

Molecular Semiconductor Fullerite C₆₀



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Outline

New allotropic forms of carbon

Fullerene C₆₀ molecule; scientific issues and possible applications

Fullerite C₆₀: energetics, thermodynamics, rotational dynamics

Roto-electric effect

Two types of disorder

Effect of orientational ordering on other properties

Diffusion phenomena

Saturation kinetics

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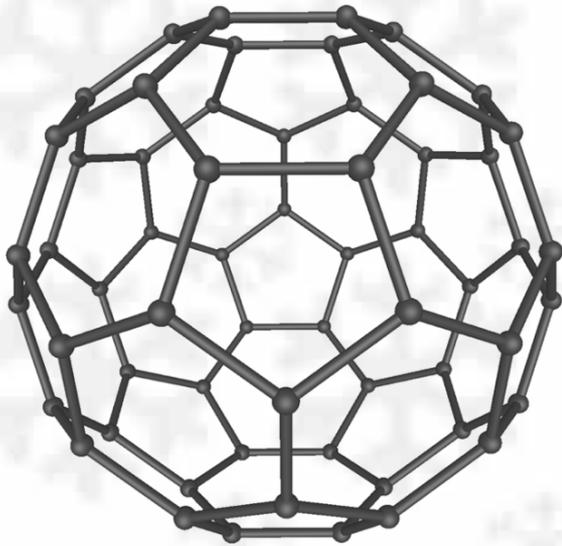
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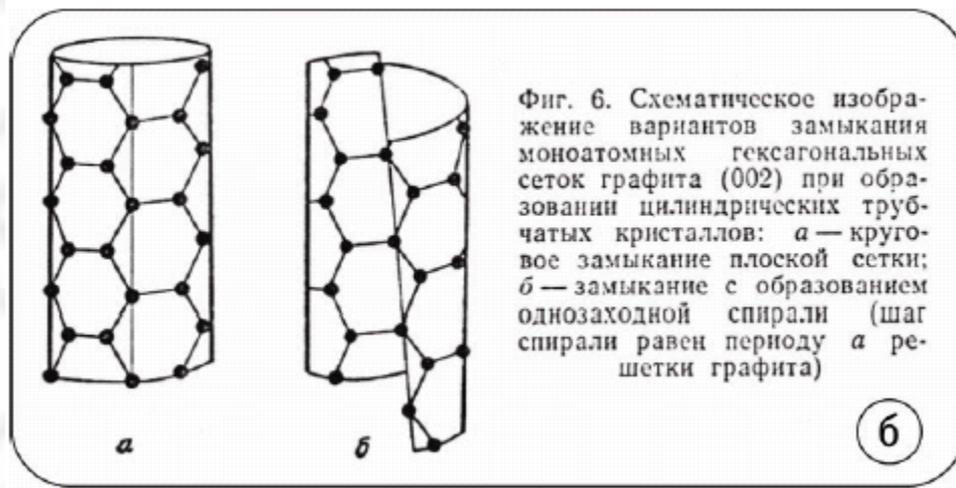
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Funding: Science and Technology Center in Ukraine (grant 2669)
Ukrainian-Austrian Collaboration Program (grant M/140)

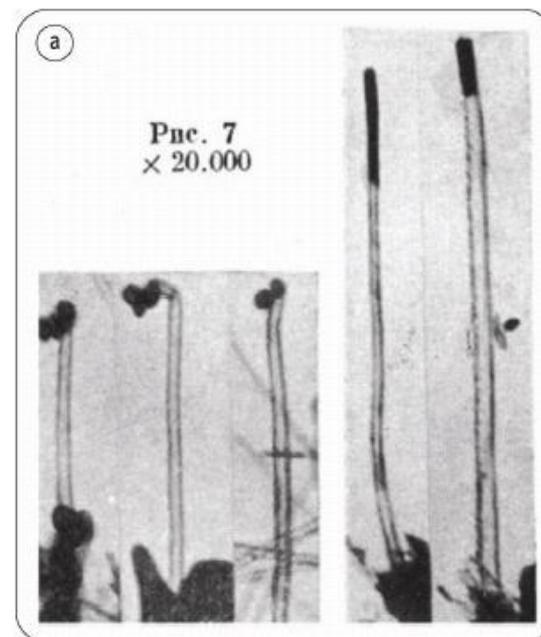


Fullerenes have been discovered in 1985 by **Robert Curl, Harold Croto, and Richard Smalley** and named after Richard Buckminster Fuller fullerenes or bucky-balls. In 1996 these scientists were awarded the Nobel prize

C_{60} molecule is an ideal truncated icosahedron, formed by 12 pentagons and 20 hexagons with the respective number 5-fold and 3-fold (not 6-fold !) axes.



⁴Нестеренко А.М., Колесник Н.Ф., Ахматов Ю.С., Сухомлин В.И., Прилуцкий О.В. и др. "Известия АН СССР. Серия Металлы", 1982, № 3.

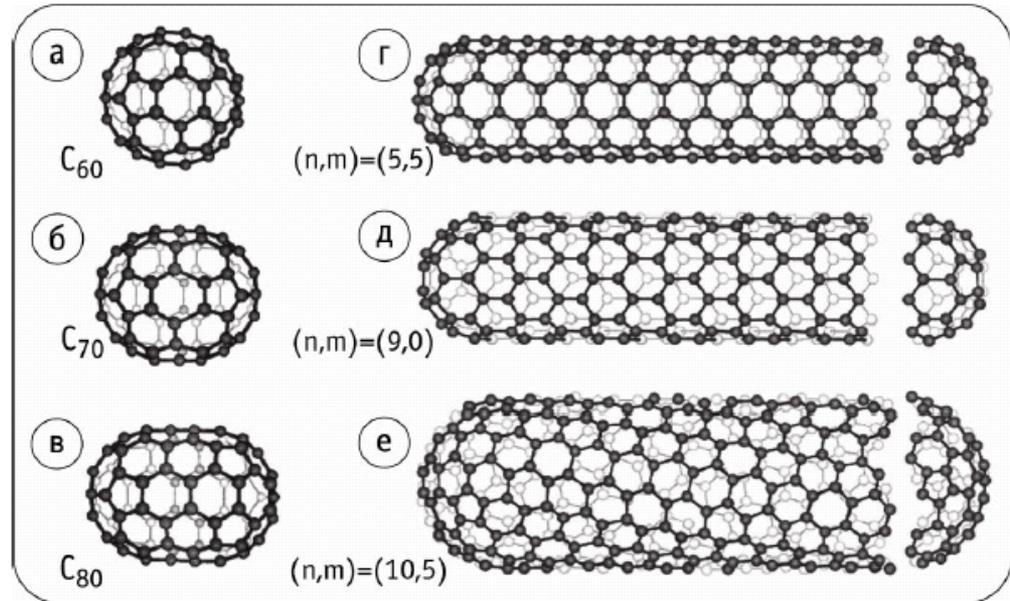


New allotropic forms of carbon



1. Fullerenes

2. Nano-tubes



3. Graphene, a one-atom-thick planar sheet of sp^2 -bonded carbons

4. Astorlenes, self-connected tubular torus, a doughnut (or Russian publik)

Possible applications



Fullerene C_{60} can be utilized in applications for these areas:

- Combined with porphyrin, ferrocene, etc. in supramolecular structures for various electrical technologies (molecular wiring in batteries, switching devices, variable capacitors)
- Conversion of photon energy to electricity (wide response spectrum, high light-to-current transformation efficiency above 50% etc.)
- Medicine (transporting carrier of medical molecules)
- Hydrogen energetics (as part of the media for storing molecular hydrogen)

One of the important properties of the fullerene molecule in various combinations is its ability to slow down the annihilation of separated charges. This is true for separate molecules in supra-structures and for fullerite, especially in film forms.



Charge distribution

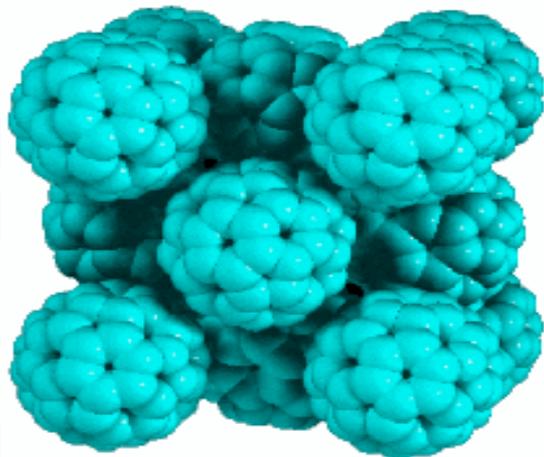
Bonds within a **hexagon** are not equivalent: the bonds shared by two neighboring hexagons are double; the bonds shared by a hexagon and a **pentagon** are single. It means that every hexagon has an excess of electrons while every pentagon has a deficit of electrons.

Charge distribution anisotropy

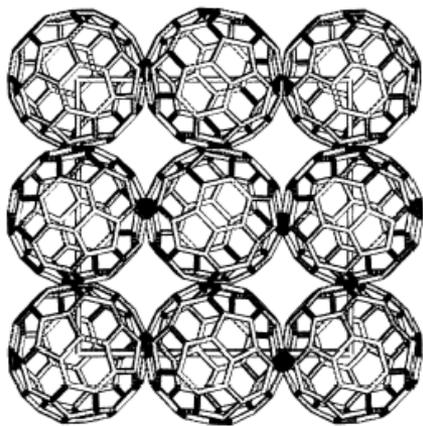


Anisotropy of intermolecular charge transport

Фуллерит C_{60} , энергетика, термодинамика, вращательная динамика

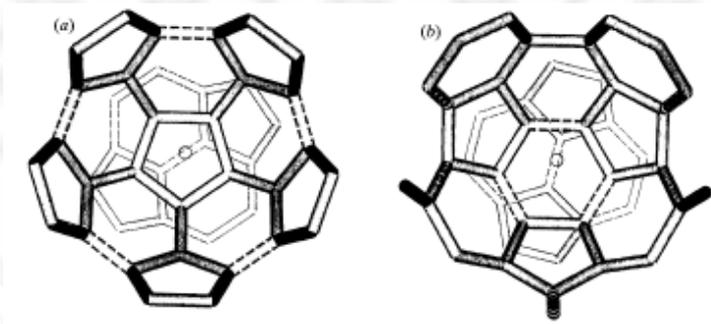


At room temperature, C_{60} molecules rotate fast (reorientation times below 8 ps): the charge distribution anisotropy at atomic level averages out to zero and C_{60} forms a fcc (Fm3) lattice, mainly owing to vdW forces, with a lattice parameter of $a \approx 14.16 \text{ \AA}$ and a nearest neighbor distance of about 10 \AA .

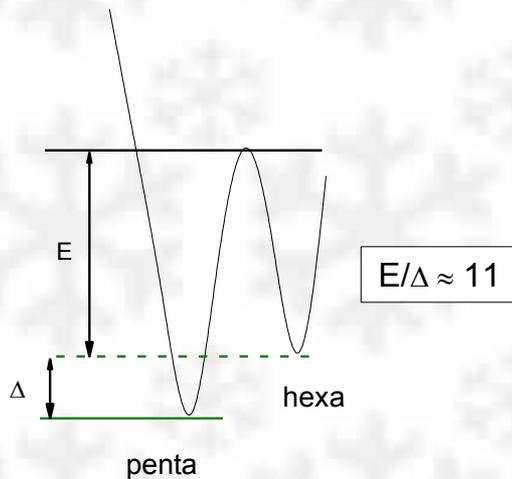


At 260 K the almost free rotation ceases, the crystal transforms from fcc (Fm3) to simple cubic (Pa3) lattice with 4 sublattices, in which the 5-fold axes are directed along the cube diagonals. The molecules go on rotating, yet not freely but around certain axes, performing jump-like reorientations.

Projection along (100)



The crystallographic motive is such that the double bond (excess of electrons) of a C_{60} molecule, which below $T_c = 260$ K performs infrequent reorientations, can face a **hexagon** (excess of electrons) of the neighboring molecule or its **pentagon** (deficit of electrons). Hence, the energetic preference of the so called pentagon mutual orientation.

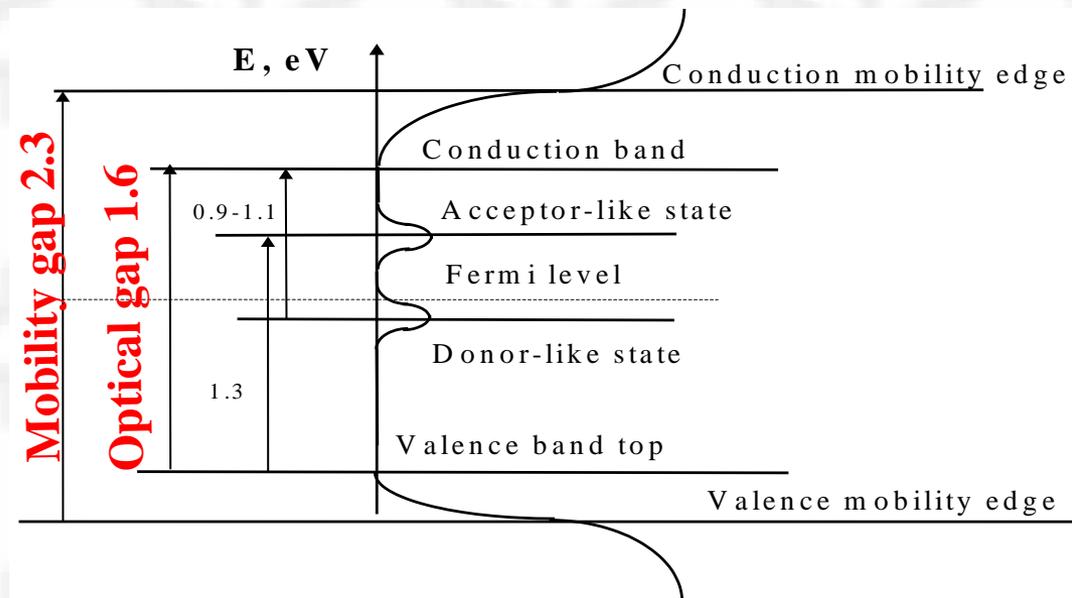


Slightly below T_c the **hexa** and **penta** states are occupied almost equally. As the temperature is lowered, the fraction of pentas increase but the reorientation frequency, which is proportional to $\exp(-E/kT)$, drops and at 95 K the reorientations stop: the system finds itself in the state of orientational glass.



As follows from calculations for $T = 0$ and experimental data, given a complete preferable mutual molecular orientations in pure bulk crystalline C_{60} , the fullerite is a typical semiconductor with a forbidden band width of about 2,3 eV and half filling.

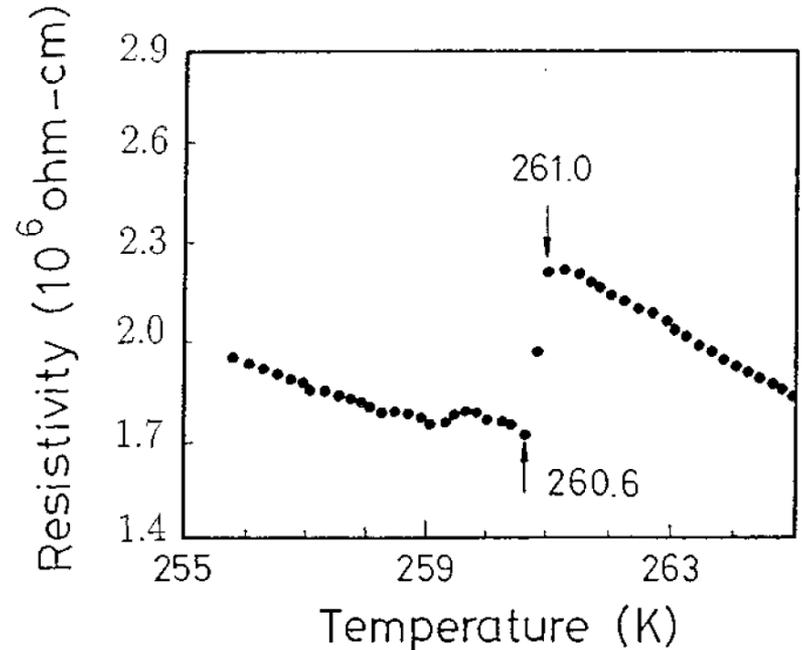
In films, donor and acceptor systems of different nature are inevitably present.



Roto-Electrical Effects



In a bulk high-quality polycrystal [Chiu et al., Appl. Phys. Lett. (1996)] the conductivity suffers an appreciable (40-70%) positive jump when going down in temperature across the critical temperature T_c



«Our result clearly indicates that the underlying mechanism of the PPC effect involves the motion of the C60 molecule.»



Results concerning the effect of orientational ordering on charge transport in C_{60} **films** were in shear contradiction between themselves, depending on sample neatness morphology, film preparation techniques, measurement schemes, etc.

As in crystals (positive jump)

Mort et al., Appl.Phys.Lett. (1996)

H.Yamaguchi et al. J.Phys.Soc.Jpn. (1995)

Balberg et al, Fuller.Sci.Technol. (1998)

No effect

Hosoya et al., Phys.Rev.B (1994)

Kazaoui et al., Solid State Commun. (1994)

Balberg et al., Fuller.Sci.Technol. (1998)

Opposite effect

Kaiser et al., Solid State Commun. (1993)

H.Yamaguchi et al., J.Phys.Soc.Jpn. (1995)

Chiu et al., Jpn.J.Appl.Phys. (2002)

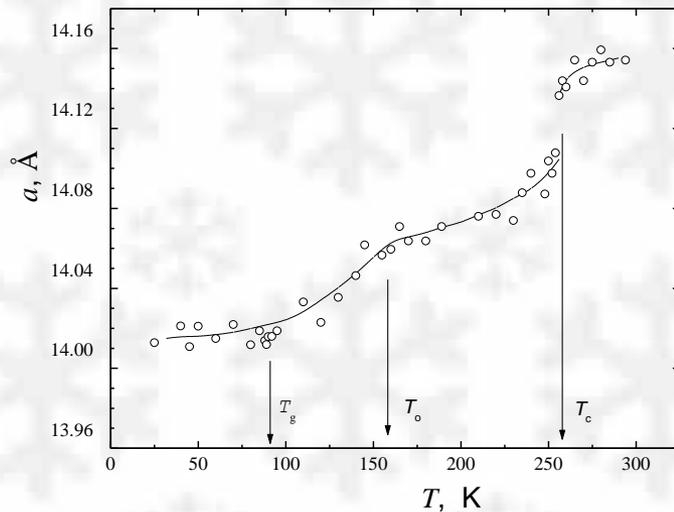
Структурные исследования

Katz, Faiman, Isakina, MAS, *et al.* J.Appl.Phys. **93** (2003)



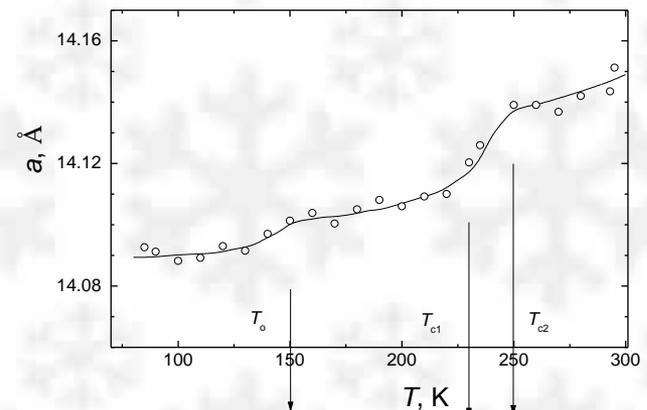
High-quality films

Good quite narrow Bragg reflections.
Clear-cut lattice parameter jump across T_c ($\Delta a/a = 0,22\%$ instead of $\Delta a/a = 0.32\%$ in bulk samples)



Low-quality films

Broadened reflections, intensive halo due to amorphous fraction. No lattice parameter jump at the transition

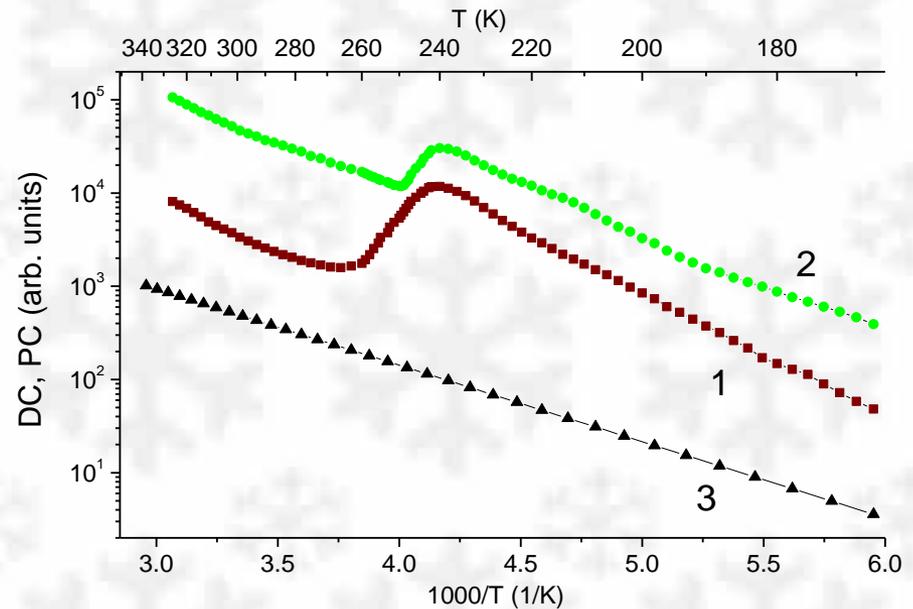


Electrical measurements



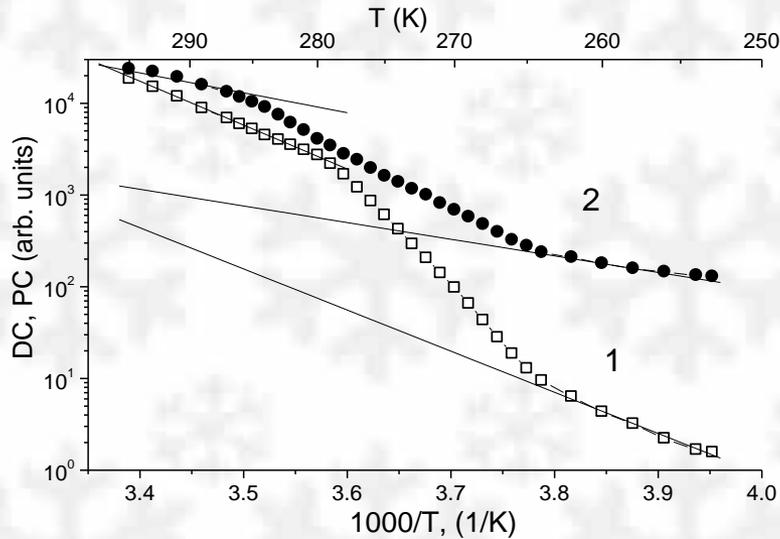
High-quality films

Temperature dependence of the **dark current** (1) and **photocurrent** (2) for a textured large-grain C_{60} film on mica. A **positive surge** near T_c .



Curve 3 is for the same film sample after a 15 minute saturation with oxygen at 100 bar.

Low-quality film samples



When cooled below the orientational ordering point, the currents drop faster with lowering temperature

1 – dark current

2 – photo current

C_{60} SPV Spectra

Surface Photo Voltage Spectroscopy

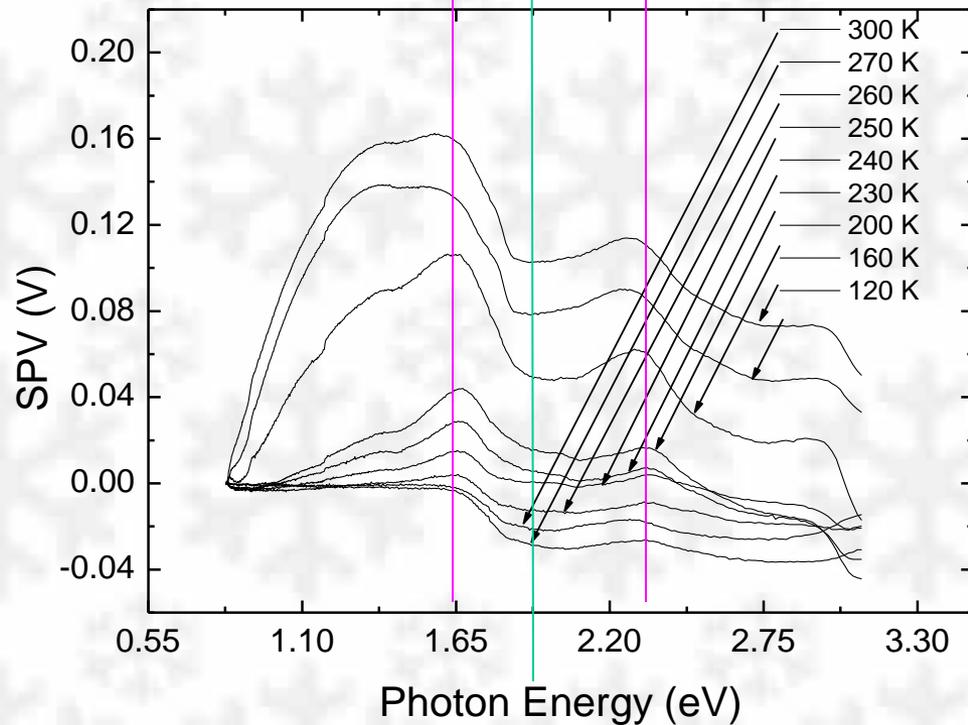


Sub-gap
photoexcitation

I

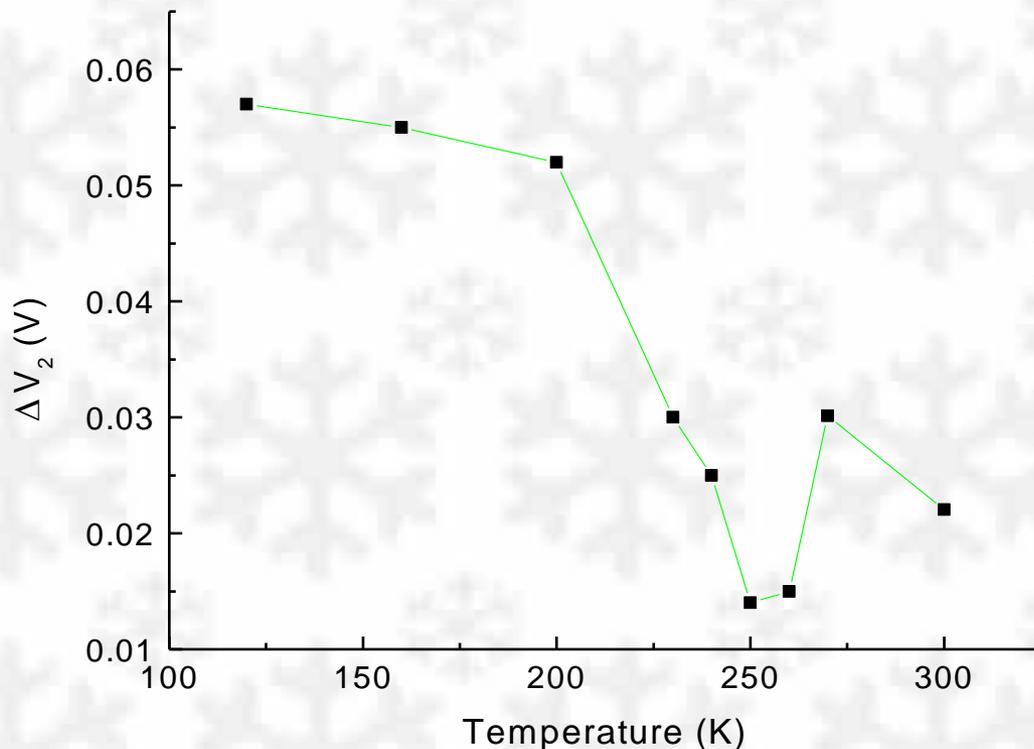
III

Valence-to conduction
inter-band excitation





All SPV regions are in correspondence with the well resolved relevant features in photo-conductivity spectra as found by different groups [cf. A.Hamed, in *Organic Conductive Molecules and Polymers*, ed. S.Nalva, Wiley (1997)]. This correspondence suggests that **SPV spectra can be employed to monitor the bulk electronic properties of films.**



Non-monotone behavior of SPV signal across the transition qualitatively reproduces the temperature dependence of the dark conductivity

Nature of anomalies



Since the characteristic energy of the intermolecular tunneling is 0.02-0.04 eV, while the intramolecular attraction energy is 0.1-0.3 eV, solid C_{60} can be treated as a system with strong coupling and with relatively strong electron correlations.

Ignoring the correlations, the Hamiltonian of an electron in the conduction band is

$$H = T + V$$

Here V describes **(quasi)-static disorder**, i.e. scattering on phonons and lattice irregularities, and T is the kinetic term of tunneling from site i to site j

$$T = \sum_{ij} t(\mathbf{w}_i \mathbf{w}_j \mathbf{n}_{ij}) a_i^+ a_j$$

The jump probability t essentially depends on the mutual orientation of neighbor molecules i and j . This term is the source of **dynamic disorder**.

Summing up, the unusual property of fullerite as a current-carrying solid consists in that the mutual orientations (which govern intermolecular transport) are controlled by an independent rotational dynamics

Variation of the conductivity is determined by the varying relation of the static and dynamic disorders.



In pure systems (**high-quality** films), static disorder is irrelevant. So, transition to the orientationally ordered state, in which mutual orientations **favor** intermolecular charge transport, causes a conductivity surge.

In «dirty» systems (**low-quality** films), scatterers are numerous and strong. Transitions to any ordered state, in which all motions are progressively hindered, will generally entail strengthening (previously rotationally averaged close to low levels) of irregularities. This, in particular, was documented through an appreciable broadening of Bragg reflections across the ordering transitions in our “dirty” samples or when entering the region of the orientational glass in “good” samples. Then one could expect a certain increase of the efficiency of scatterers and, as a consequence, a decrease in the conductivity.

Presence of oxidizers (oxygen or iodine) not only drastically changes the band structure but also tends to fix molecular positions and orientations.

Intermediate conclusions



A complex of specially planned studies of the roto-electric effect in pure C_{60} films have been carried out. As a result, a model was suggested which consistently explains the basics of the phenomena observed as well as the existing controversies.

In high-quality films the conductivity is essentially higher in the orientationally ordered state. In films containing numerous defects an opposite effect is observed.

Our explanation is based on the fact that in C_{60} semiconductor two types of disorder can compete, the effect of which depend differently on the temperature and the structure morphology and defects of C_{60} films.

Utilization of the promising properties of C_{60} in any form, especially as a basis of various semiconductor devices encounters certain problems

Problems to tackle



Theory

Overlap integral \mathbf{t} is not known as a function of mutual molecular orientations

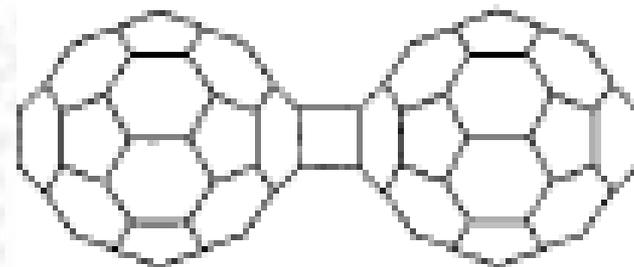
In the orientationally ordered state the conduction problem is clear [cf. Loktev et al., Fiz. Nizk. Temp. (2002)], whereas for the ordered or intermediate cases no theory is available

Polymerization

Two double bonds in molecules in a hexagon configuration can open up to form a covalently bonded (polymeric) dimer or longer polymeric chains.

High temperatures and/or pressure and ultraviolet are the hazards promoting polymerization

The dimer state is negligible higher in energy compared to the ground state of two non-bonded molecules; these two state are also close in space [Suzuki et al. (2000) Phys. Rev. B].



Mechanical softness

The material is inconveniently soft

Tackling the technologic problems with C_{60} (oxygen poisoning, ultraviolet hazard, softness) involved a few protection measures (coating, implantation of strengthening elements, etc.), which all proved inefficient.



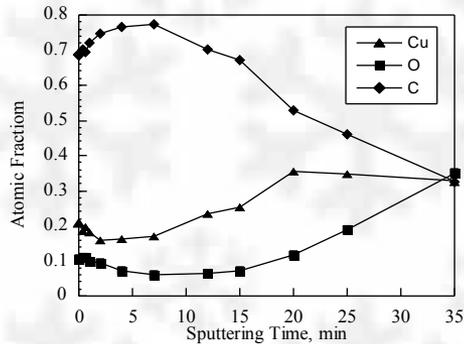
Our main idea was:

To saturate fullerite C_{60} with a dopant which would prevent oxidized poisoning, would strengthen mechanically and – simultaneously – would not essentially deteriorate its electric properties.

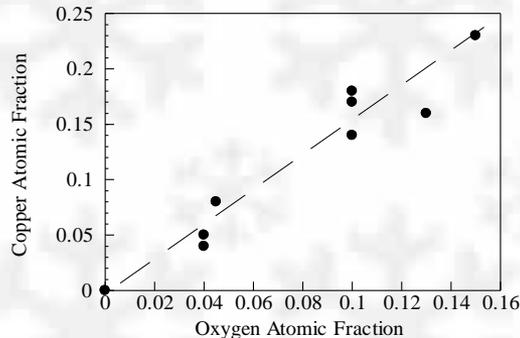
Sequence of studies:

1. Detailed saturation kinetics for various chemically neutral species
2. Strength characteristics and the means to affect them
3. Comparative resistometric measurements

Joint penetration from two sides of C₆₀ films of O₂ molecules and Cu atoms



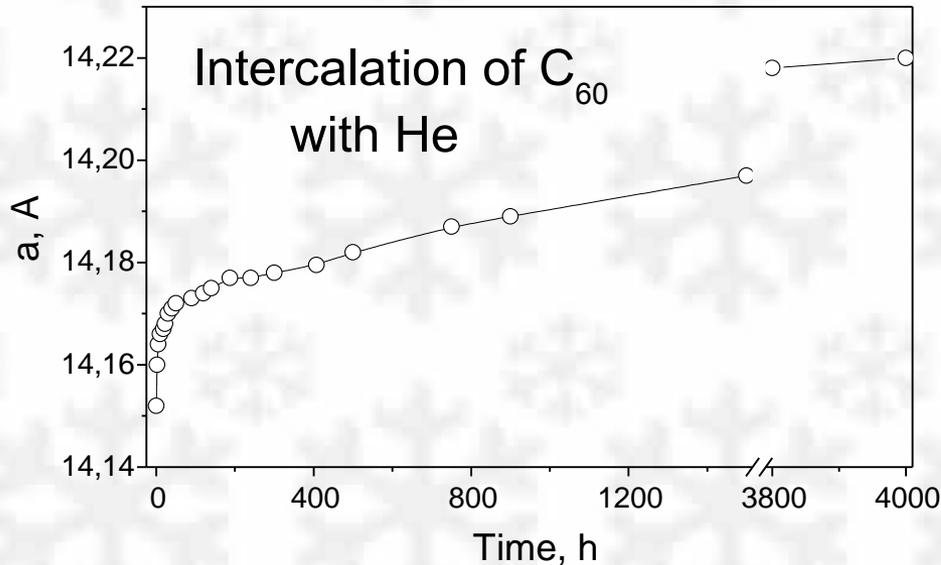
Distribution of atomic fractions of Cu, O, and C (in units corresponding Ar ion impact time) in a C₆₀ film on Cu substrate after a 10 months of exposure to air.



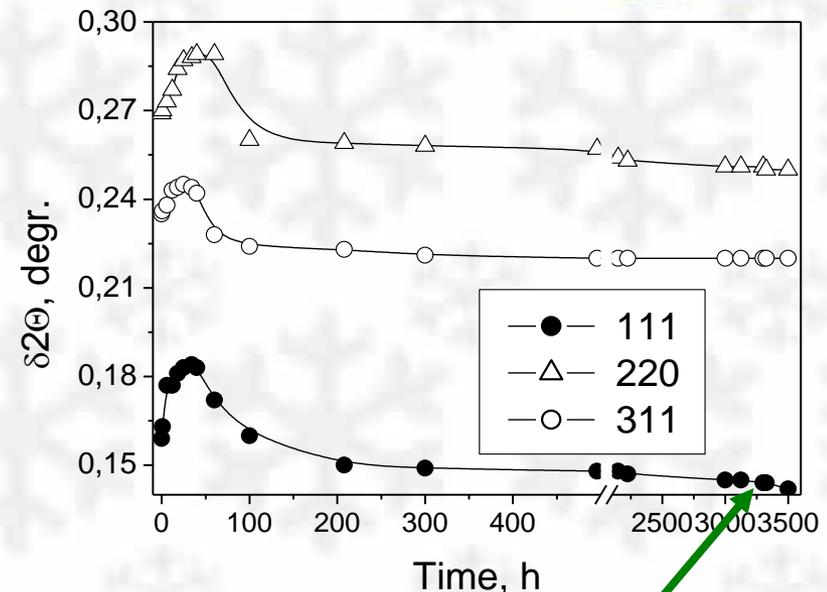
Correlation between atomic fractions of Cu and O as measured at a fixed depth (after 1 min sputtering) at several points of the film

Conclusion: because of the counter-flow up-diffusion (double electric layer) the fullerite with an oxygen inflow from the “external” film side tends to “eat up” copper and other metal substrates at a rate 10-100 Å per month

Saturation with helium: two-stage process



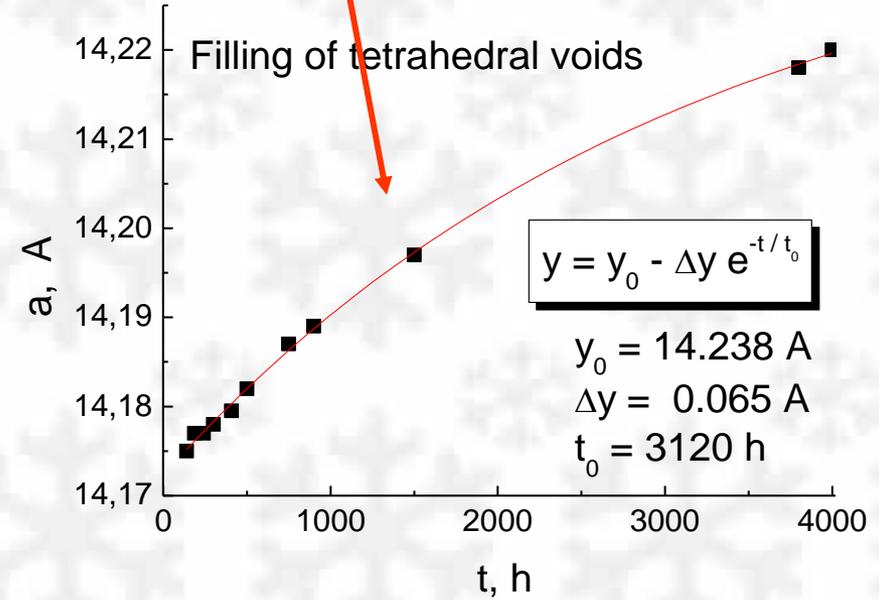
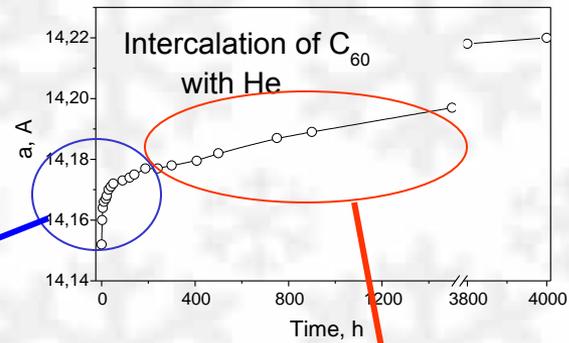
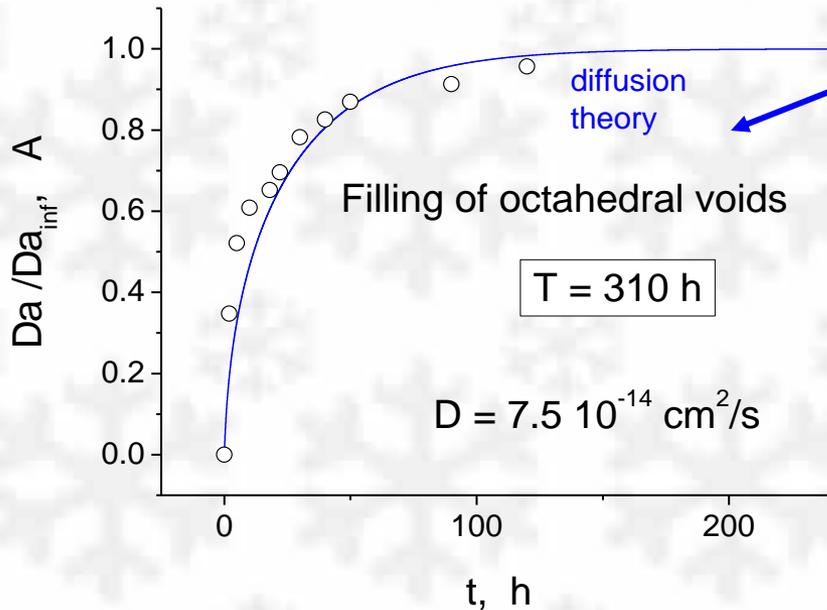
Lattice parameter vs. saturation time;
pressure ≈ 1 bar; room temperature



Reflection width vs. intercalation
time

Conclusion: since the reflections are appreciably and systematically narrower upon filling than in the initial state and remain so after degassing, saturation tends to “purge” part of the defects (dislocations) from crystallites.

Filling of voids

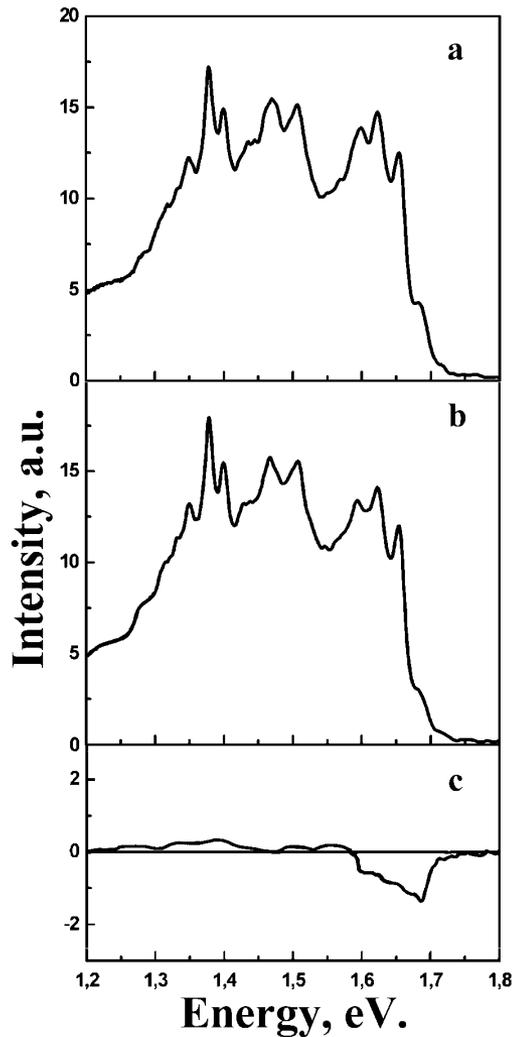


Conclusion: saturation with helium proceeds in **two stages**: first, octa-voids are filled (inhomogeneously, from surface into inside) and then tetra voids are filled, homogeneously over the volume.

Effective infusion to tetra-voids is about $10^{-19} \text{ cm}^2/\text{s}$, i.e. by 5-6 orders slower, than to octa-voids

rattle

Comparison of luminescence spectra



a) pure C_{60}

b) C_{60} saturated by helium during 440 h under normal conditions. Octa-system is virtually completely filled

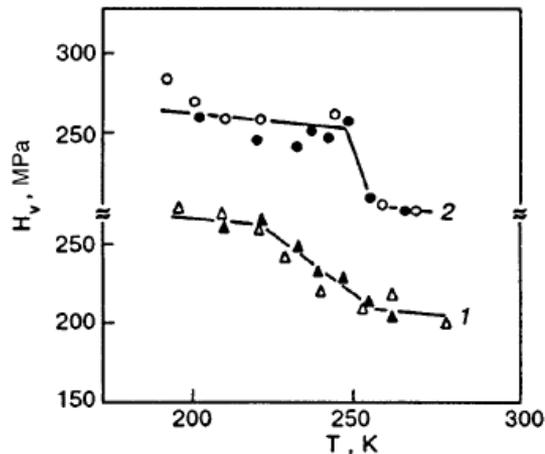
c) Difference luminescence spectrum (a) - (b)

Finding: luminescence intensity of saturated C_{60} is lower **exactly** in the range where emission from polymeric dimers is expected.

Conclusion: C_{60} with He in octa-voids contains **less** dimers than the starting material.

Remember also that saturation purges defects out of sample.

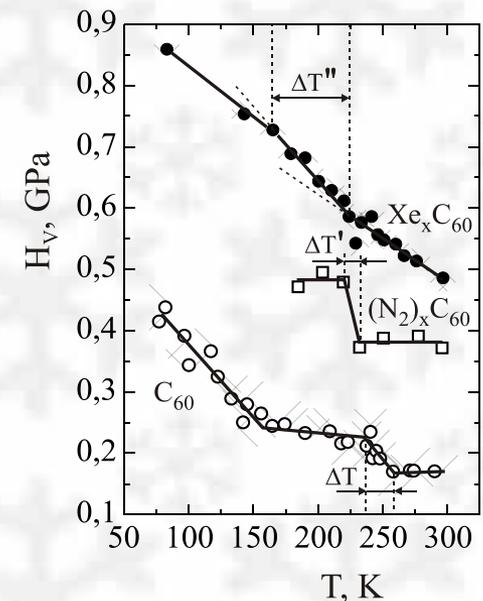
Correlation between hardness of C_{60} and orientational ordering



Temperature dependence of the microhardness close to the orientational phase transition (260 K) ориентационного фазового перехода. Curve 1: polished non-annealed sample; curve 2: polished and then annealed (for 24 h at 10^{-3} Torr and 300 K) sample.

The correlation is evident; it is more clearly seen in a pur (without oxygen) sample

Saturation with chemically neutral particles entails an essential hardening of C_{60}



Conclusions



1. Investigation into the effects of orientational ordering on the conductivity of C_{60} film allowed us to explain the relevant roto-electrical phenomena in this molecular semiconductor. The explanation is based on the idea about two types of disorder.
2. The saturation process of C_{60} with helium and hydrogen was studied, showing that for He two stages exist. Room-temperature diffusion coefficients have been determined. The cause behind the anomalous volume **in**crease of C_{60} during infusion of particles (He), smaller than the size of octahedral voids, was explained.
3. Saturation with helium and neon was found to purge part of defects and to enhance the ability of C_{60} to counteract polymerization by light.
4. It was found that orientational ordering essentially influences the hardness of C_{60} . Saturation of this material with chemically neutral particles results in a substantial increase of its hardness



Thank you for your attention

Experimental



Sample preparation

Two types of films were grown, both about 100 nm thick. One (**high crystallinity**) on mica, the other (**low crystallinity**) on glass, as in [Yagotintsev et al., Physica B (2003), [Katz et al., Thin Solid Films \(2000\)](#)]

Electrical measurements

Dark-current and photo-current measurements at 130-310 K on samples that underwent preliminary in situ at 150 C during 2 hr. The low voltages used ensured Ohmic regimes [[Katz et al., J. Appl. Phys. \(March 2003\)](#), Yagotintsev et al., Physica B (2003)].

Surface Photo Voltage Spectrometry was used [[Katz et al., J. Appl. Phys. \(December 2003\)](#)] in order to check the conclusions of the current measurements for consistency.

Structure studies

Temperature resolved (80 to 300 K) powder x-ray diffraction

Motivation



Basic aim: to **establish correlation** between the morphology / structure state and charge transport properties, especially, with varying orientational order

What to avoid:

- (i) Oxygen poisoning of the film surface
- (ii) Metal substrates

Both factors influence drastically the electrical properties of films and even their structure, especially in combination

Trapping present

$$\sigma_{DC} = e \mu n F$$

$F (< 1)$ is the dimensionless factor that accounts for carrier trapping

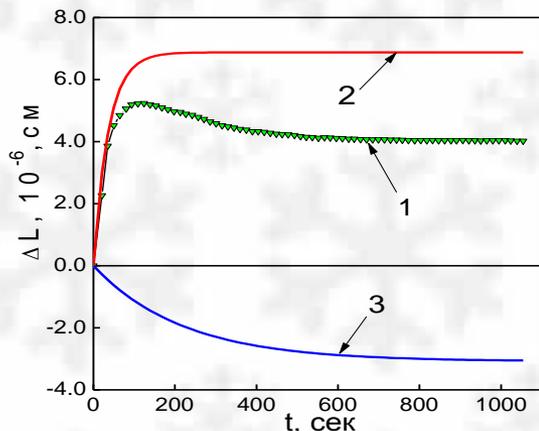


What changes across T_c - F or μ ?

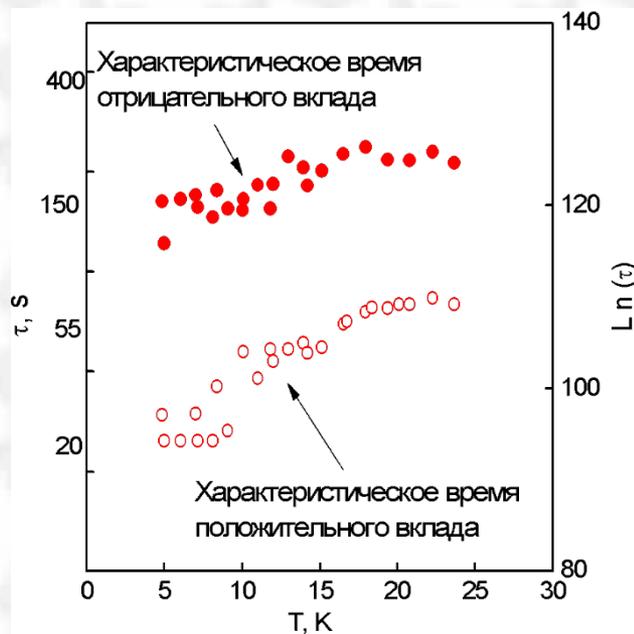
In single crystals μ is known to increase by 40-70% in the ordered state.

Of course, the trapping parameters that determine the magnitude of F (concentration, capture probability, energy distribution) may change in the same way, though a clear understanding how this could occur is absent.

КЛТР в области ориентационного стекла



В исследованных растворах газов в фуллерите C_{60} наблюдались как положительный, так и отрицательный вклады в тепловое расширение, имеющие различные характеристические времена. Показано, что положительный вклад обусловлен низкочастотными возбуждениями решетки (фононами и либронами), а отрицательный вклад, по-видимому, обусловлен туннельными переориентациями молекул C_{60}



V.G. Manzhelii, A.V. Dolbin, V.B. Esel'son, V.G. Gavrilko, D. Cassidy, G.E. Gadd, S. Moricca, and B. Sundqvist, ФНТ (2006).

