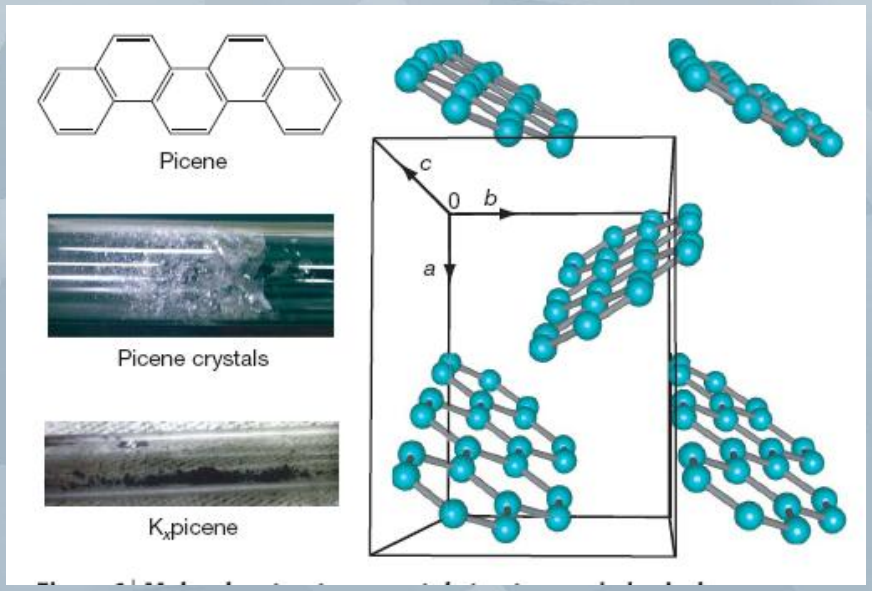
nature

Vol 464|4 March 2010|doi:10.1038/nature08859

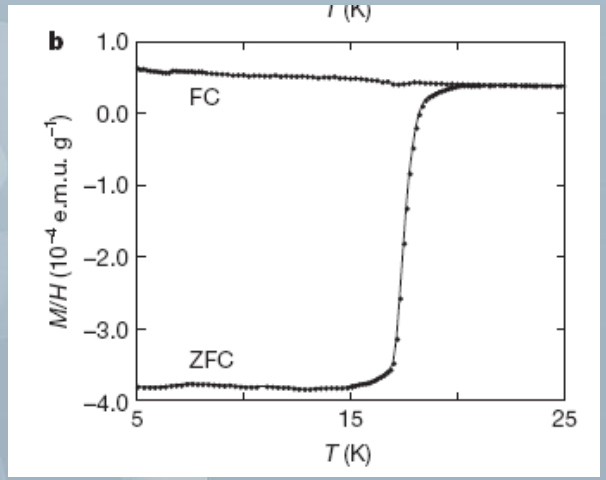
LETTERS

Superconductivity in alkali-metal-doped picene

Ryoji Mitsuhashi[1], Yuta Suzuki[2], Yusuke Yamanari[2], Hiroki Mitamura[1], Takashi Kambe[2], Naoshi Ikeda[2], Hideki Okamoto[3,4], Akihiko Fujiwara[5], Minoru Yamaji[6], Naoko Kawasaki[1], Yutaka Maniwa[7] & Yoshihiro Kubozono[1]

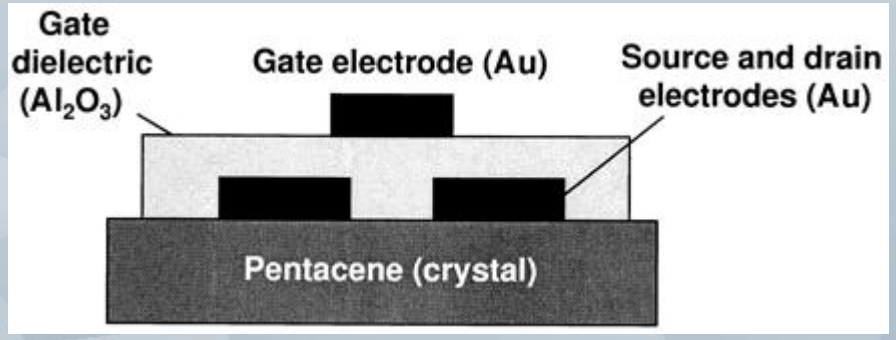


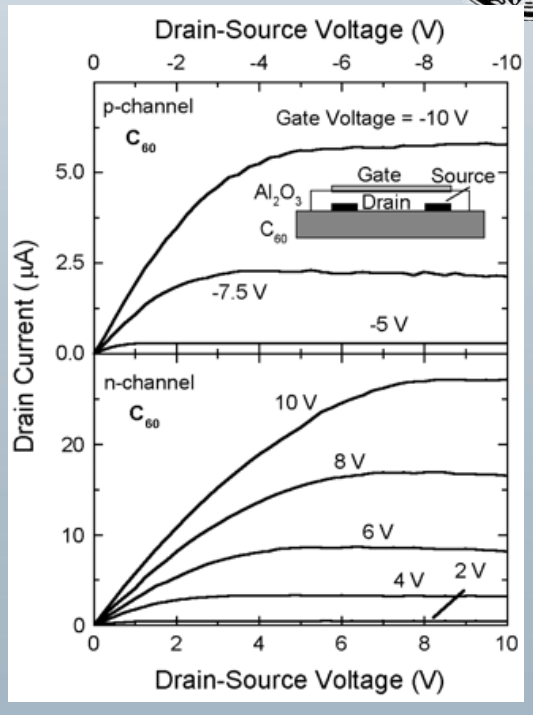
$K_{3.3}$-picene

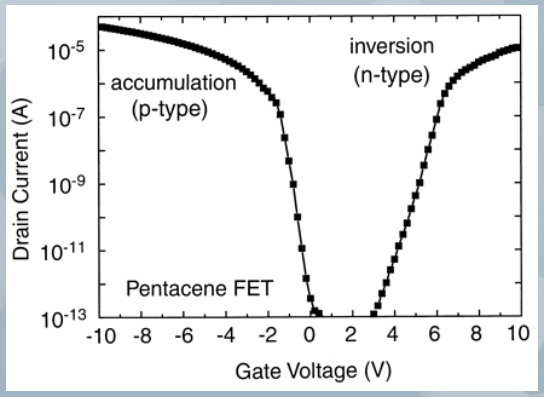


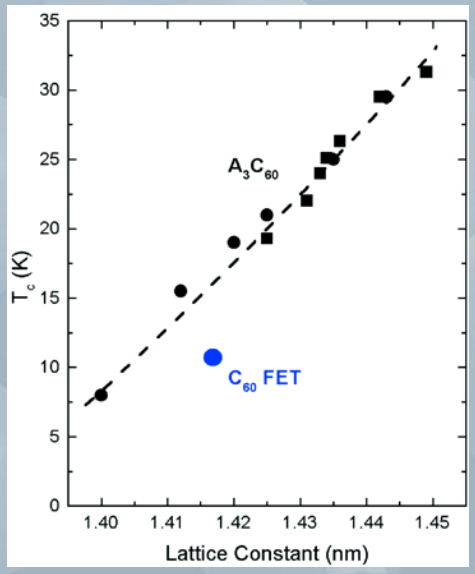


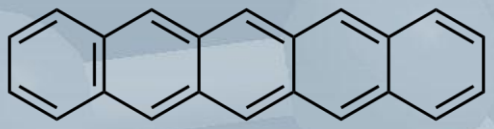
Batlogg-Schon research

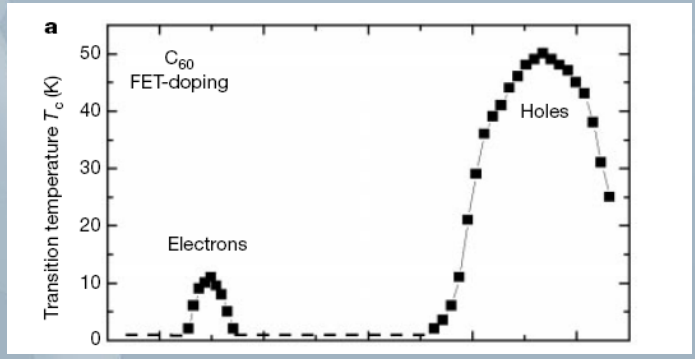












Schön, J. H., Kloc, Ch. & Batlogg, B. Superconductivity at 52K in hole-doped C_{60}. Nature 408, 549-552 (2000).



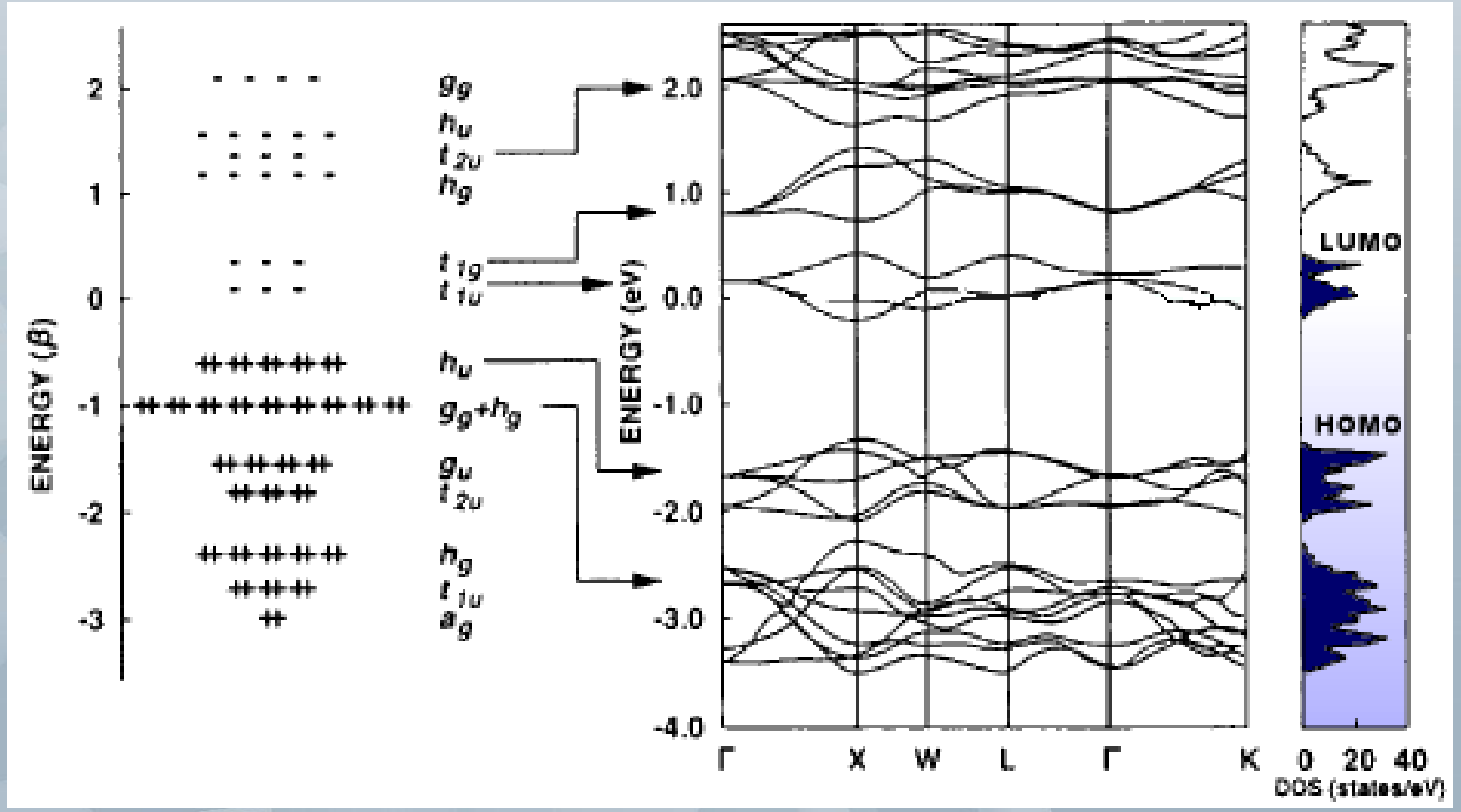
Superconducting Fullerites

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
KRb_2C_{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



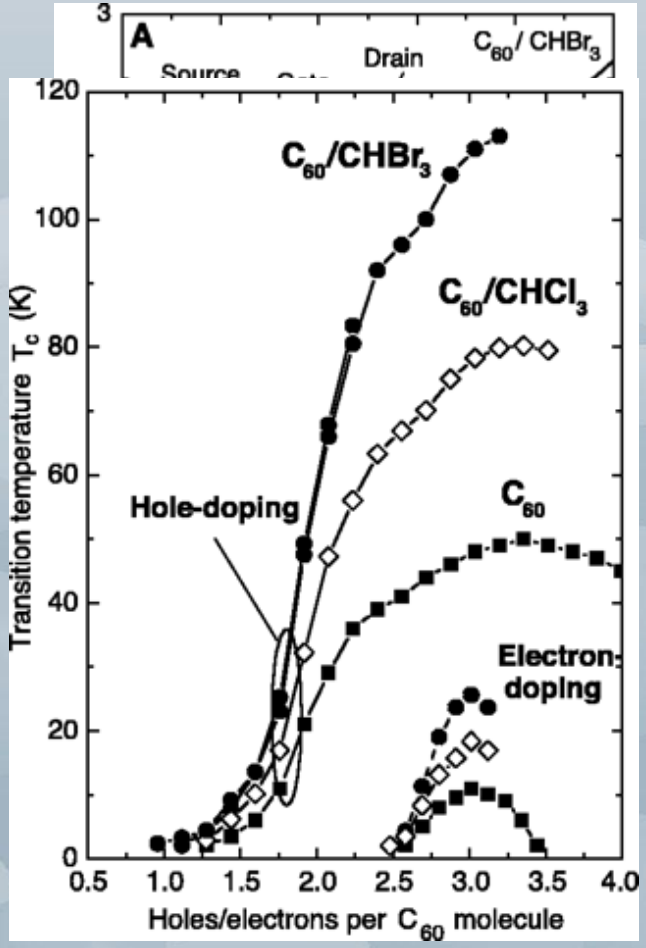
Electronic structure



C_{60} A_3C_{60}



Batlogg-Schon research



High-Temperature Superconductivity in Lattice-Expanded C_{60}

J. H. Schön,[1,2*] Ch. Kloc,[1] B. Batlogg[1,3]

C_{60} single crystals have been intercalated with $CHCl_3$ and $CHBr_3$ 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 $C_{60}/CHBr_3$. The increasing spacing between the C_{60} molecules follows the general trend of alkali metal–doped C_{60} 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 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*). C_{60} 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_c is well documented in alkali metal–doped bulk samples (A_3C_{60}) (*12*, *13*). The observation of gate-induced hole doping of C_{60} resulting in a T_c of 52 K suggests that significantly higher T_c's could be anticipated in suitably "expanded" C_{60} crystals. Indeed, here we report on raising T_c to 117 K with such methods.

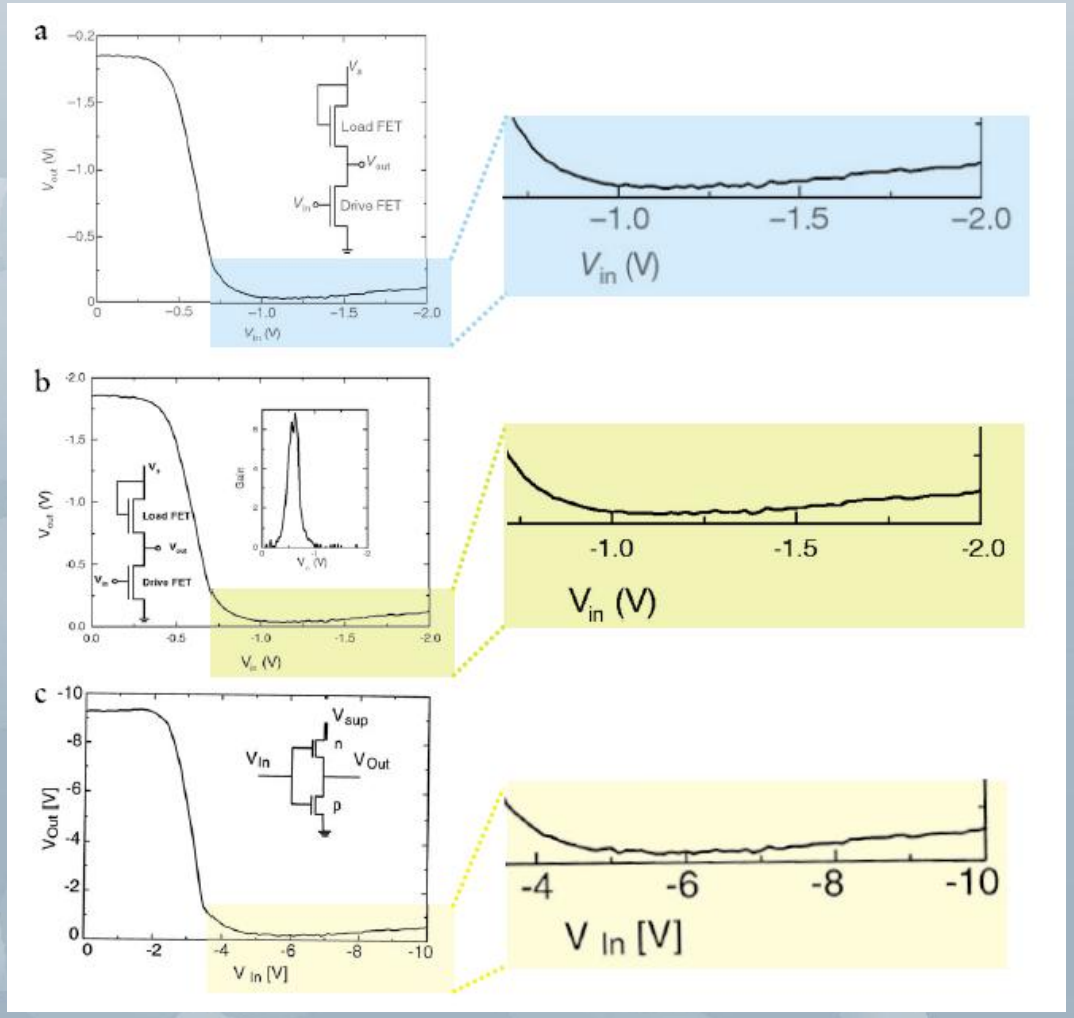
Undoped C_{60} single crystals have been grown from the vapor phase in a stream of hydrogen (*14*). $CHCl_3$ and $CHBr_3$ are interca-

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Batlogg-Schon story 2002….initial suspicions





Batlogg-Schon story 2002….initial suspicions

- 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

- 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
Retracted articles

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)

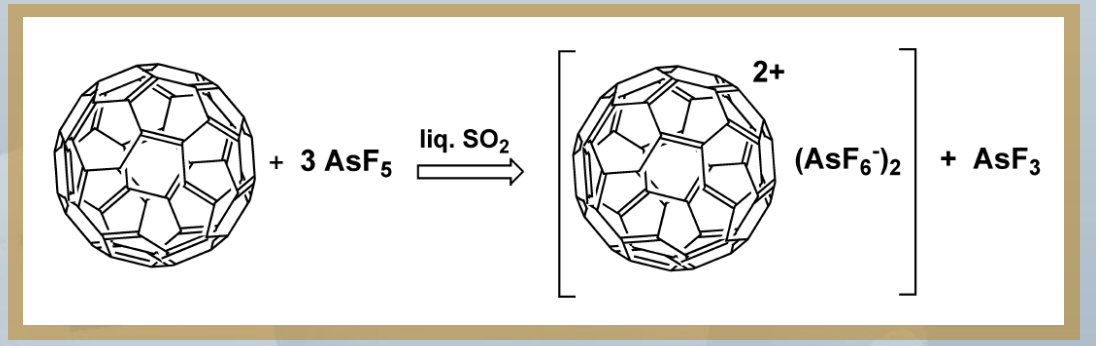
On March 5, 2003, Nature withdrew seven papers written by Schön:

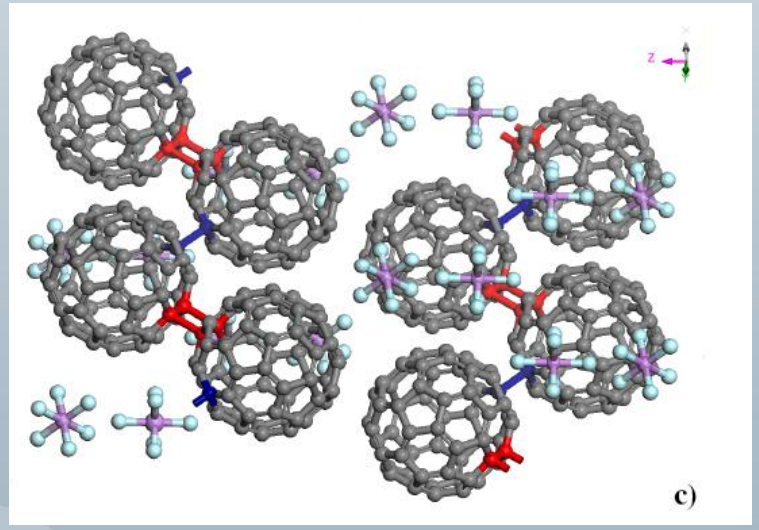
http://www.nature.com/nature/journal/v422/n6927/index.html

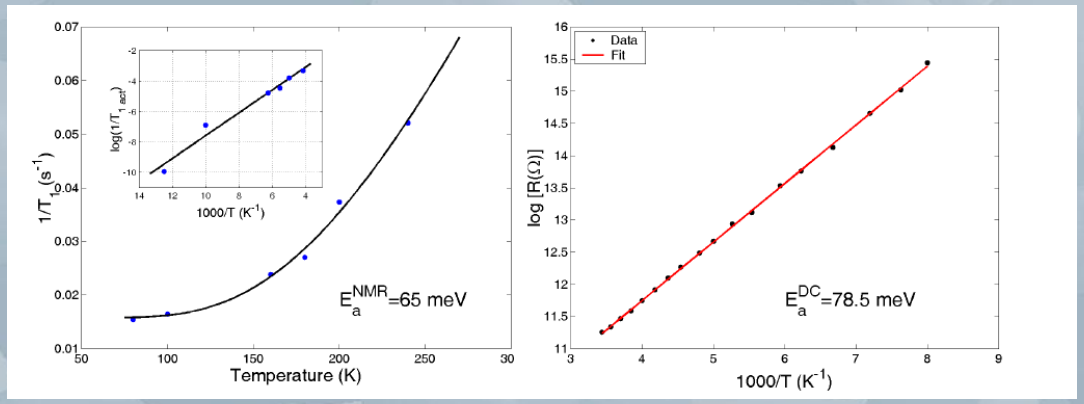
- * Schön, J. H., Kloc, Ch. & Batlogg, B. Superconductivity at 52K in hole-doped C60. Nature 408, 549-552 (2000).
- * Schön, J. H. et al. Gate-induced superconductivity in a solution-processed organic polymer film. Nature 410, 189- 192 (2001).
- * Schön, J. H., Meng, H. & Bao, Z. Self-assembled monolayer 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).



Fullerenium salts







J|A|C|S ARTICLES

Published on Web 01/26/2010

Fullerenium Salts: A New Class of C_{60}-Based Compounds

Mauro Riccò,*,† Daniele Pontiroli,† Marcello Mazzani,† Fabio Gianferrari,† Massimo Pagliari,† Angelo Goffredi,† Michela Brunelli,‡ Giorgia Zandomeneghi,§ Beat H. Meier,§ and Toni Shiroka||

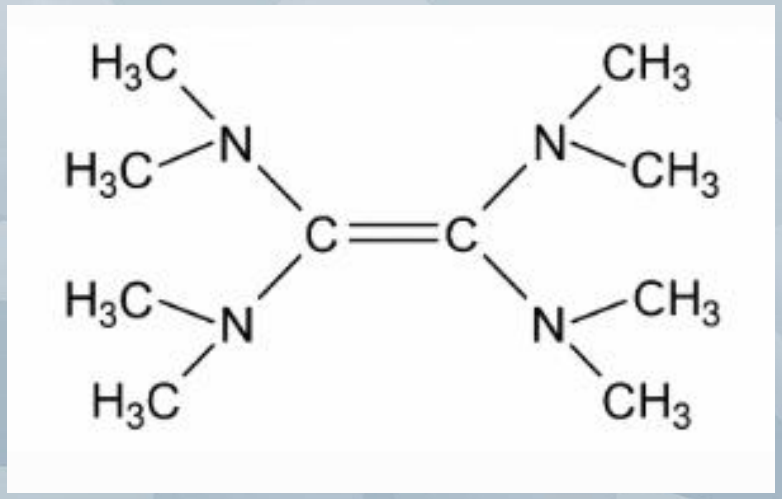
Dipartimento di Fisica, Università di Parma, Via G. Usberti 7/a, 43100 Parma, Italy, Institut Laue Langevin, BP 156, 6, rue Jules Horowitz, 38042 Grenoble Cedex 9, France, Physical Chemistry Laboratory, ETH-Zurich, Wolfgang-Pauli-Strasse 10, CH-8093 Zurich, Switzerland, and Laboratorium für Festkörperphysik,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

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



Magnetism in C_{60}

TDAE-C_{60} Tc = 16K, Ms=0,9 μ_B/C_{60}

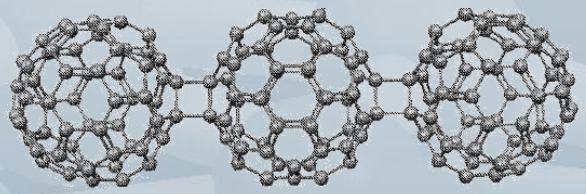


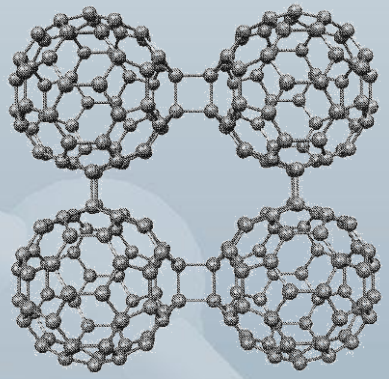
TDAE (tetrakisdimetilaminoethylene)

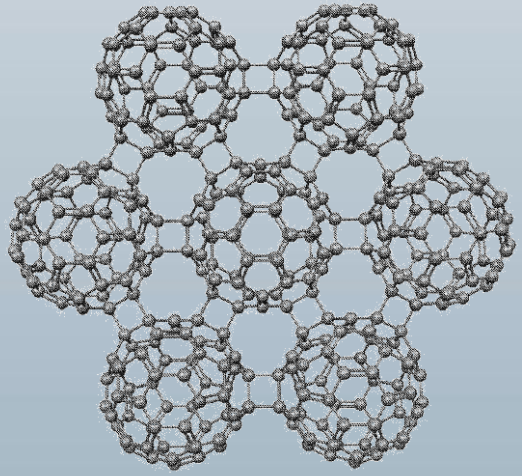




C_{60} polymers



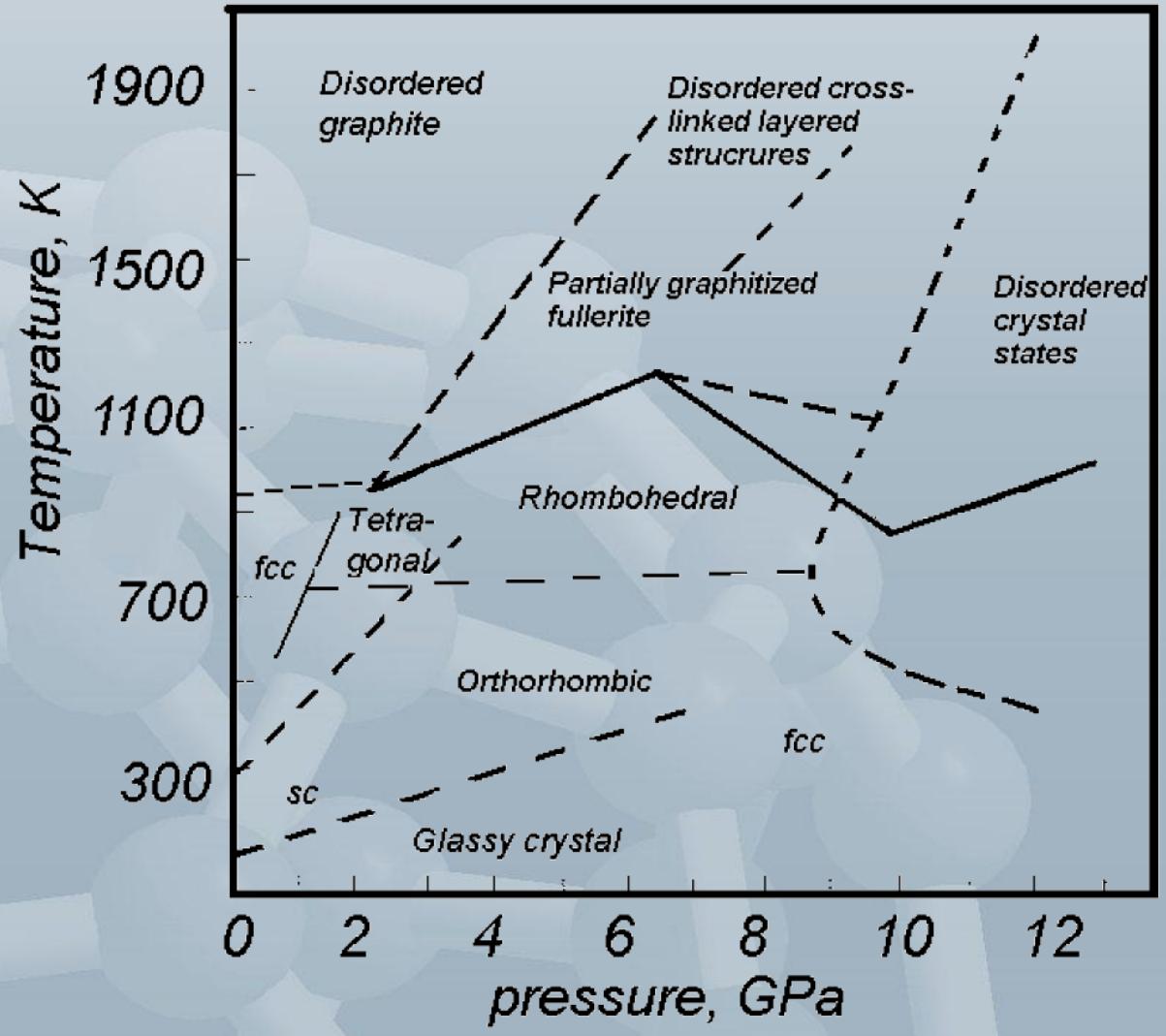




Orthorhombic (1D)	Tetragonal (2D)	Rhombohedral (2D)
a=9.26Å b=9.88Å c=14.22Å	a=9.09Å c=14.95Å	a=9.19Å c=24.5Å
Sp. gr: **I m m m**	S. g.: **?**	Sp. Gr.: **R -3 m**
1-8 GPa 300°C	3 GPa 600°C (mixed phase)	4 GPa 700°C



C_{60} polymers





Rh-C_{60}

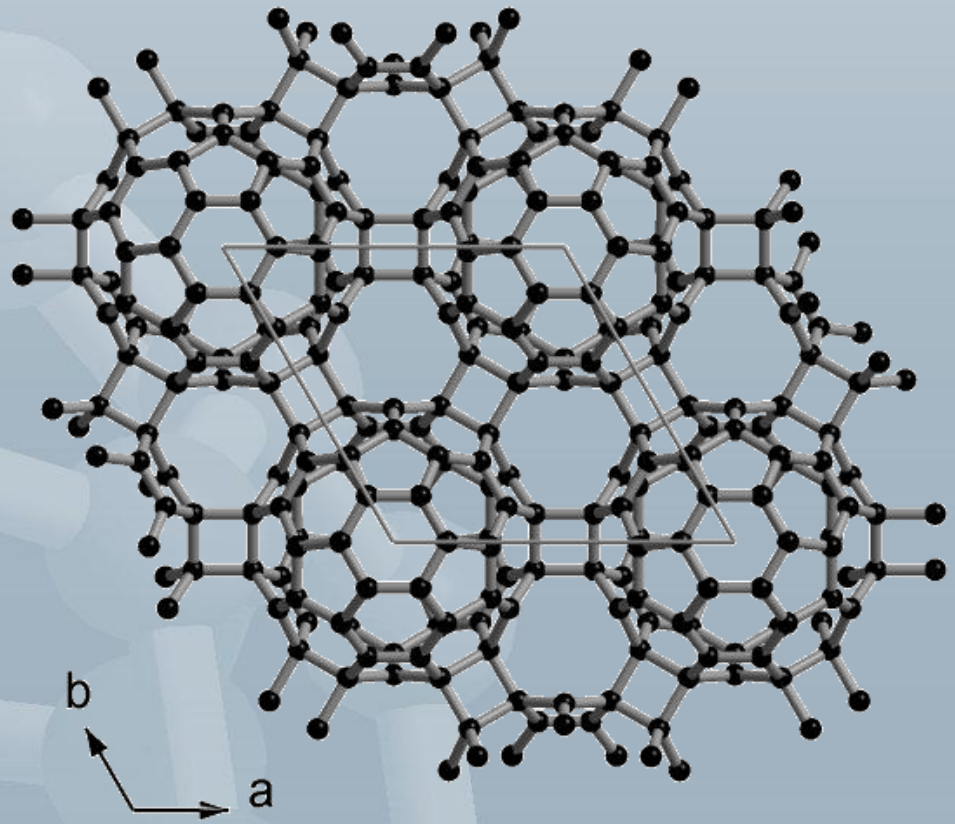
- Observed for the first time in 1994 (**Y. Iwasa *et al.*, Science 264, 1570 (1994)**)

Single crystal

a=9.17 Å
c=24.57 Å

Sp. Gr.: R-3m

5 GPa 500°C





Rh-C_{60} magnetic?

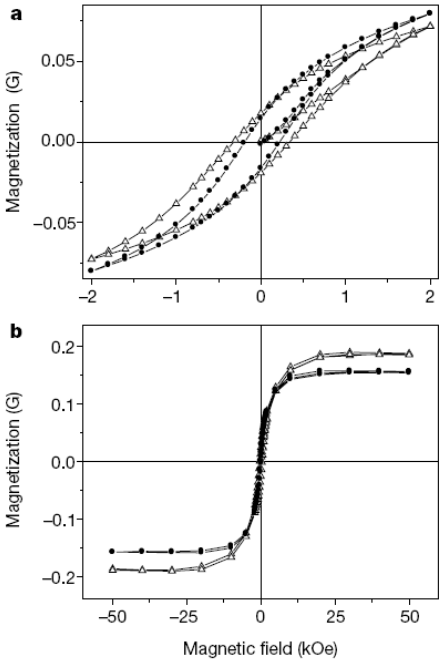


Figure 3 Hysteresis loops for Rh-C_{60}. Data were obtained at $T = 10$ K (triangles) and 300 K (circles). **a**, Hysteresis is observed in the field range $-2\,\text{kOe} < H < 2\,\text{kOe}$; **b**, saturation of the magnetization is clearly seen in a broader field region.

NATURE|Vol not known|0 2006

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 impurities[1]. 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 C_{60} samples mixed with iron before polymerization had a similar Curie temperature (500 K) to those we described[1], owing to the presence of the compound Fe_3C (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 C_{60} phase is not ferromagnetic[5].

Nevertheless, magnetic order in impurity-free carbon structures at room temperature has been demonstrated independently[6]. 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 results[1] are totally invalidated by these subsequent findings[2–5].

1. 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).
6. Murakami, Y. & Suematsu, H. Magnetism of C_{60} 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.



Magnetic carbon?

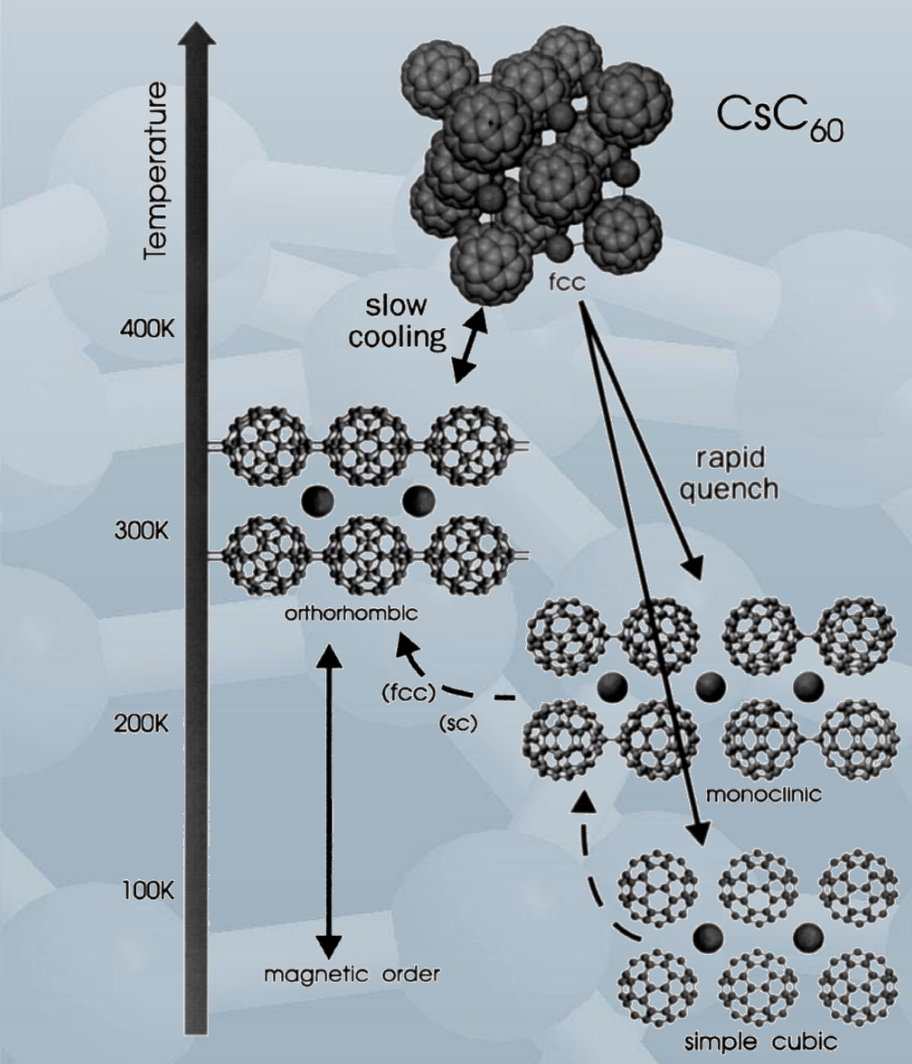


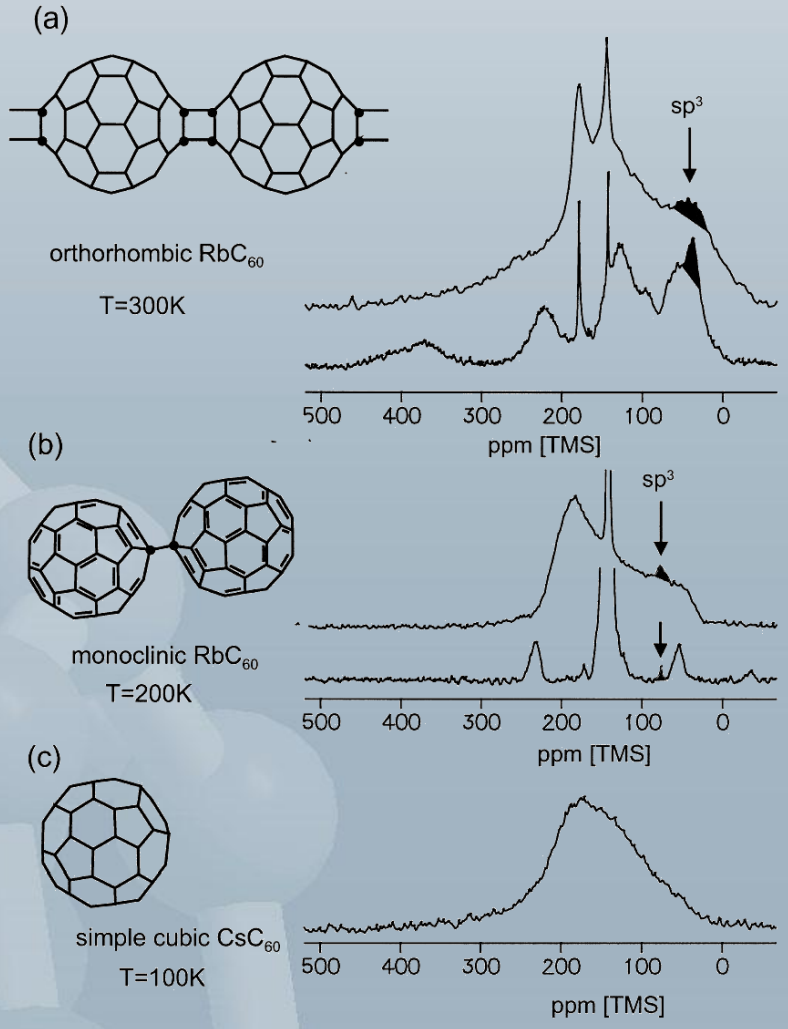
http://www.ferrocarbon.it/



Polymeric fullerides A_1C_{60}









CP-MAS NMR





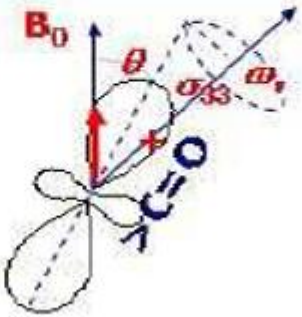
Distribution of electrons is not symmetrical and is not motionally averaged

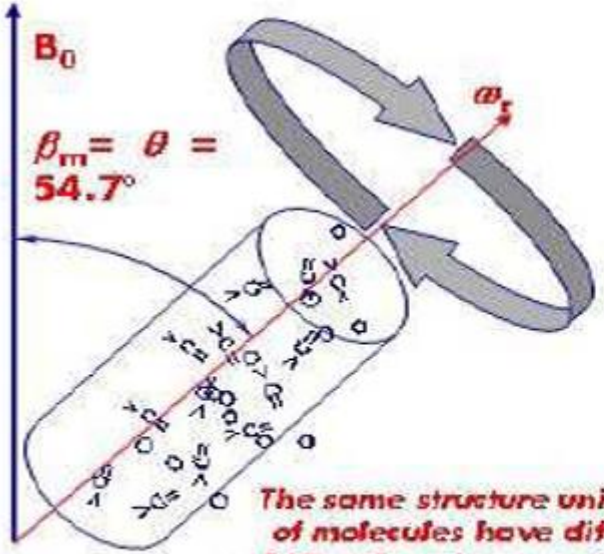
Static sample

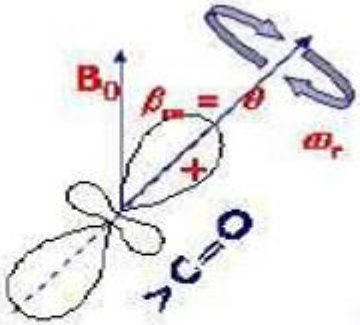
Anisotropy interactions dominate

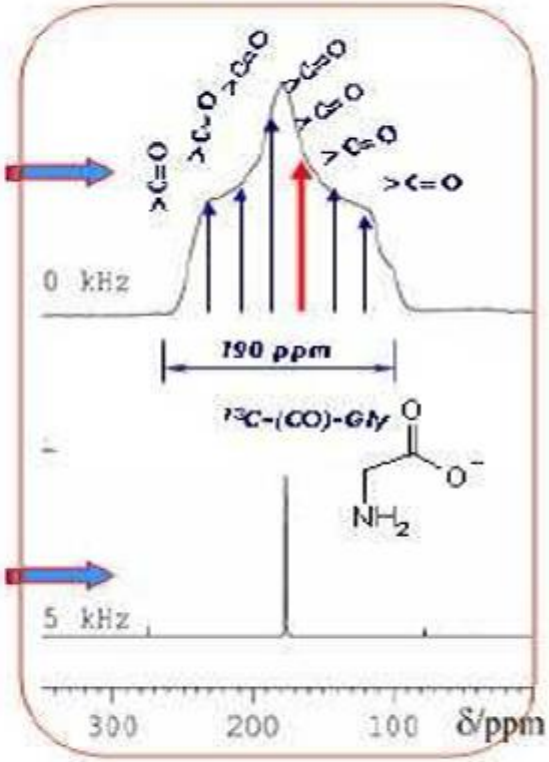
Limited mobility

Chemical shift anisotropy







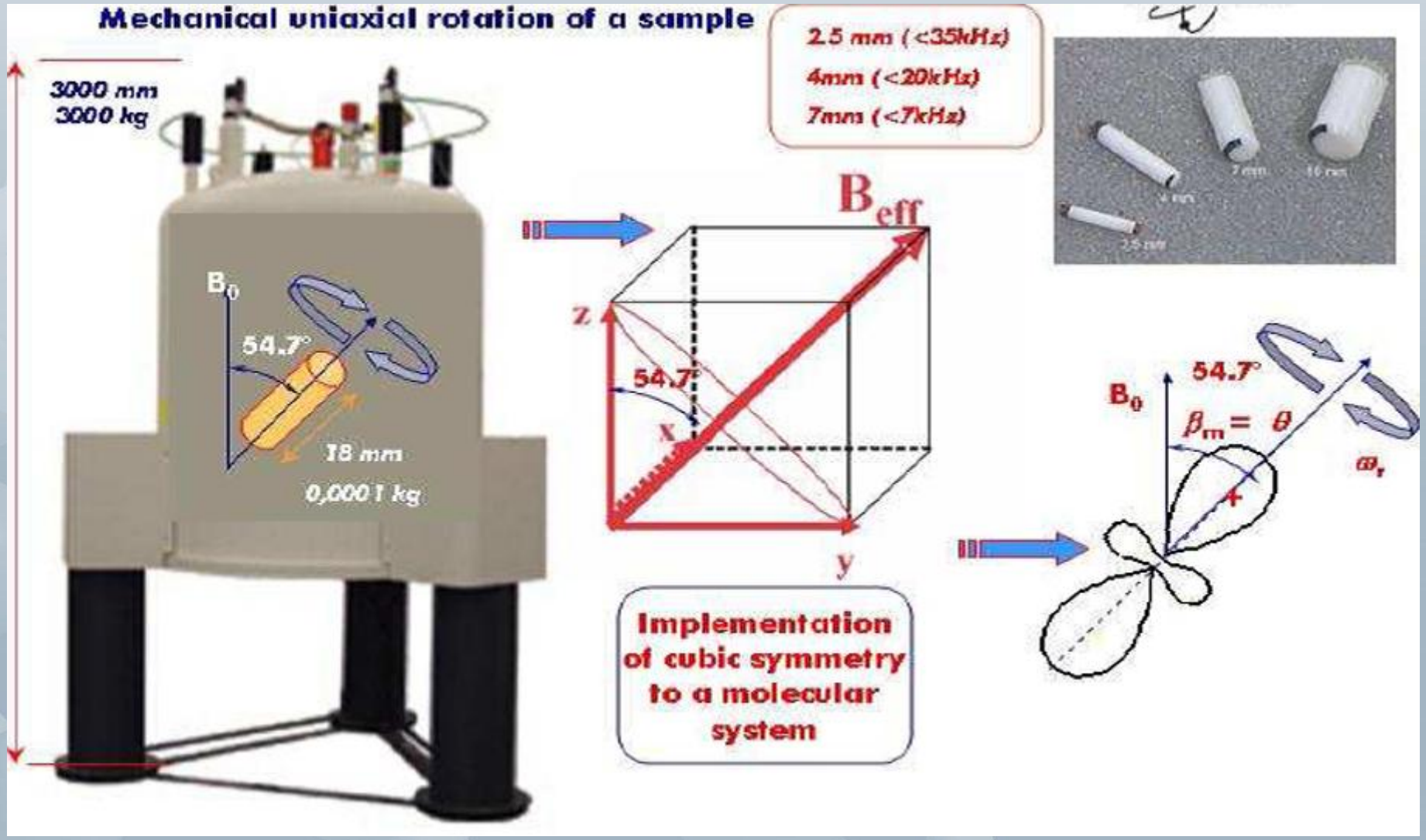


The same structure units in a collection of molecules have different chemical shifts – there is no equivalence at it was in solution.

Magic Angle Spinning (MAS)

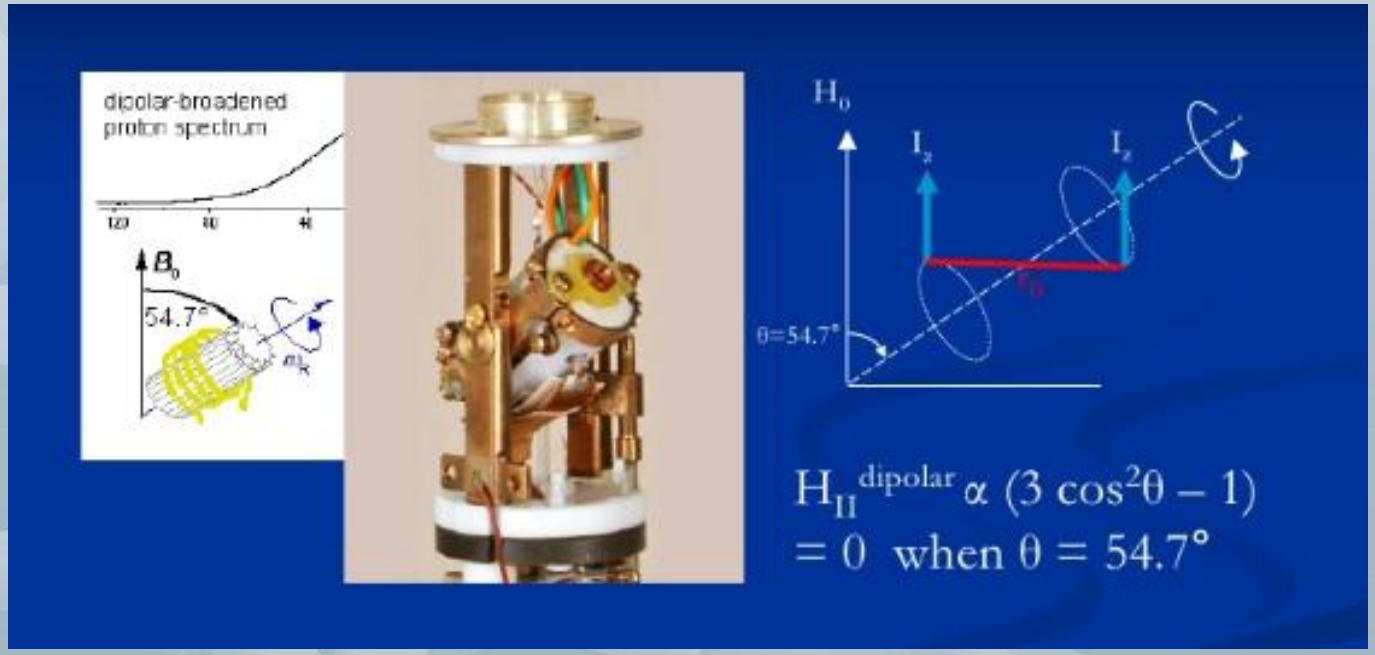


CP-MAS NMR


Mechanical uniaxial rotation of a sample
3000 mm
3000 kg
B0
54.7°
18 mm
0,0001 kg
2.5 mm (<35kHz)
4mm (<20kHz)
7mm (<7kHz)
Beff
z
54.7°
x
y
Implementation of cubic symmetry to a molecular system
B0
54.7°
βm = θ
ωr

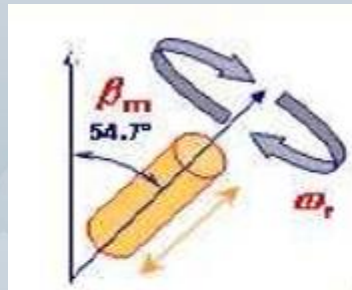


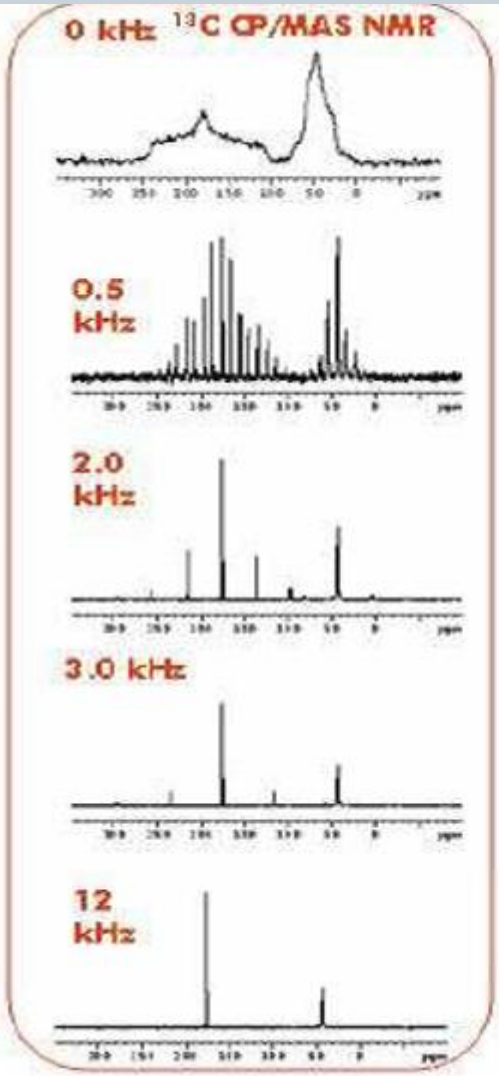
CP-MAS NMR

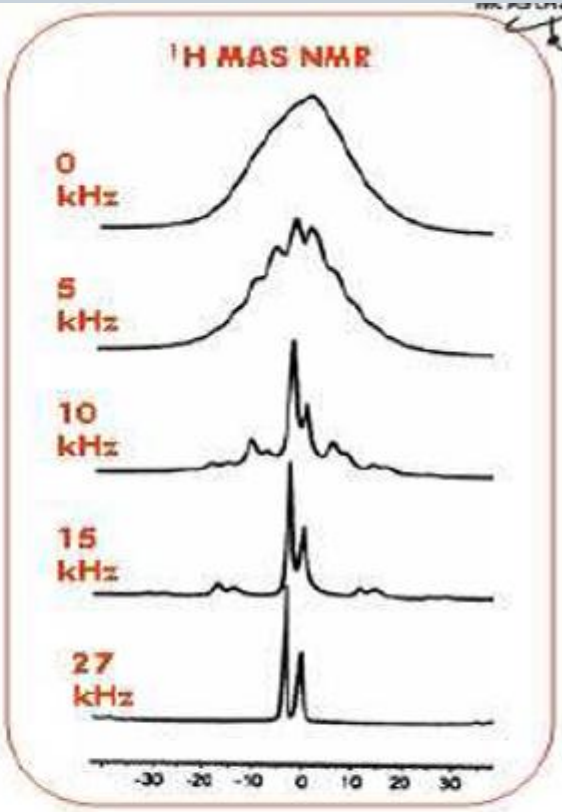

dipolar-broadened
proton spectrum
120
80
40
B_0
54.7°
H_0
I_z
I_z
θ=54.7°
$H_{II}^{dipolar} \alpha (3\cos^2\theta - 1)$
$= 0$ when $\theta = 54.7°$

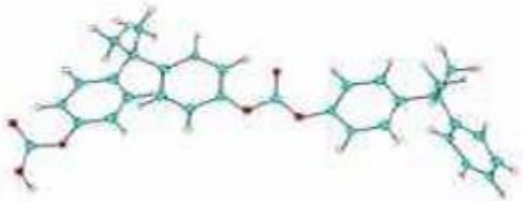


CP-MAS NMR


β_m
54.7°
ω_r


0 kHz
^{13}C CP/MAS NMR
0.5 kHz
2.0 kHz
3.0 kHz
12 kHz
Increasing frequency of MAS


^{1}H MAS NMR
0 kHz
5 kHz
10 kHz
15 kHz
27 kHz
-30 -20 -10 0 10 20 30

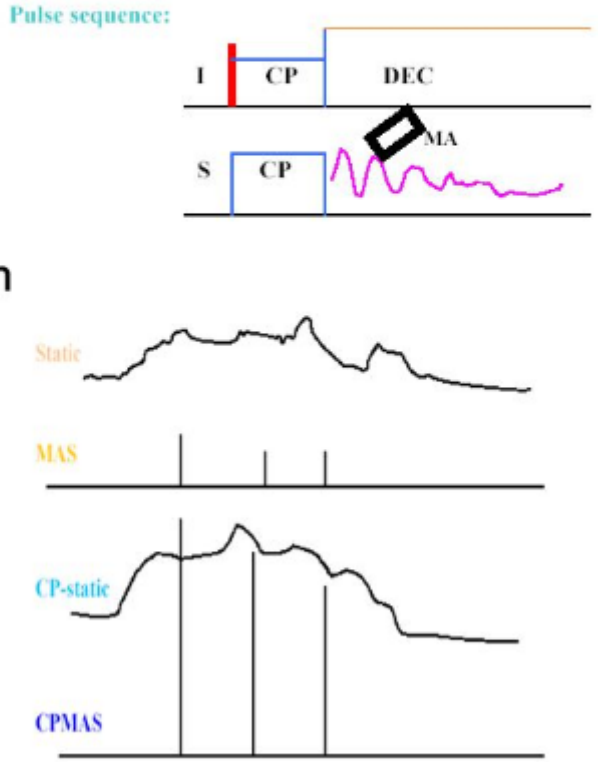




CP-MAS NMR

Cross polarization

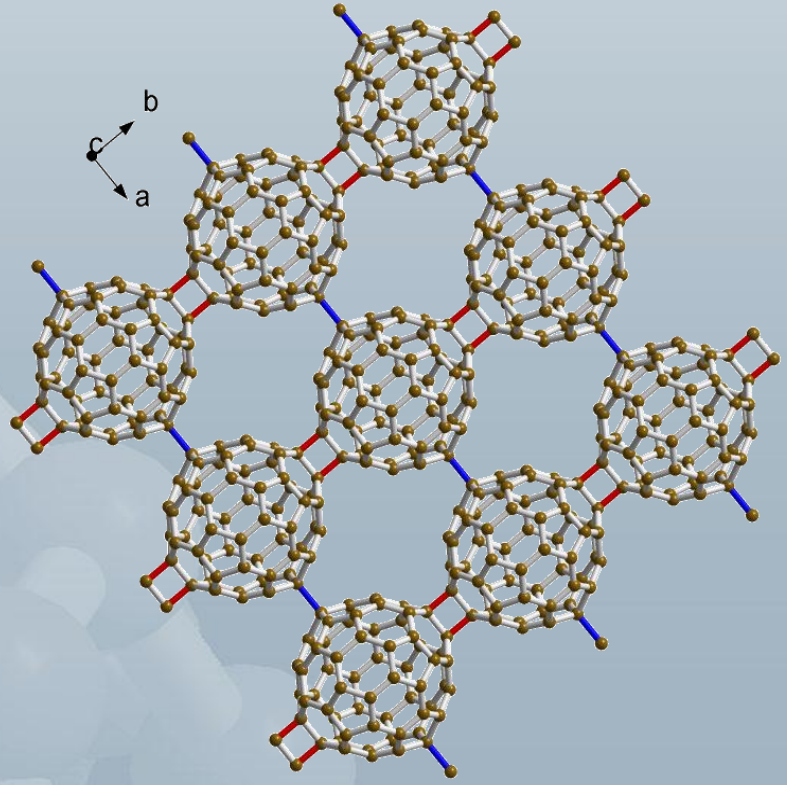
- ☐CPMAS–one of the most important solid state NMR techniques. $\omega_{1,I} = \omega_{1,S}$
- CP contact time: several hundred microseconds to tens of milliseconds.
- Purpose: To enhance the sensitivity of the lower γ spins such as carbon-13. maximal enhancement factor: γI/γS
- Other advantages: Shorter recycle delay time
- Distinguish the interconnectivity of nuclear spins such as the protonation of a certain carbon nucleus.





Li_4C_{60} Fullerite

- **Polymer at T = 300 K: 2 + 2 cycloaddition**
- **The polymer bonds break at about 300 °C, and a cubic monomeric phase is formed → metallic phase**



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



Superionic conductivity in Li_4C_{60}

Physical Review Focus

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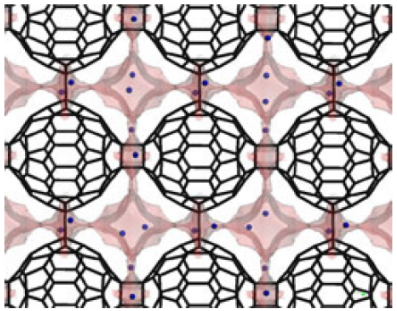
Phys. Rev. Lett. **102**, 145901
(issue of 10 April 2009)
Title and Authors

10 April 2009

"Superionic" Buckyball Crystal

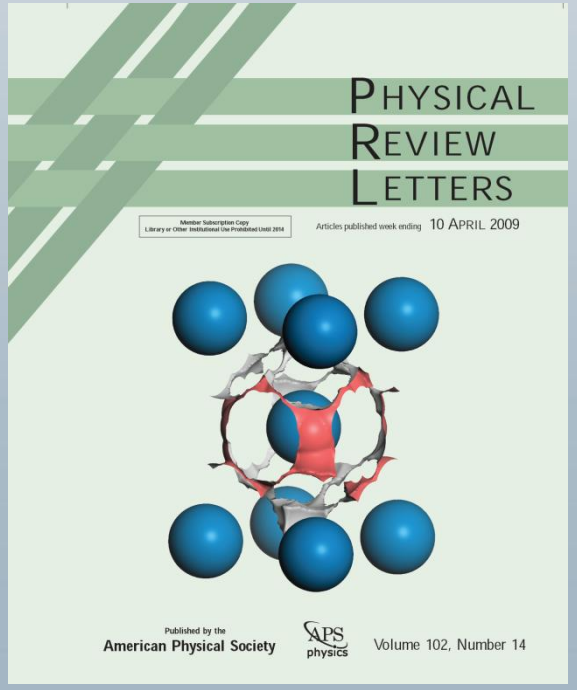
Materials that conduct electricity with ions rather than electrons are essential for batteries, fuel cells, and more exotic technologies. Providing enough space in the molecular structure for the movement of ions usually requires a disordered (non-crystalline) material. But a paper in the 10 April *Physical 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 C_{60} 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

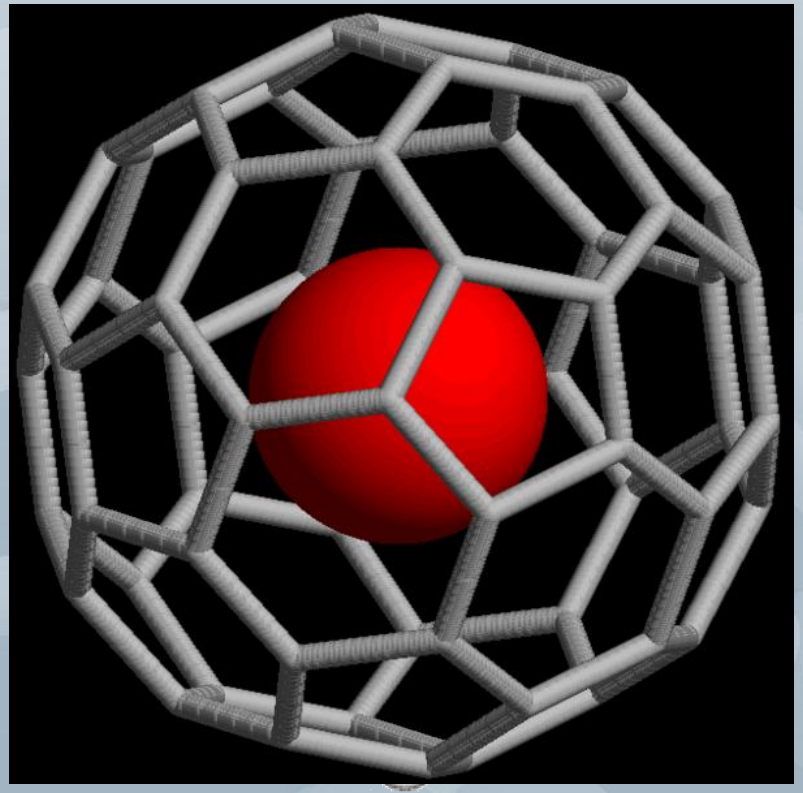
Buckyworld. A new highly-conductive material consists of a crystalline network of negatively-charged buckyballs (black) with positively-charged lithium ions (blue) inhabiting the spaces between them (pink). The lithium ions move easily through the structure. (See animation of the rotating structure below.)





Endohedral fullerenes

$X@C_{60}$



Production methods:

- **Directly in the reactor but in the presence of the atomic species to be trapped**
- **Treatment at high temperatures and pressures**
- **Cage opening with a chemical approach**

Nanopharmaceuticals, Quantum Computing ecc.



Fullereni endoedrici

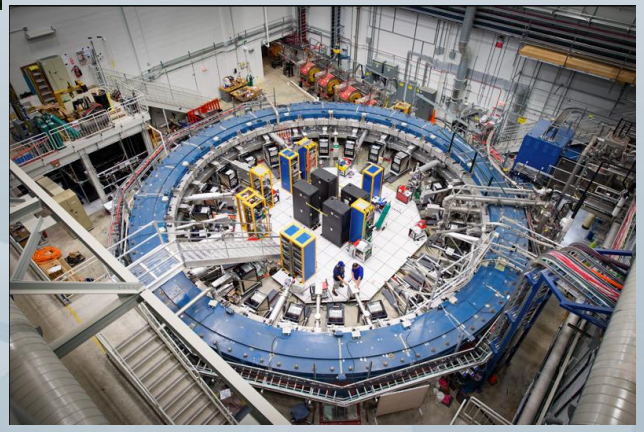
$X@C_{60}$

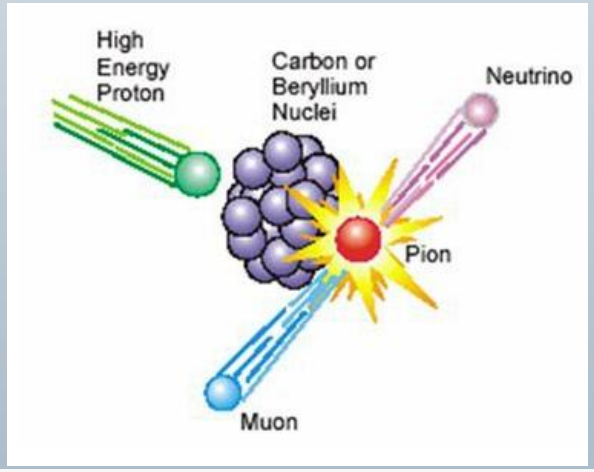
Reported Species

I	II	IIIb	IVb	Vb	VIb	VIIb		VIIIb		Ib	IIb	III	IV	V	VI	VII	0
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	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	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac**	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub		Uuq		Uuh		
Lanthanides *			Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
Actinides **			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

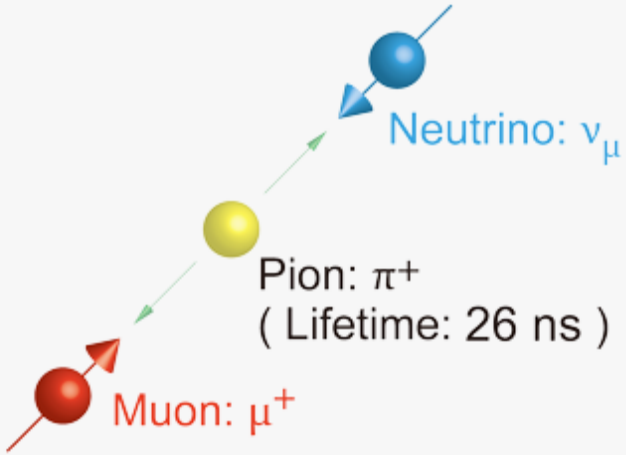


μSR



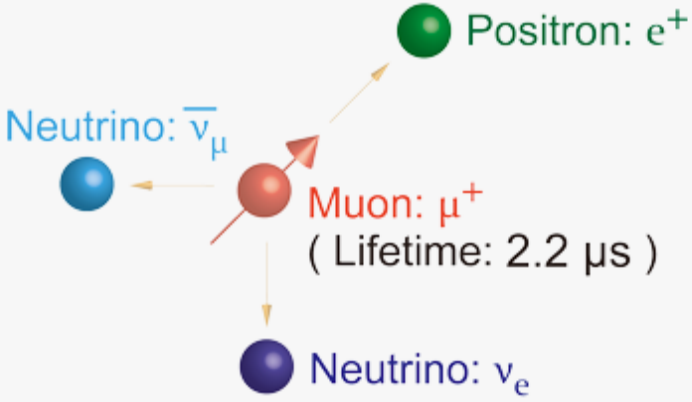


$\pi^+ \rightarrow \mu^+ + \nu_\mu$



Muon spins are 100% polarized.

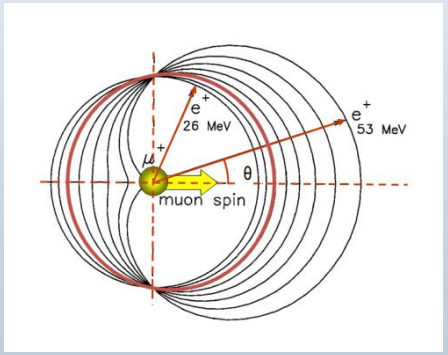
$\mu^+ \rightarrow e^+ + \nu_e + \overline{\nu}_\mu$



Positron selectively emitted in the direction of the muon spin.

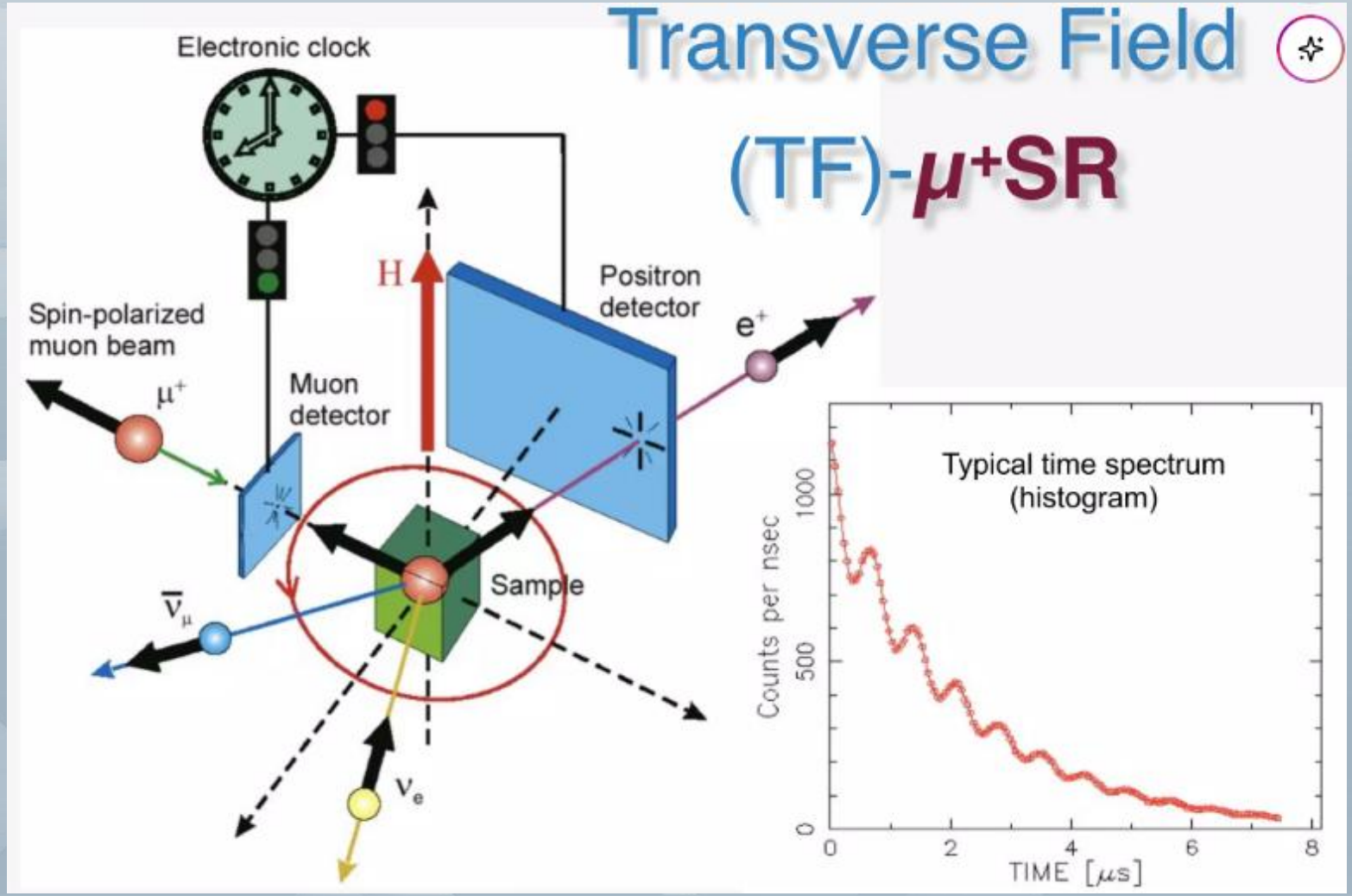


μSR



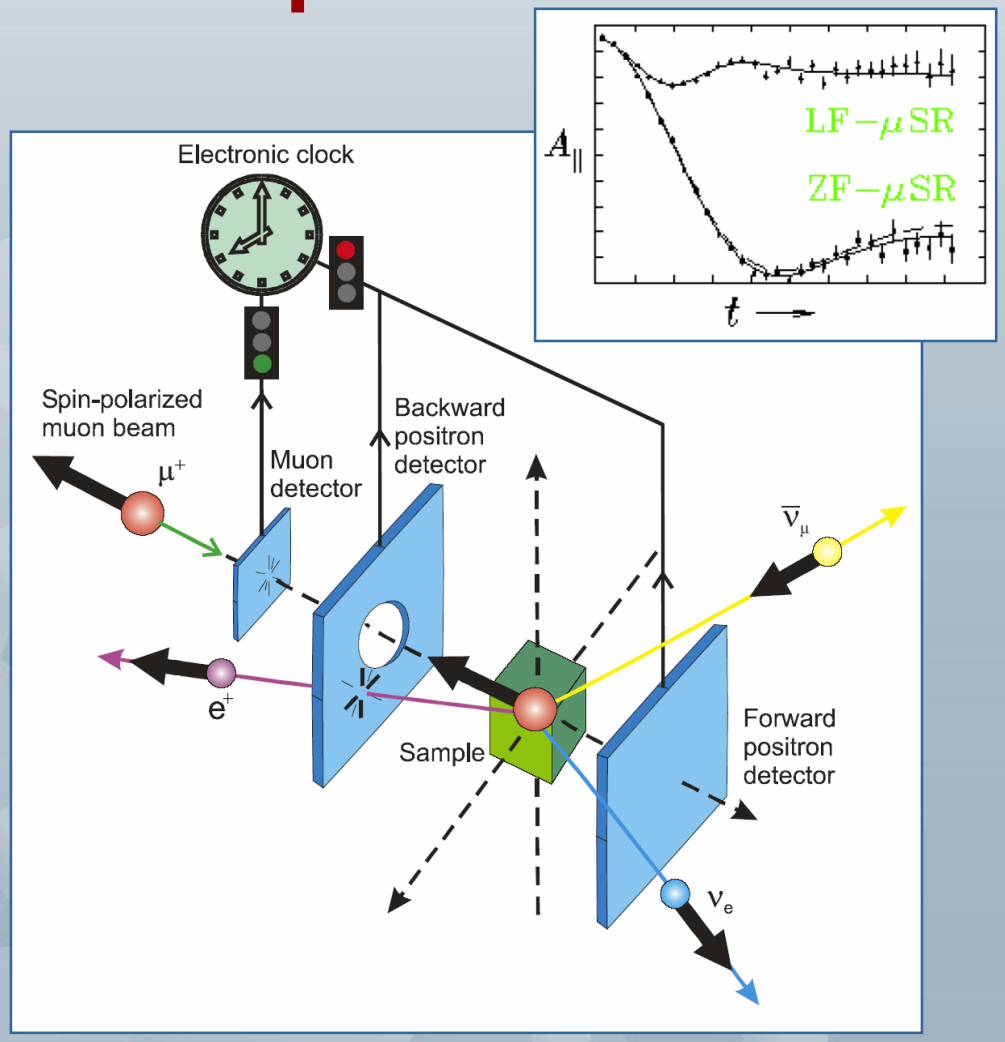
Transverse Field

(TF)-μ+SR





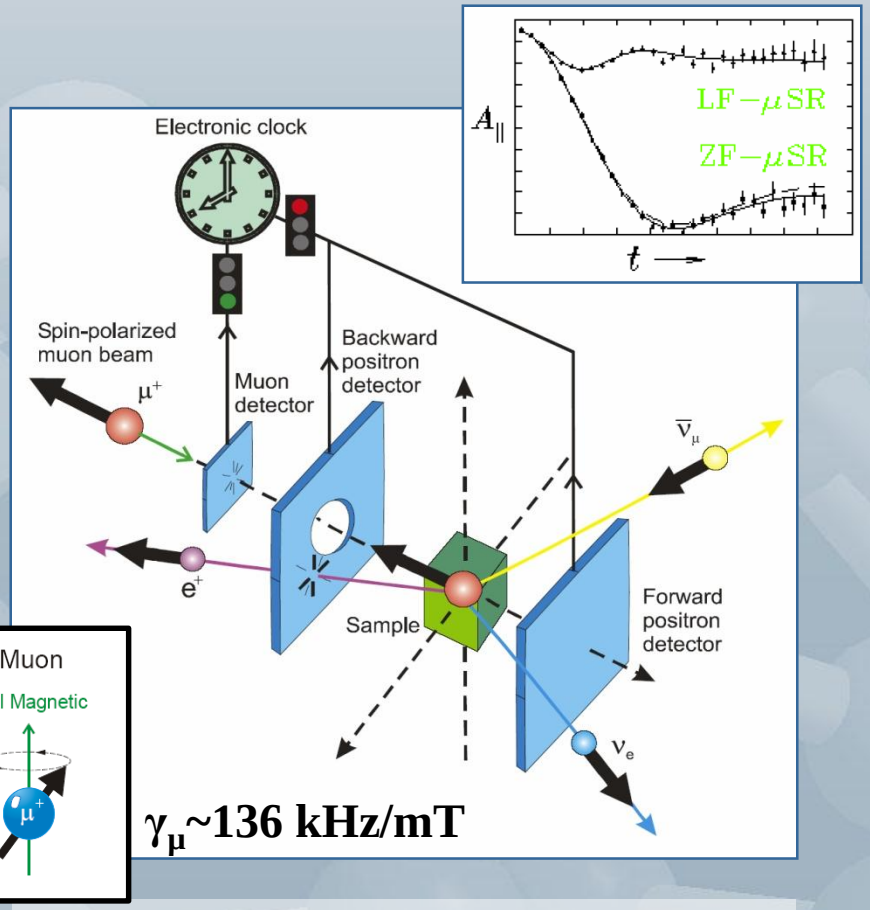
μSR



Schematic LF (ZF) μSR experiment



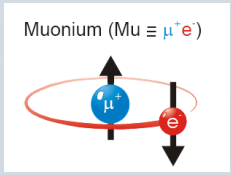
μSR



Schematic LF (ZF) μSR experiment

- Muons ($I = ½$, $\tau \sim 2.2$ μs):
  - Light isotope of proton
  - Implantation of polarized μ^+
  - Localise at an interstitial site
  - Decay: emitted positron to spin direction of μ^+
- Muonium:

Insulators:



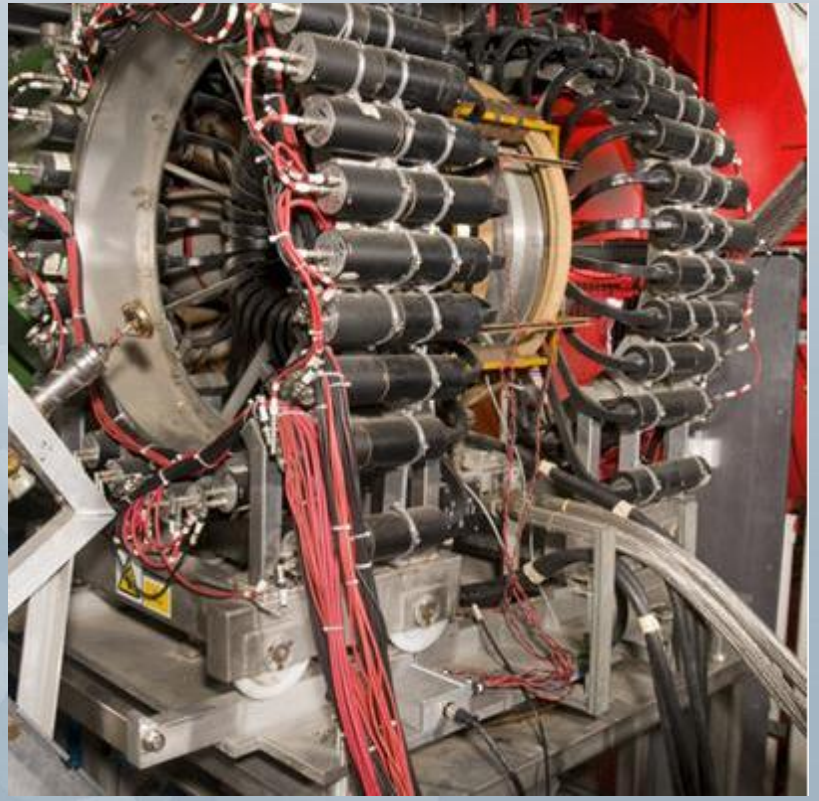
≡ **Hydrogen**

$$H/\hbar = -\gamma_\mu \boldsymbol{I}\cdot\boldsymbol{B} + \gamma_e \boldsymbol{S}\cdot\boldsymbol{B} + A\boldsymbol{S}\cdot\boldsymbol{I} = -\gamma_\mu I_z B + \gamma_e S_z B + A\boldsymbol{S}\cdot\boldsymbol{I}$$



μSR







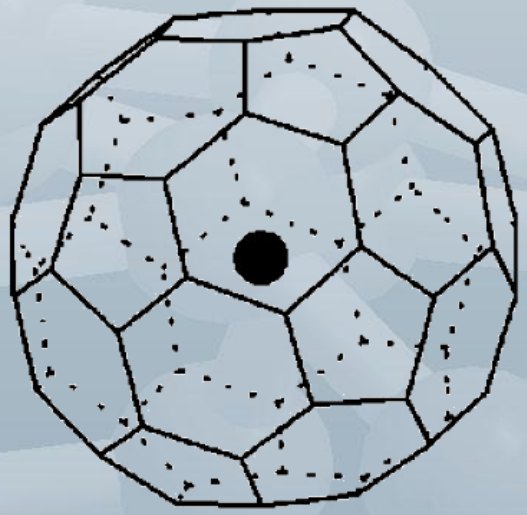
μSR in the world

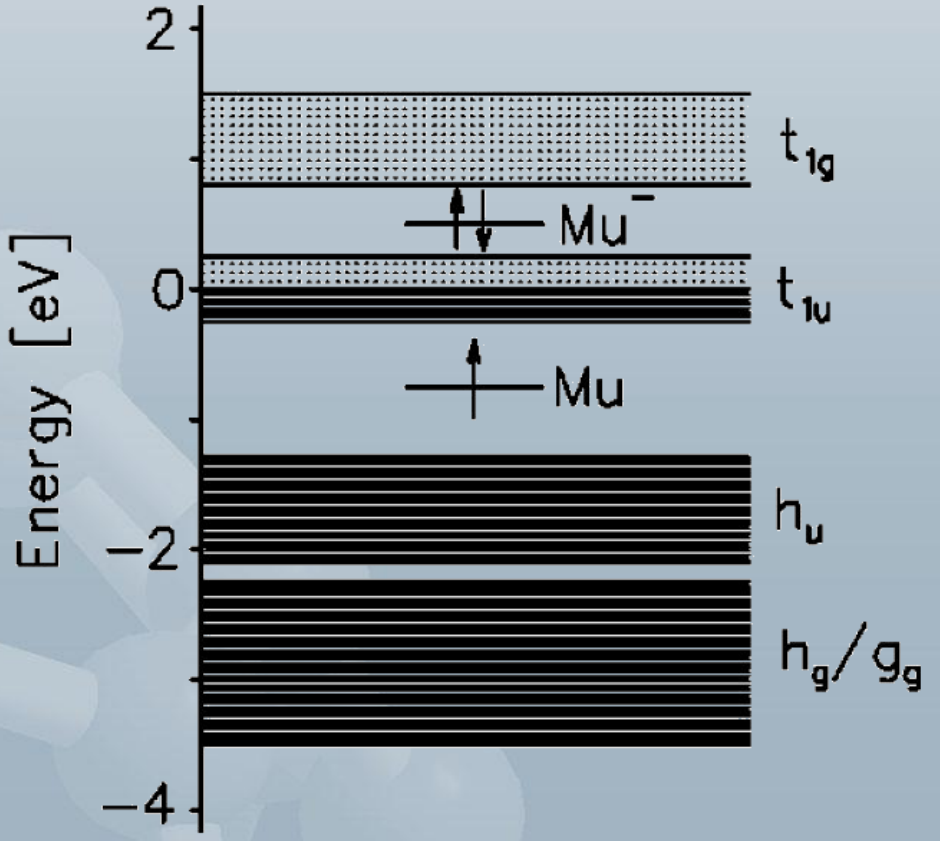


Facility	Proton Energy	Proton Power	Repetiton Rate	Muon Rate	Experiments
MUSE[1]	3 GeV	1 MW	25 Hz	2×10^8 μ^+/s	μSR, Muon g-2/EDM,COMET, MuSEUM
MELODY[2]	1.6 GeV	500 kW	2.5 Hz	1×10^6 μ^+/s	μSR
ISIS[3]	800 MeV	160 kW	50 Hz	6×10^5 μ^+/s	μSR
CERN[4]	400 GeV	0.5 kW	DC	1×10^8 μ^+/s	MuonE, NA64μ
SμS[5]	590 MeV	1.4 MW	53 MHz (DC)	2×10^8 μ^+/s	μSR, MIXE, muEDM, mu3e, MEG, MuLAN, Mu-MASS, MuSUN
CMMS[6]	520 MeV	75 kW	23 MHz (DC)	10^6 μ^+/s	μSR
MuSIC[7]	390 MeV	400 W	17 MHz (DC)	5×10^5 μ^+/s	μSR
CiADS[8]	600 MeV	3 MW	DC	5×10^{10} μ^+/s	μSR
HIAF[9]	Ion / proton (9.3 GeV)		Pulsed / DC	8×10^6 μ^+/s	μSR, muongraphy, BSM search
SMS[10]	Electron (8 GeV)		50 kHz	3×10^6 μ^+/s	μSR, muEDM, MACE



$Mu@C_{60}$





$Mu@C_{60}$: also present in A_3C_{60} in which it shows a particular stability due to a weak interaction with the conduction band