Electronic properties of partially fluorinated graphene

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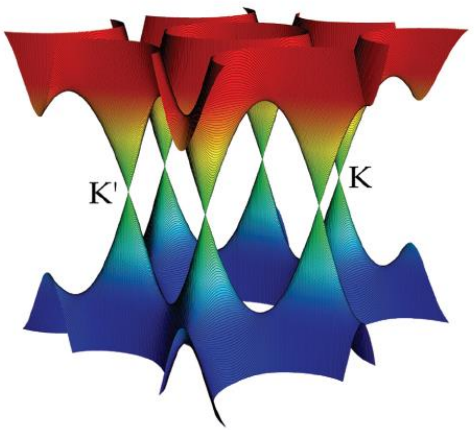
Graphene



New carbon material with unique electronic, optical and mechanical properties

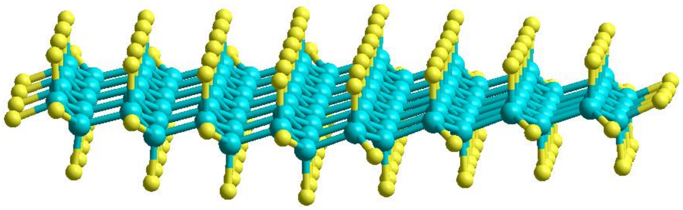
Chemical modification, what it gives ?!

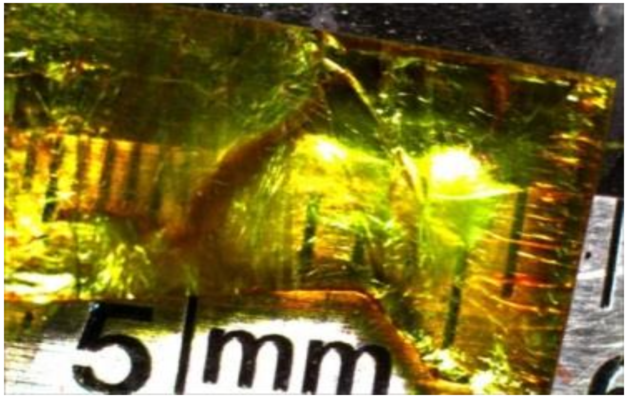
«Negative» factor:

- **Destruction of perfect system from carrier charges in graphene layer**

«Positive» factors:

- **Control of surface charge state**
- **Gap appearing and variation of value**





Synthesis of fluorinated graphite CF

High temperature fluoribation (F_2, T ~ 400°C)

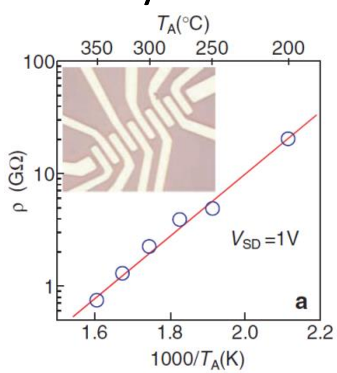
1. O. Ruff, D. Bretschneider, F. Elert, Z. Anorg. Allg. Chem., 217 (1934)
2. L.B. Ebert, J.L. Brauman, R.A. Huggins JACS, v.96, 25, (1974) 7841
3. V.K. Mahajan, R.P. Badachhape, J.L. Margrave, Inorg. Nucl. Chem. Letters, 10 (1974) 1103
4. P. Kamarchik, J. Margrave "Poly(carbon monofluoride): a solid, layered fluorocarbon" Accounts of Chemical Research, v.11, (1978) 296-300
5. Y. Kita, N. Watanabe, Y. Fujii, JACS, 101, 14 (1979) 3832

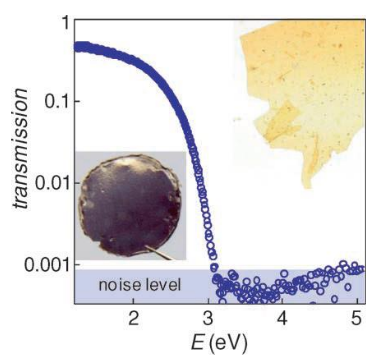
Properties of fluorinated graphite CF

Dielectric (R > 1GΩ)

The optically transparent (ΔEg > 3,8 эВ)

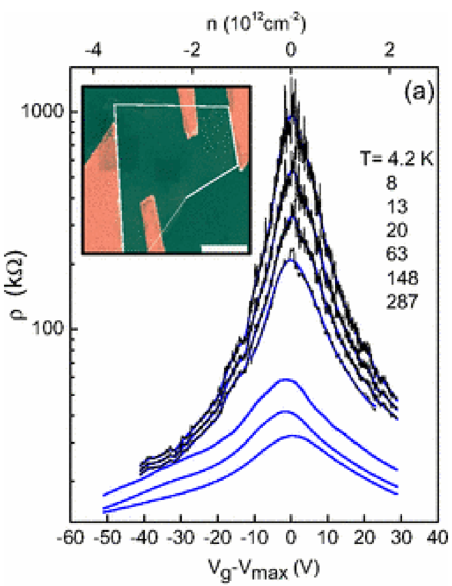
Theory calculations (ΔEg ~ 4,9 – 8,1 эВ)





Fluorographene: A Two-Dimensional Counterpart of Teflon

small 2010, 6, No. 24, 2877–2884



F. Withers, M. Dubois, A. K. Savchenko

Electron properties of fluorinated single-layer graphene transistors

Phys. Rev. B **82**, 073403 (2010)

Synthesis of C_2F fluorinated graphite

Low temperature fluorination (BrF_3)

L. Stein L. J. Amer. Chem. Soc. 1959. v. 81. № 6. P. 1273.

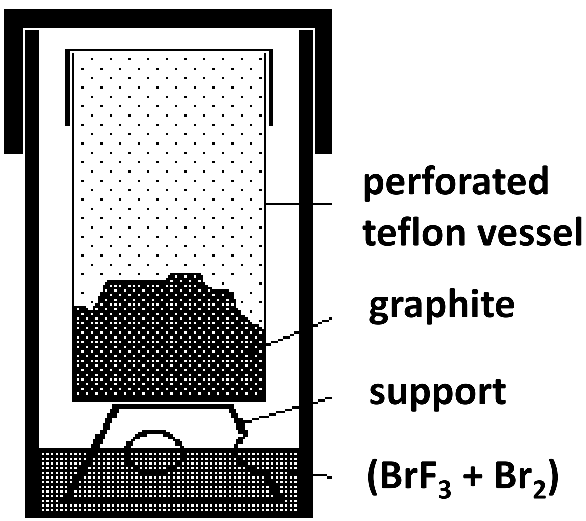
Cgraphite $\xrightarrow{Br_2}$ C_8Br

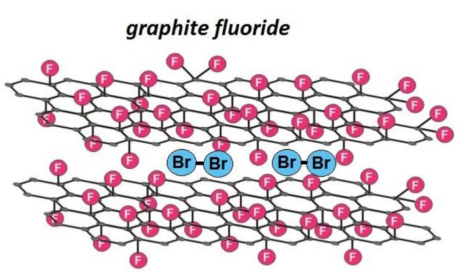
C_8Br $\xrightarrow[Br_2]{BrF_3}$ $C_2F_x \bullet yBrF_3 \bullet zBr_2$

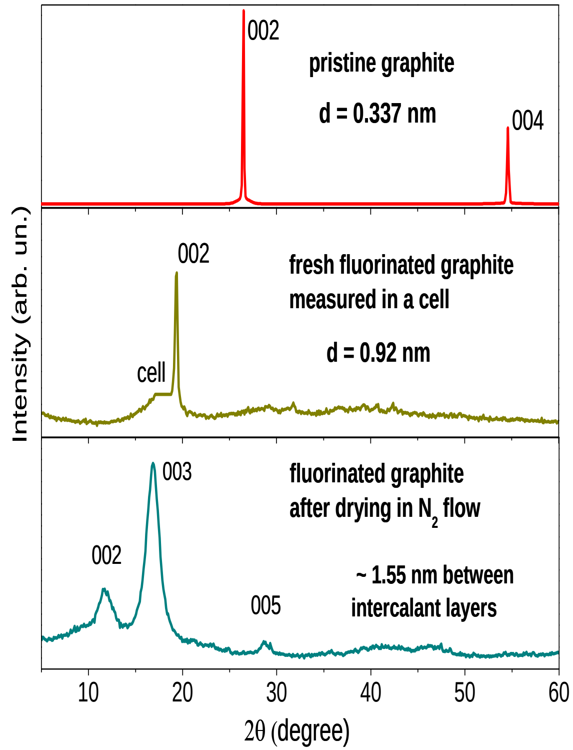
KBr (powder) ↓

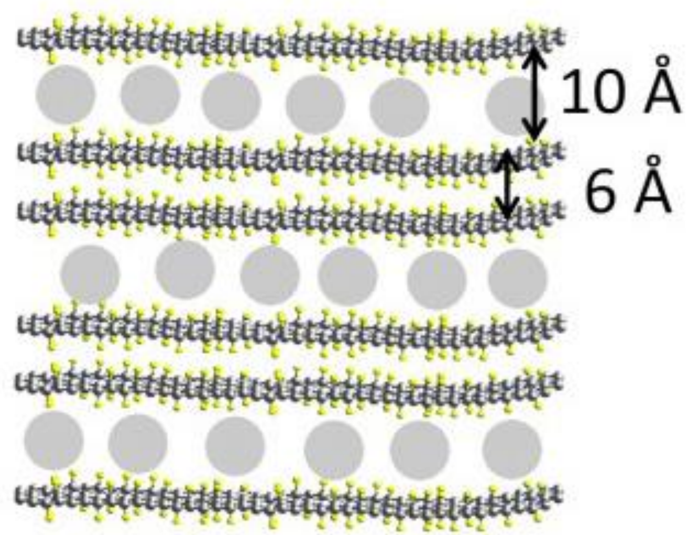
$C_2F_x \bullet zBr_2$

Teflon reactor

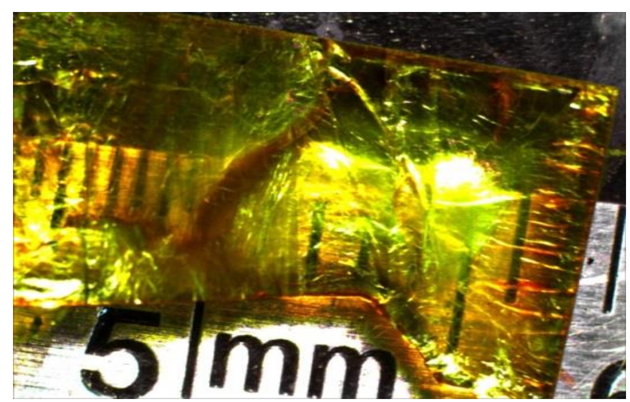




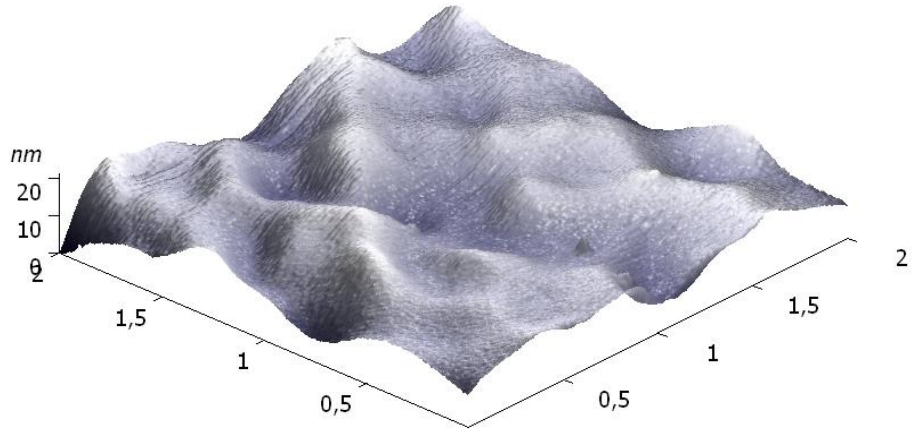


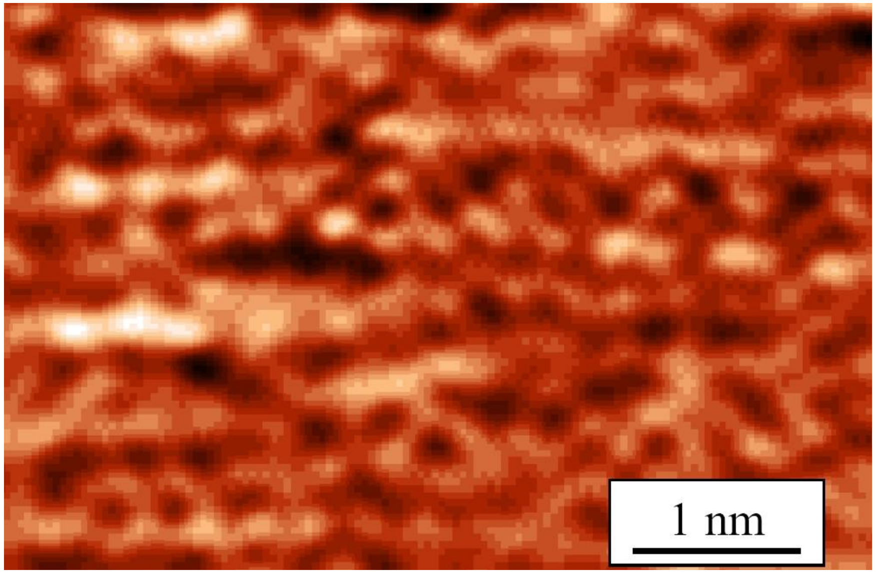


second-stage Br_2 intercalated C_2F_x compound



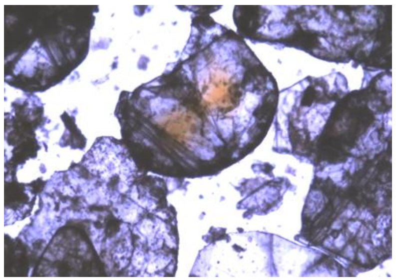
Structure of C_2F





Exchange by the guest molecules

$$C_2F_x \cdot z_1Br_2 \xrightarrow{CH_3CN} C_2F_x \cdot z_2CH_3CN$$

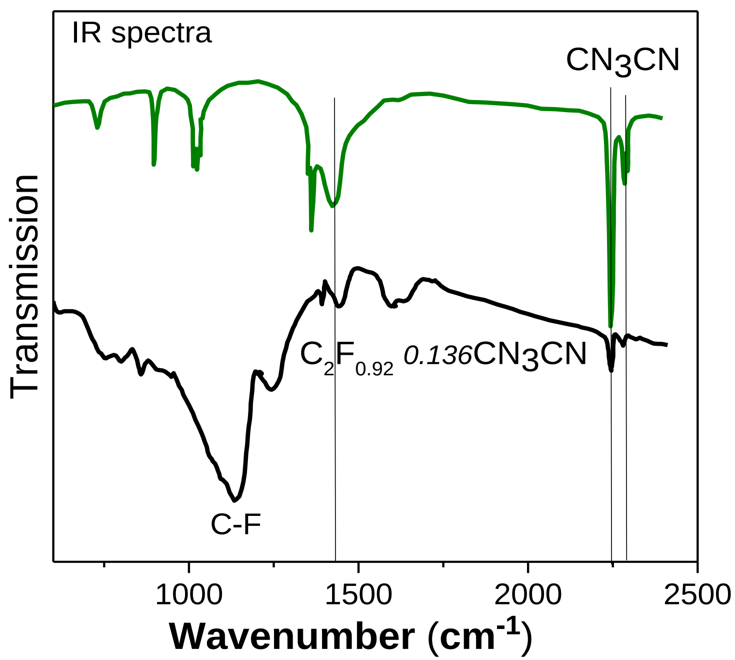


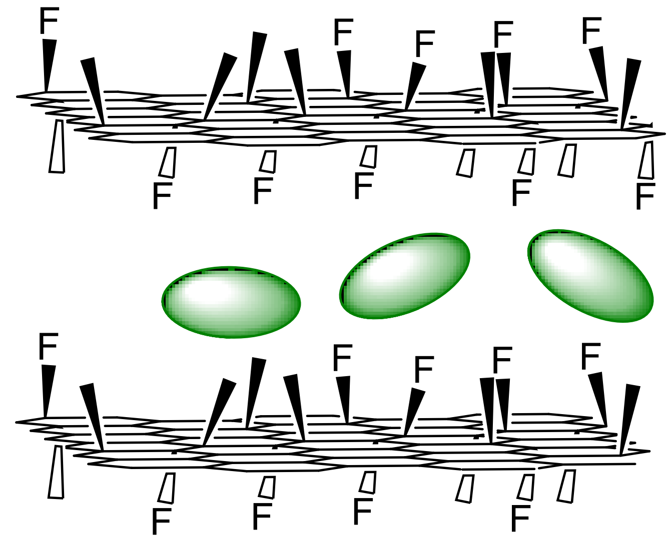
CH_3CN

or

$(CH_3)_2CHNH_2$

$(C_2F)_n$ dispersion





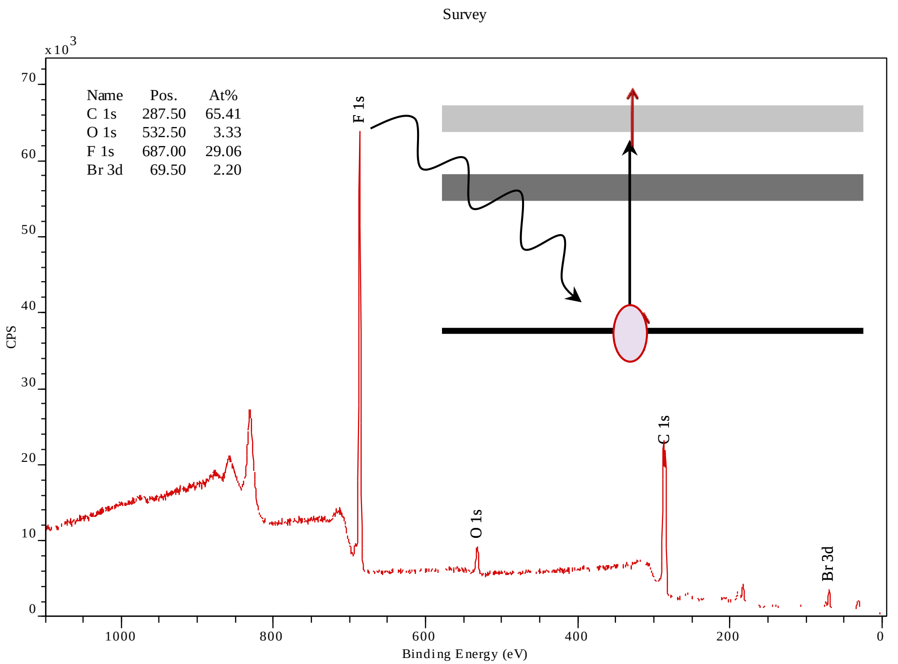
$$C_2F_x \cdot z_2CH_3CN$$

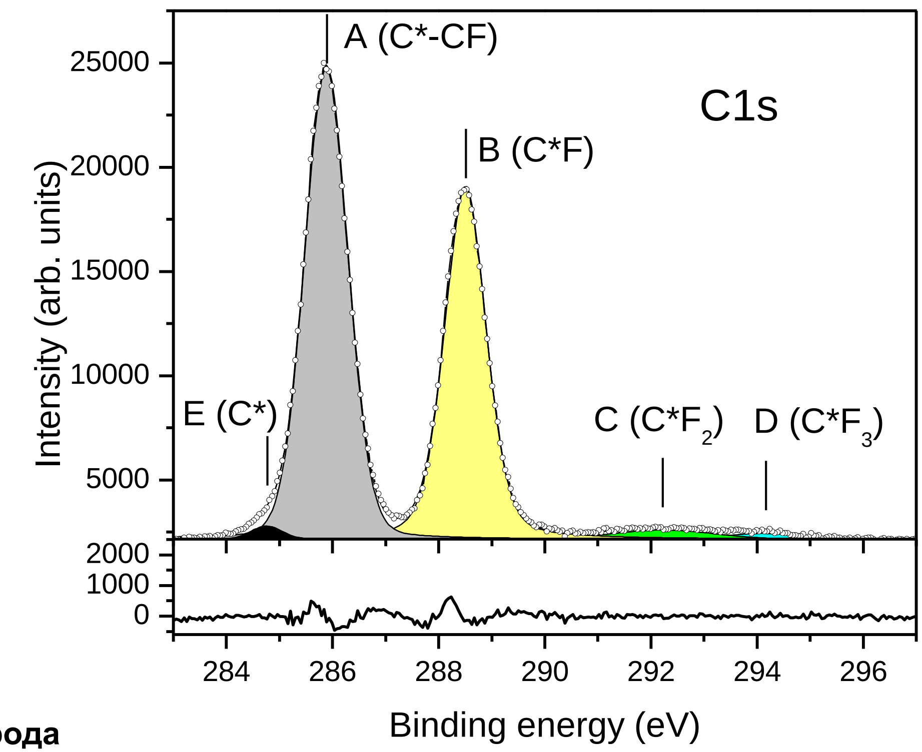
$$\downarrow \; i\text{-}PrNH_2$$

$$C_2F_x \cdot z_3(CH_3)_2CHNH_2$$

Intercalant molecules save the individuality in C_2F matrix

XPS spectra of C_2F

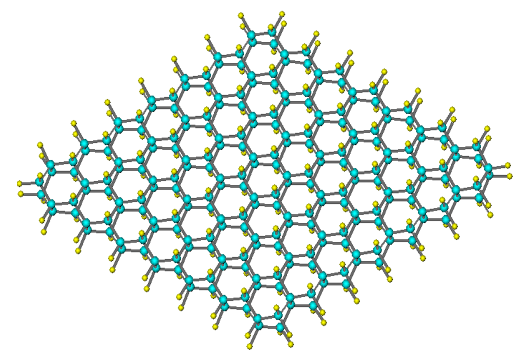




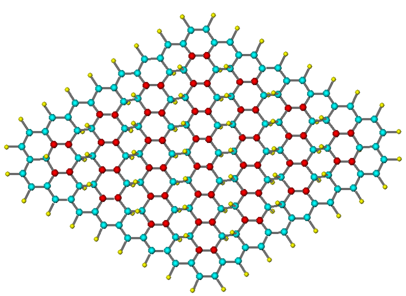
- **Два состояния атомов углерода**
- **Атомы фтора ковалентно связаны с атомами углерода**

Возможные модели C_2F слоев

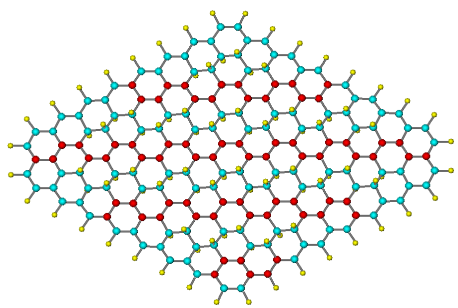
double-layered model



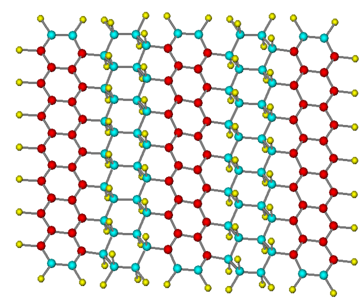
isolated double bonds



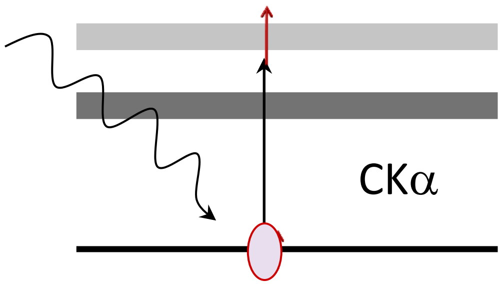
armchair chains

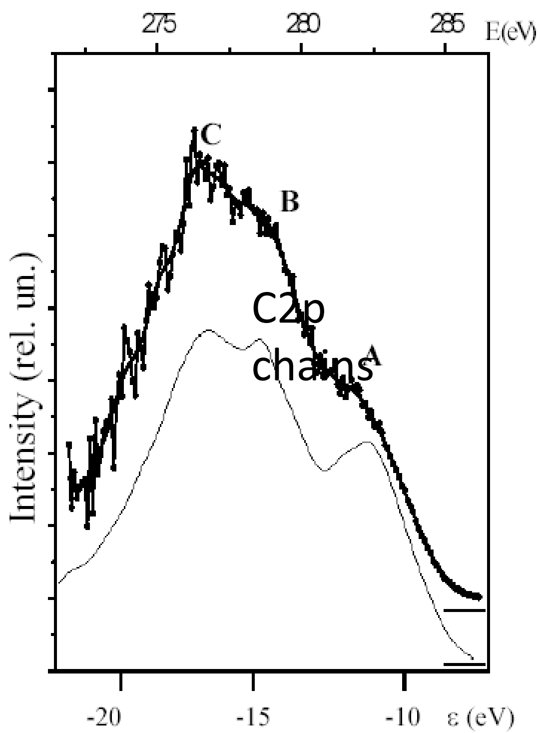


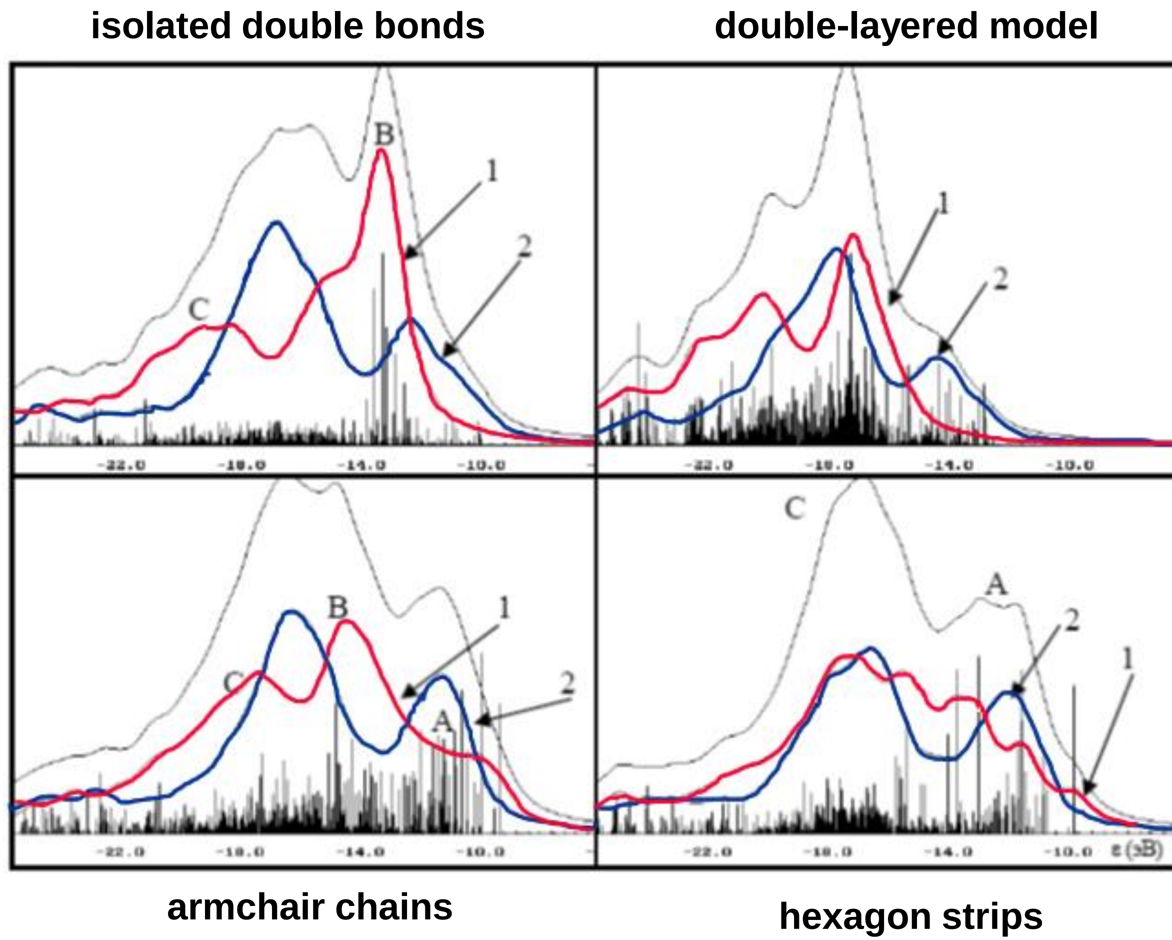
hexagon strips



Calculated CKα spectra of C_2F models





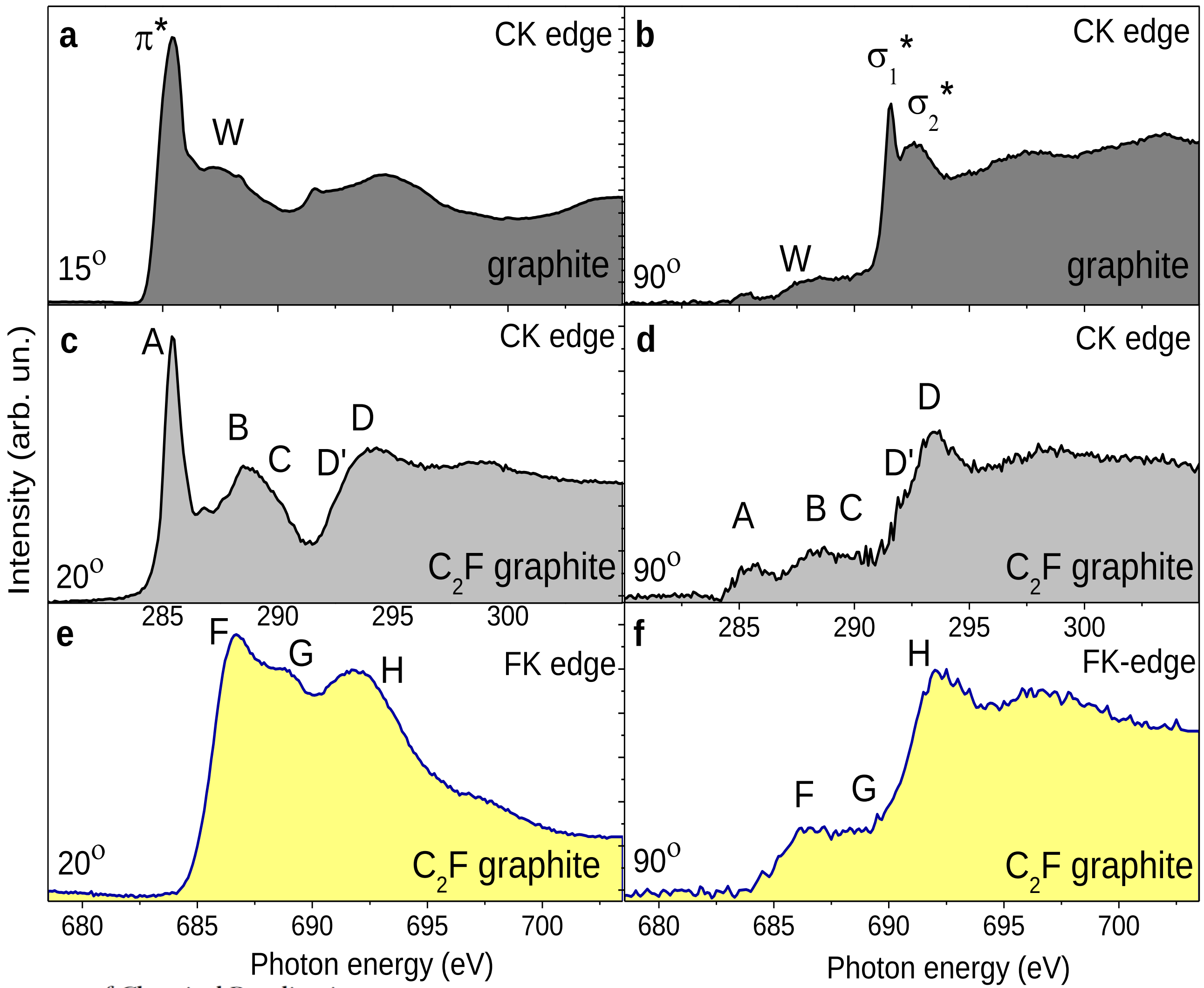


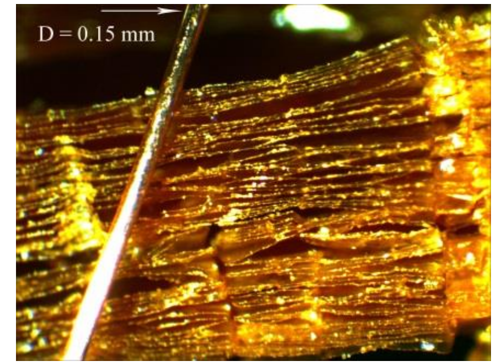
L.G. Bulusheva, A.V.Okotrub, N.F. Yudanov
Physi. Low-Dim. Struct. 7/8 (2002) pp.1-14

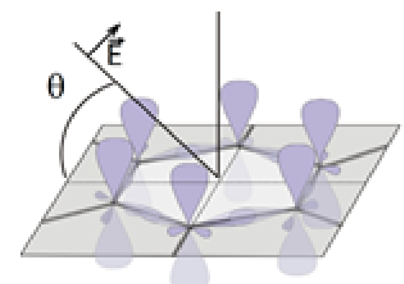
component 1 corresponds to C2p - density of states of bare carbon atoms,

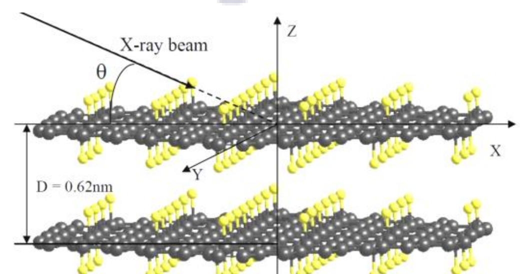
component 2 corresponds to C2p - density of states of carbon atoms of CF groups.

Experimental X-ray absorption spectra measured near CK- and FK-edge of C_2F







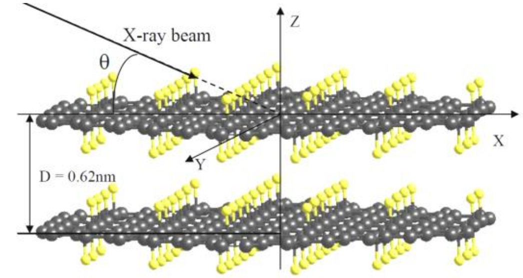


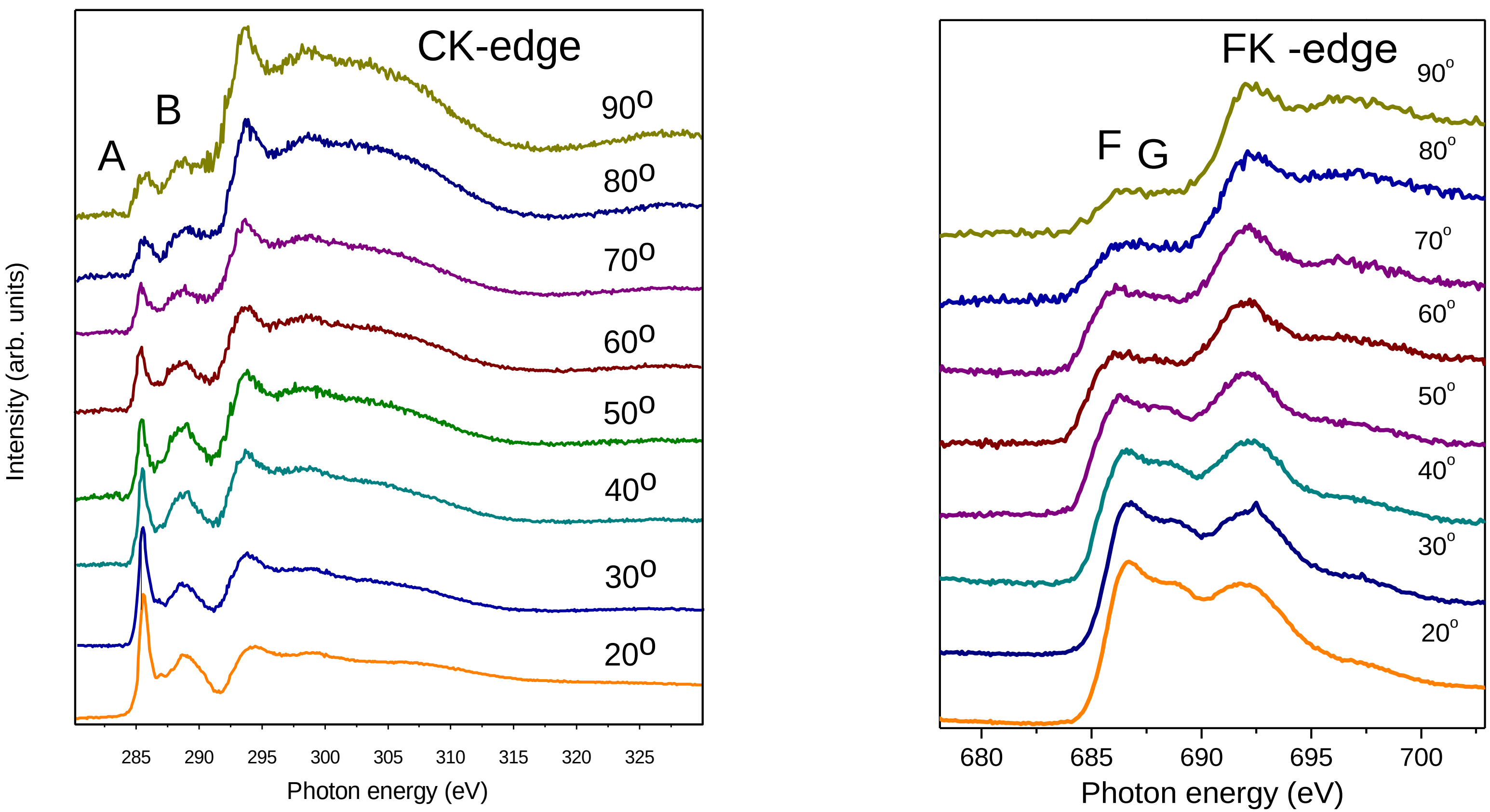
Anisotropy of Chemical Bonding in Semifluorinated Graphite C_2F Revealed with Angle-Resolved X-ray Absorption Spectroscopy

Alexander V. Okotrub,[†,*] Nikolay F. Yudanov,[†] Igor P. Asanov,[†] Denis V. Vyalikh,[‡] and Lyubov G. Bulusheva[†]

VOL. 7 ▪ NO. 1 ▪ 65–74 ▪ 2013 ACS NANO

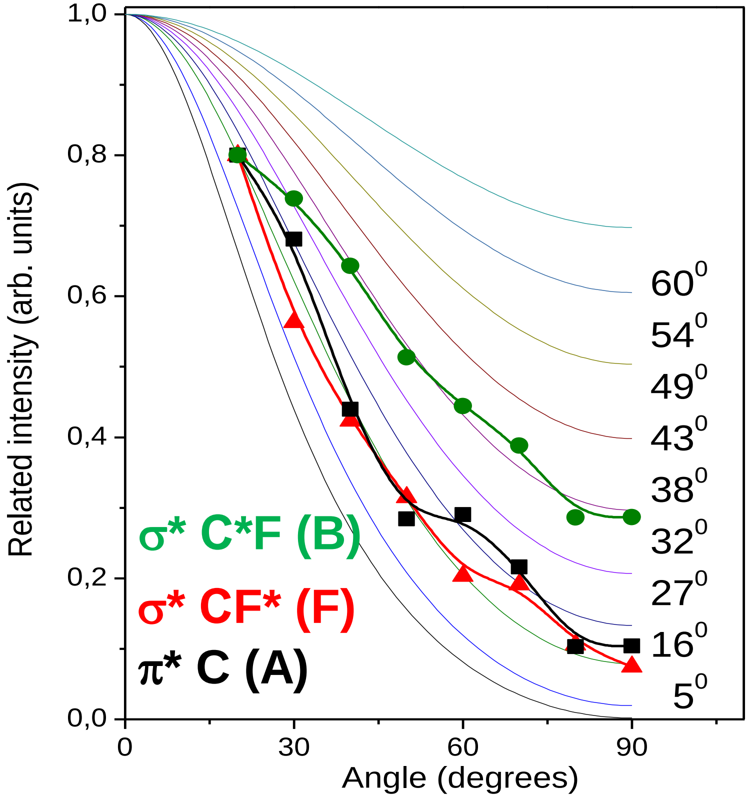
Angle-depended X-ray absorption spectra





NEXAFS spectra measured near CK edge and FK edge of fluorinated HOPG at different incidence angle of radiation.

Angular dependence of the relative intensity of the π* resonance calculated for different Gaussian distributions of graphene layers

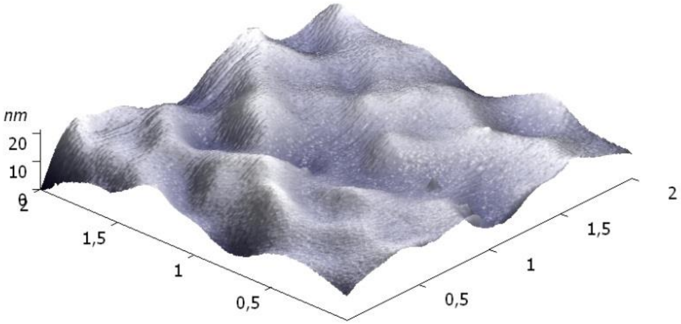


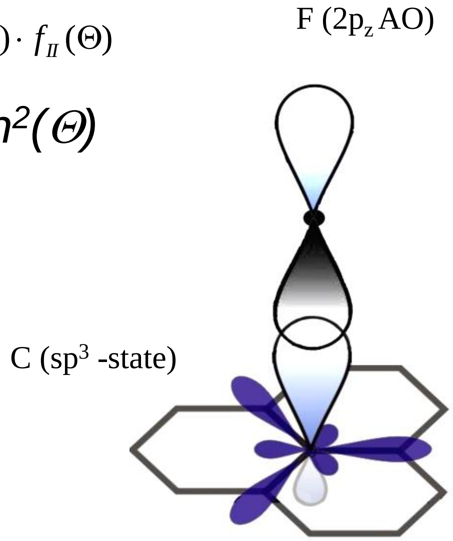
$$I(\Theta) = (I_{(\pi^*-C)} + I_{(\sigma^*-FC)\perp}) \cdot f_{\perp}(\Theta) + (I_{(\sigma^*-C)}) \cdot f_{II}(\Theta)$$

$$f_{\perp}(\Theta) \sim \cos^2(\Theta) \quad f_{II}(\Theta) \sim \sin^2(\Theta)$$

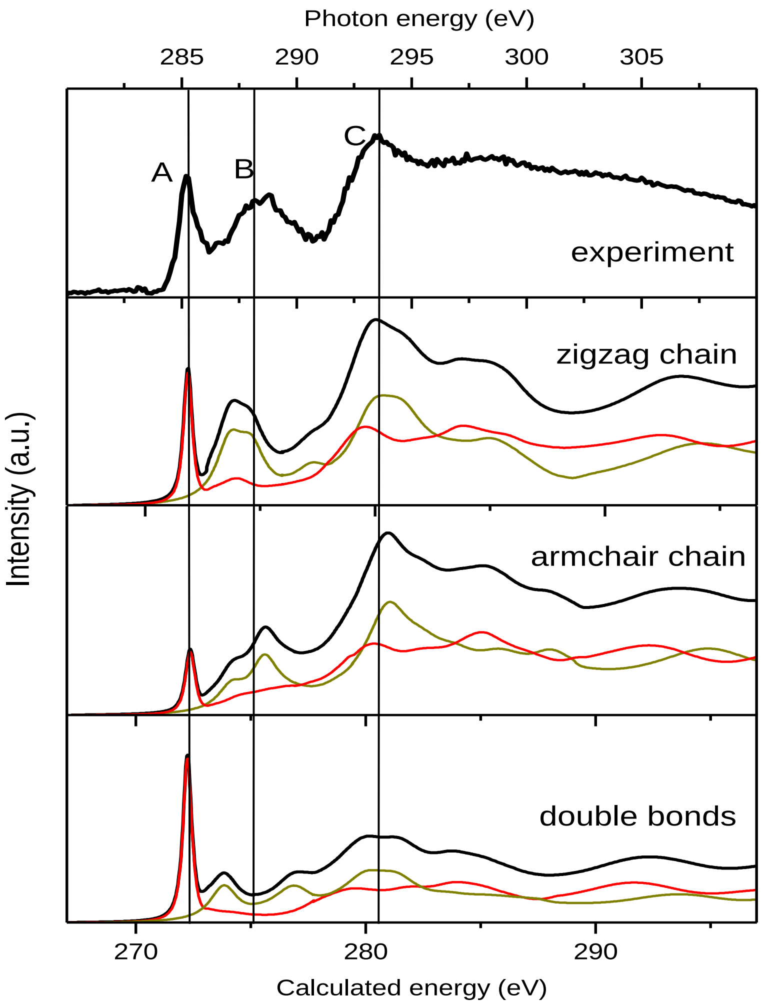
$$\rho(\theta, w) = A \cdot e^{-\left(\frac{\theta}{w}\right)^2 \cdot \ln(2)}$$

w – average deviation angle

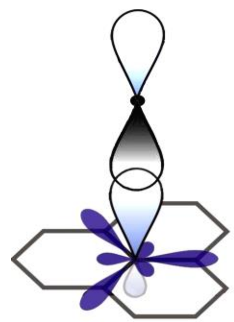


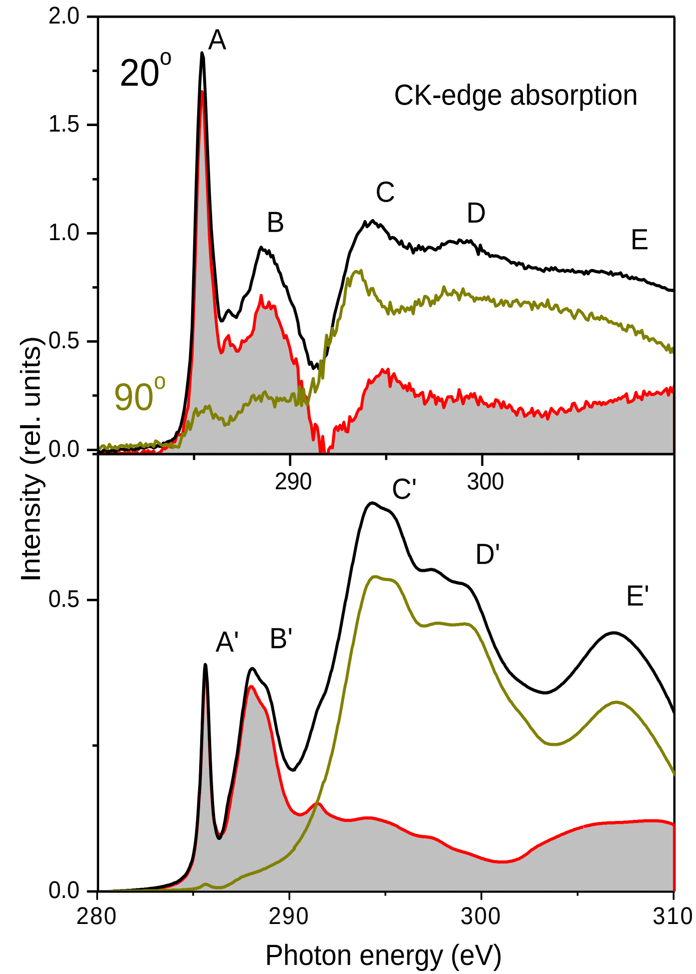


Comparison of experimental and theoretical CK absorption spectra



C*-CF
C-C*F

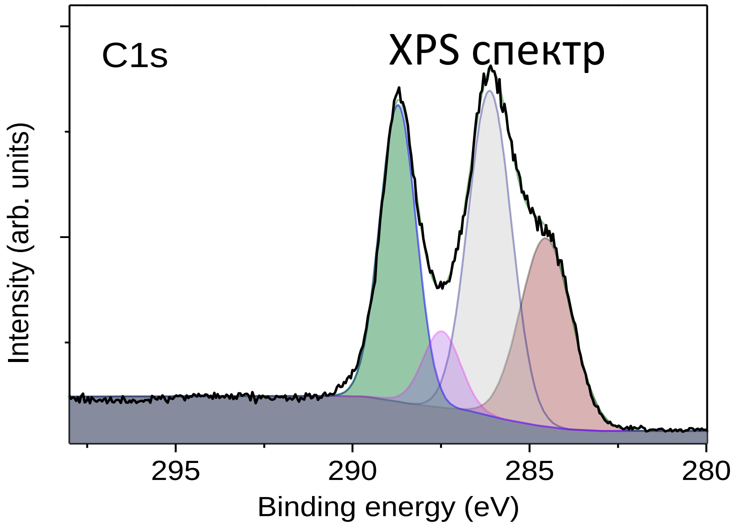




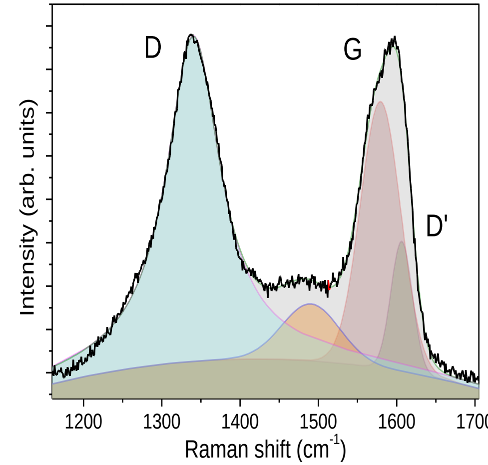
Z+1 approach, B3LYP(6-31G) level

C2p (⊥) and **C2p (II)** components in spectra

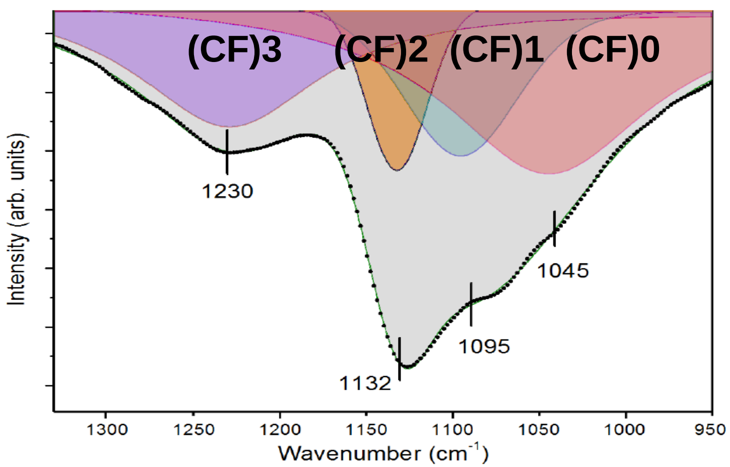
Synthesis and structure of $C_2F*0.13\ C_7H_{16}$



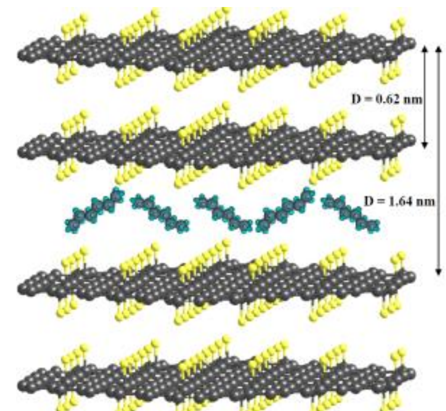
$I_D/I_G \sim 2.7$



Effective size ~ 2.6 nm [M.M. Lucchese, 2010]



IR transmittance spectra near CF bond area



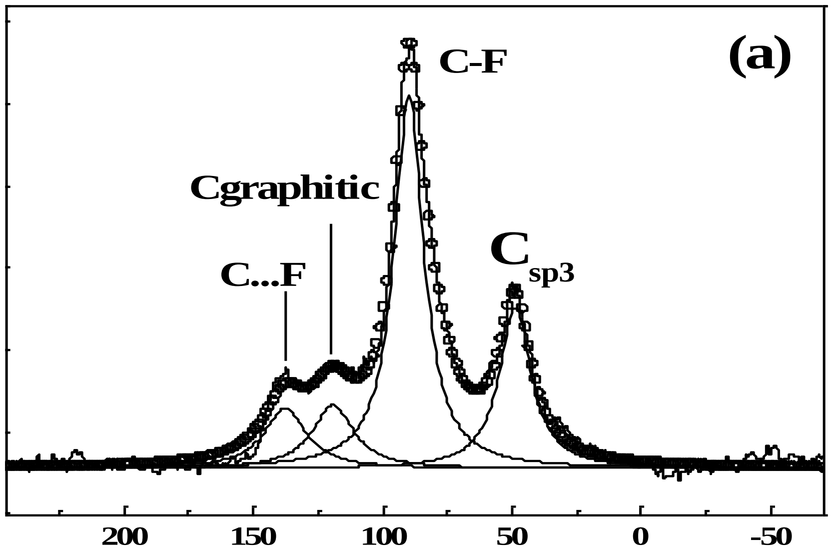
Graphene nanochains and nanoislands in the layers of room-temperature fluorinated graphite

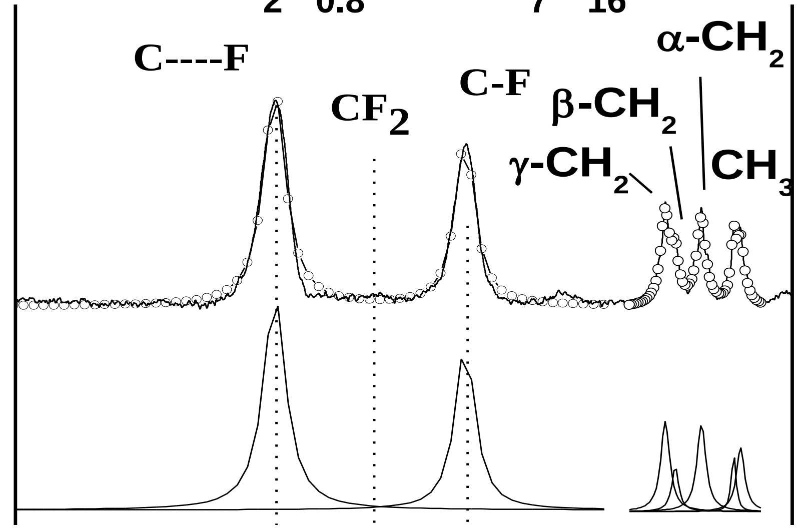
I.P. Asanov [a,], L.G. Bulusheva [a], M. Dubois [b,c], N.F. Yudanov [a], A.V. Alexeev [a], T.L. Makarova [d], A.V. Okotrub [a]*

CARBON 59 (2013) 518–529

NMR investigation of hihg and low temperature produced C_2F

$C_2F_{0.8}$*$0.13C_7H_{16}$



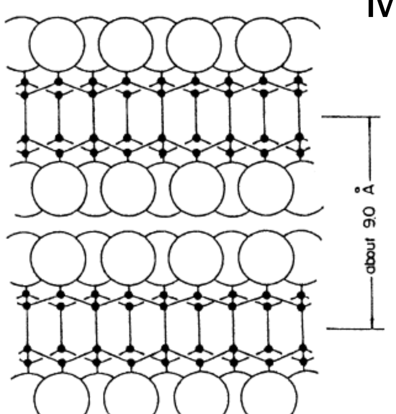


$(C_2F)_n$ type

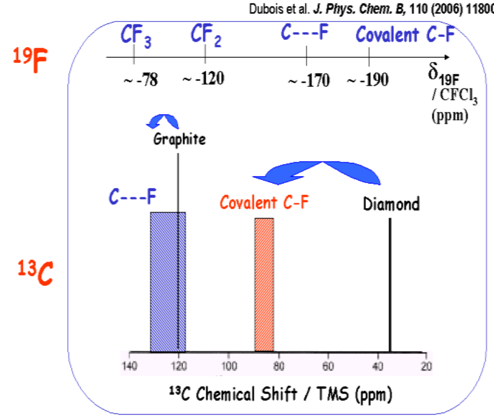
δ\13C /TMS (ppm)

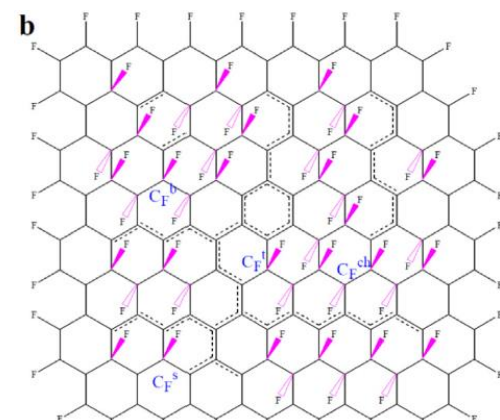
13C MAS NMR (10 kHz)

Модель Watanabe

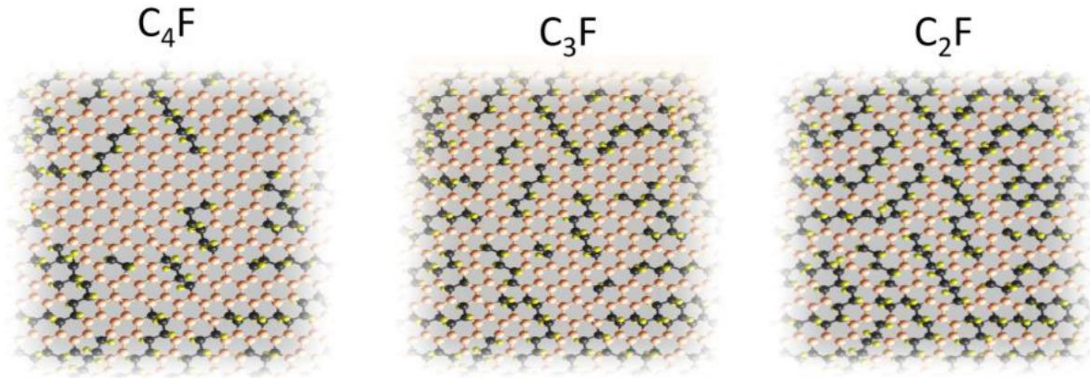


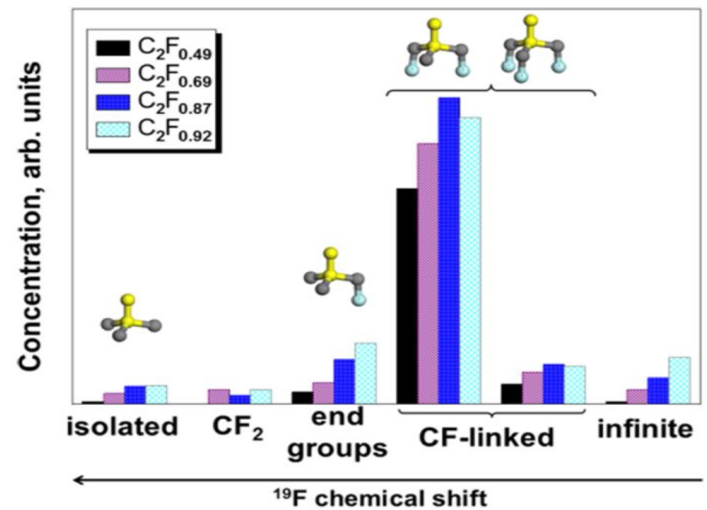
A.M. Panich, *Synthetic Metals* 100 (1999) 169-185
Giraudet et al. *J. Phys. Chem. B*, 109 (1) (2005)
Dubois et al. *J. Phys. Chem. B*, 110 (2006) 11800-11808



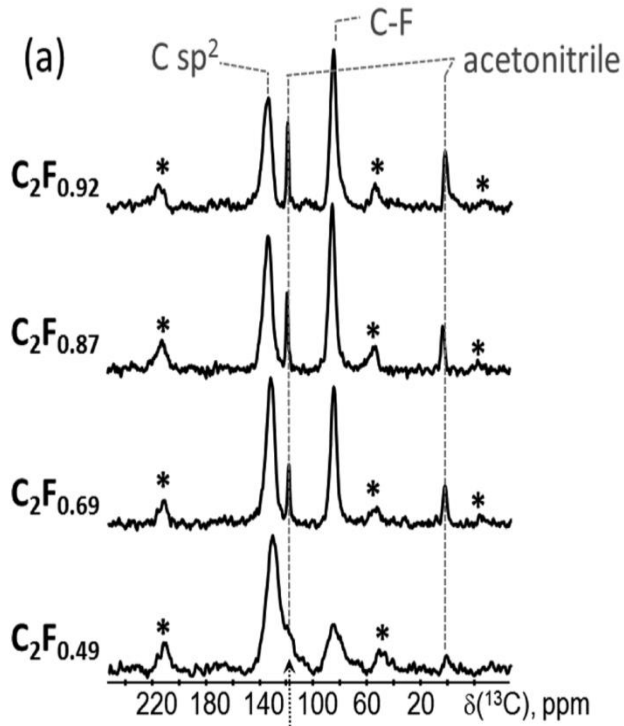


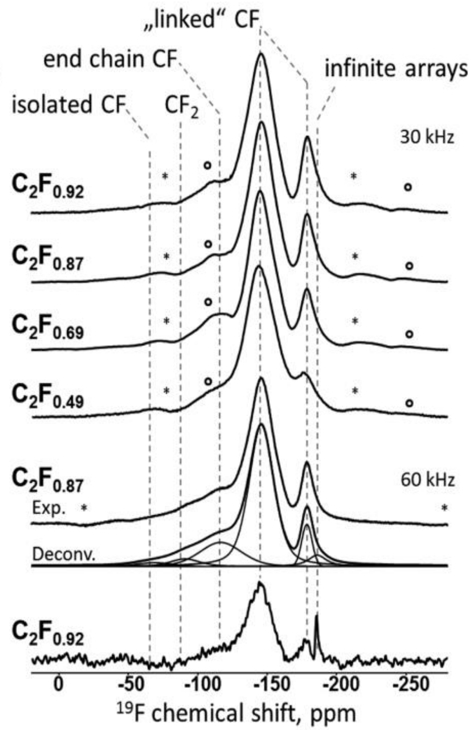
Structure of partially fluorinated graphite C_2F_x



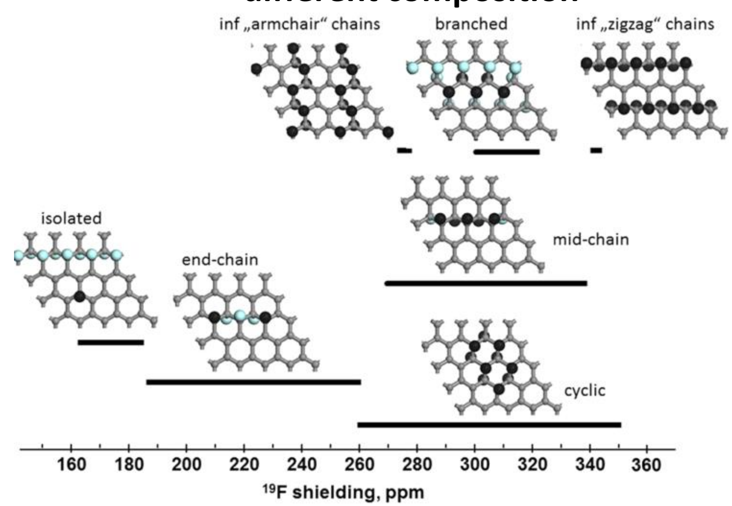


Structure motives in C_2F_x with different composition





NMR spectra ^{13}C and ^{19}F of C_2F_x samples

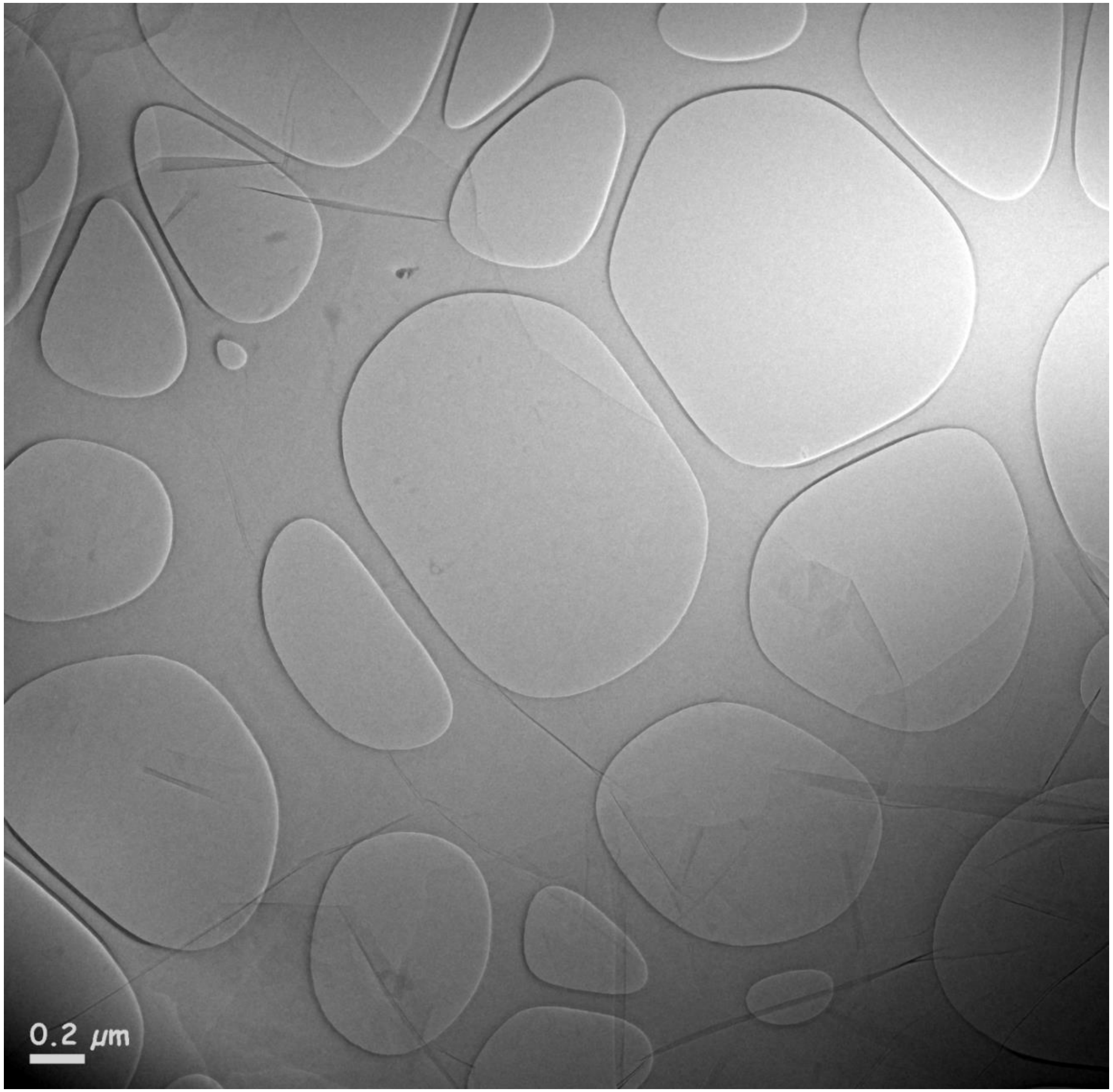


Fluorine Patterning in Room-Temperature Fluorinated Graphite Determined by Solid-State NMR and DFT

Anastasia Vyalikh,*,† Lyubov G. Bulusheva,‡ Galina N. Chekhova,‡ Dmitry V. Pinakov,‡ Alexander V. Okotrub,‡ and Ulrich Scheler†

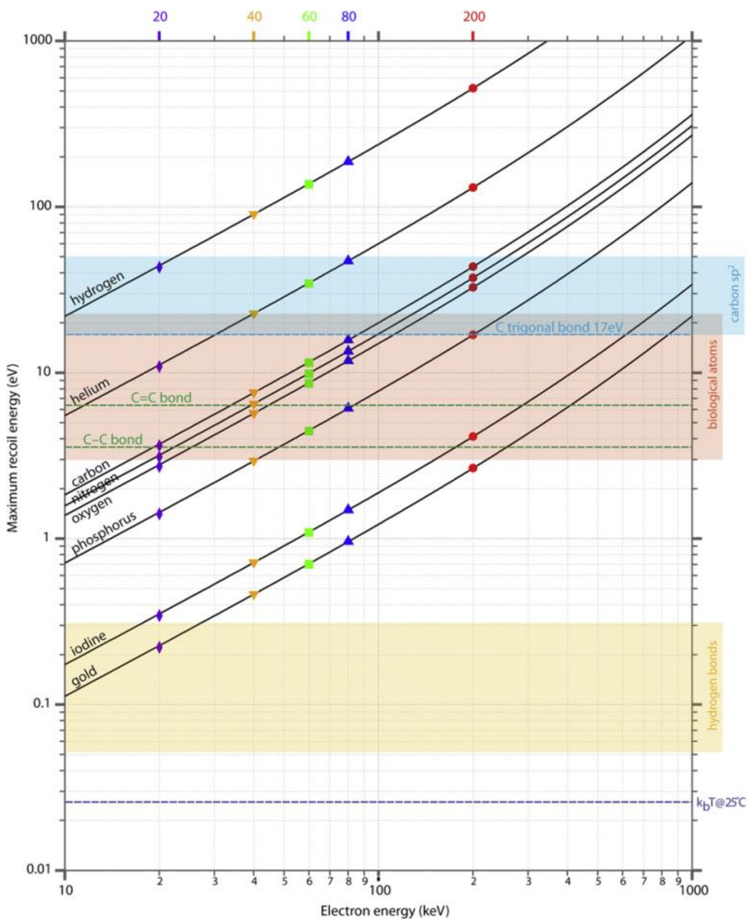
J. Phys. Chem. C 2013, 117, 7940–7948

Electron microscopy images of C_2F_x

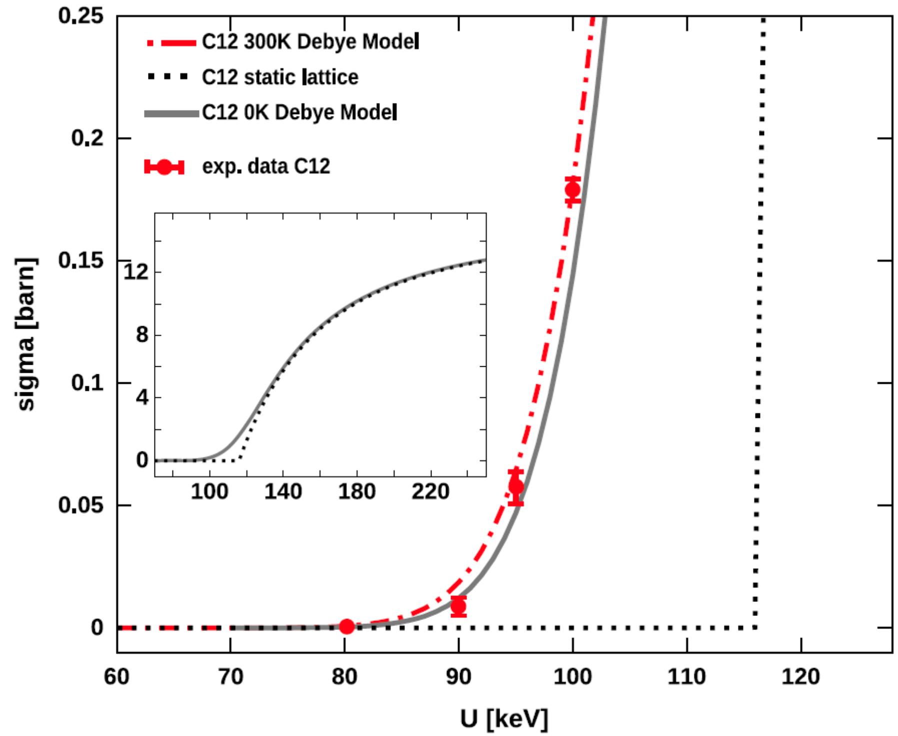


Defluorination under electron irradiation

Negative factors
1. Fluoride has a low contrast
2. Electrons knock out fluorine atoms (although the strongest single bond).
3. Deposition of pyrolysis of residual gas from the chamber of the spectrometer.

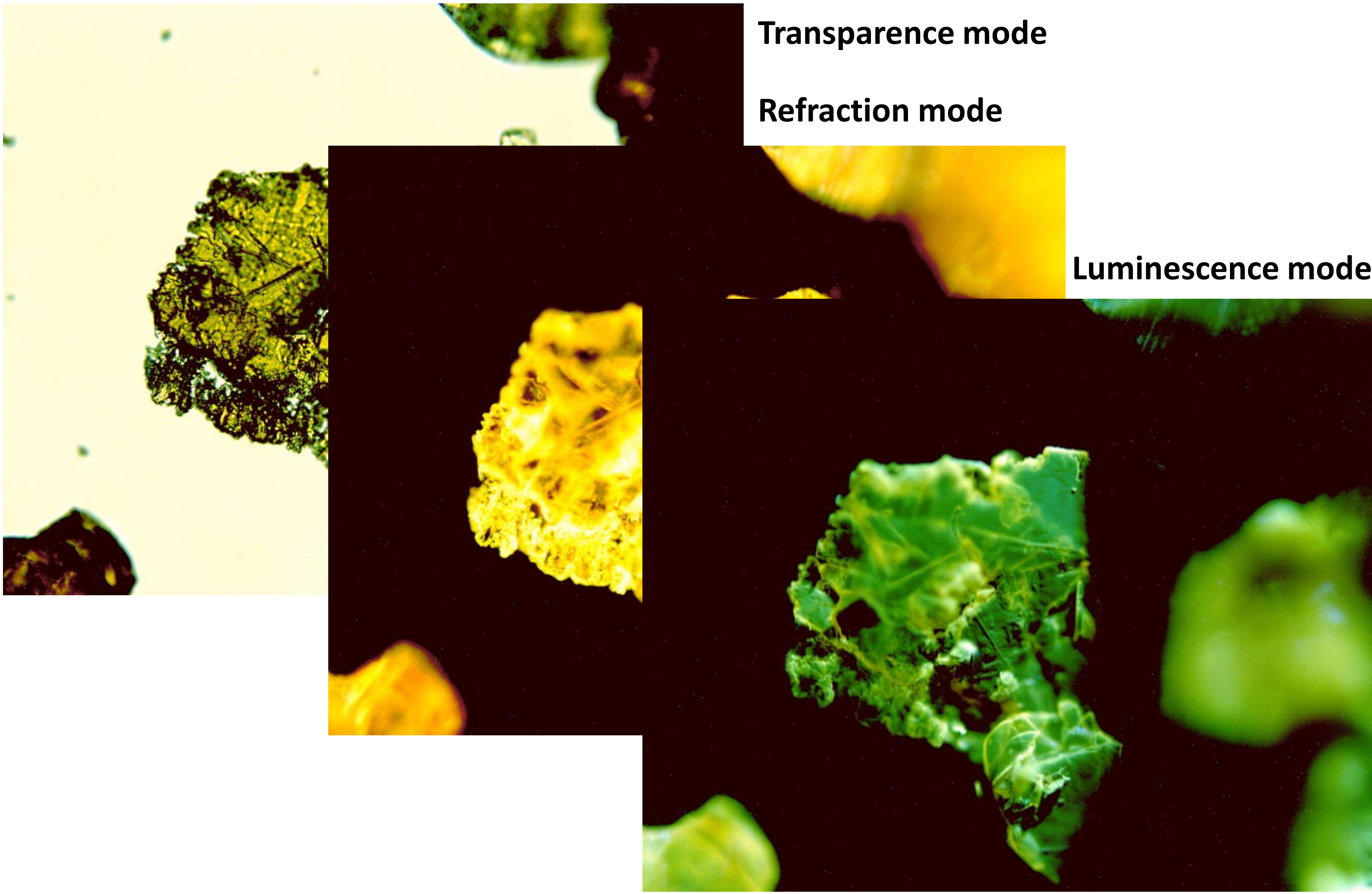


D.C. Bell et al. / Ultramicroscopy 114 (2012) 31–37

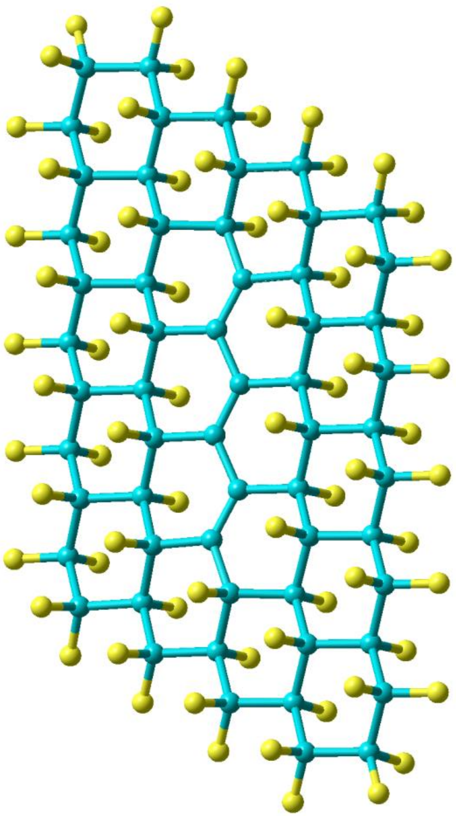


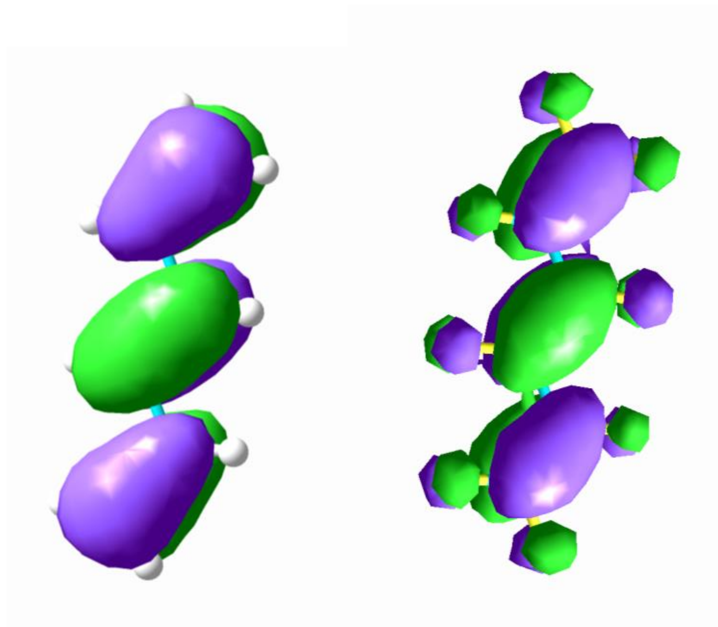
C. Mangler, J.C. Meyer / C. R. Physique 15 (2014) 241–257

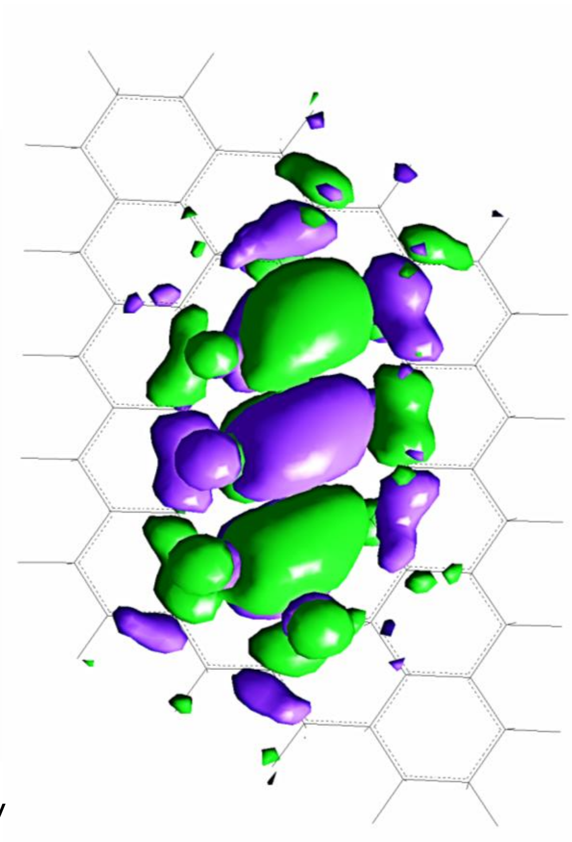
Optical microscopy study



Aromatic fragments embedded in CF matrix





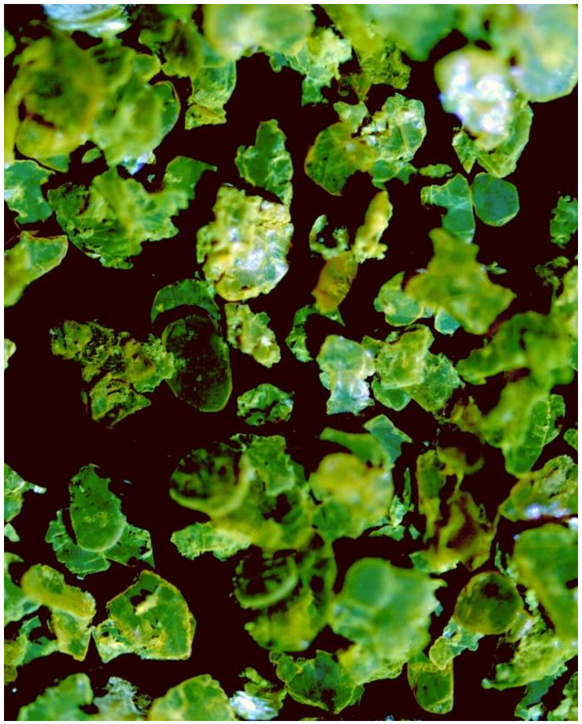


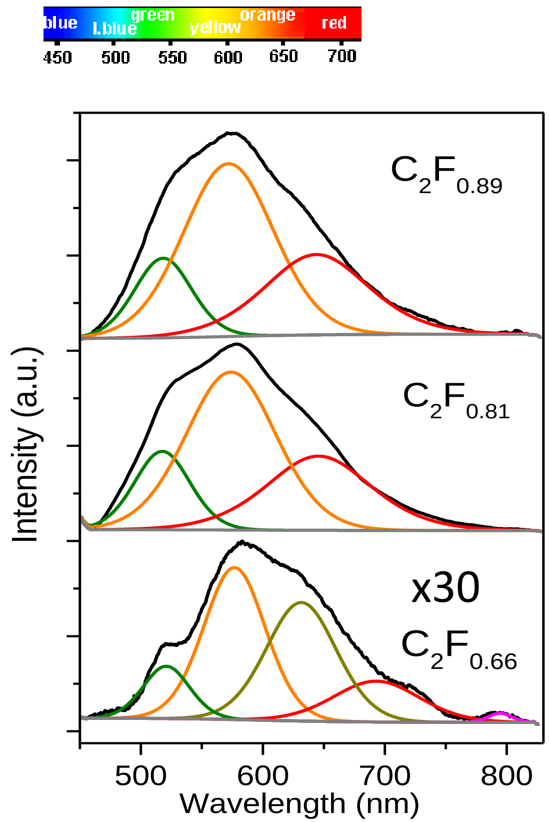
HOMO -8.90 eV, LUMO = -0.25 Δ=8.65 eV
HOMO -9.91 eV, LUMO -2.02 eV, Δ=7.89 eV
HOMO -12.55 eV, LUMO -4.34 eV, Δ8.21 eV

Photoluminescence of C_2F_x

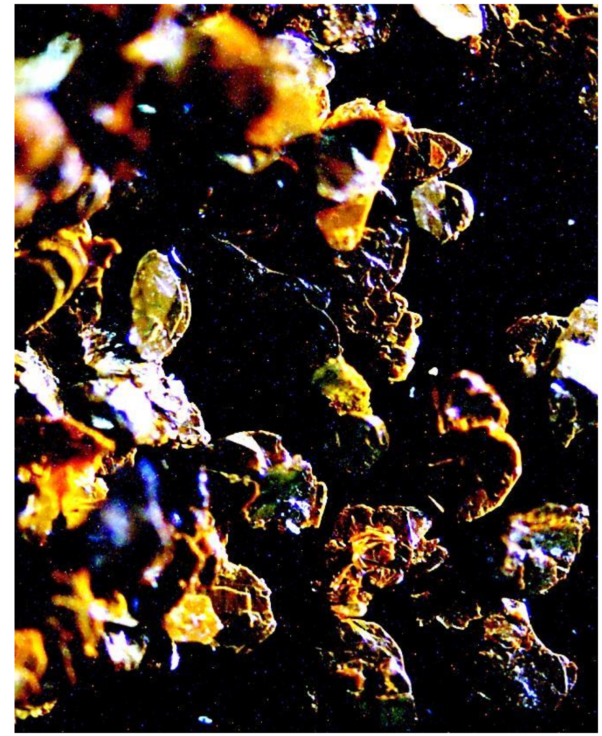
λ_{ex} ~ 405 nm

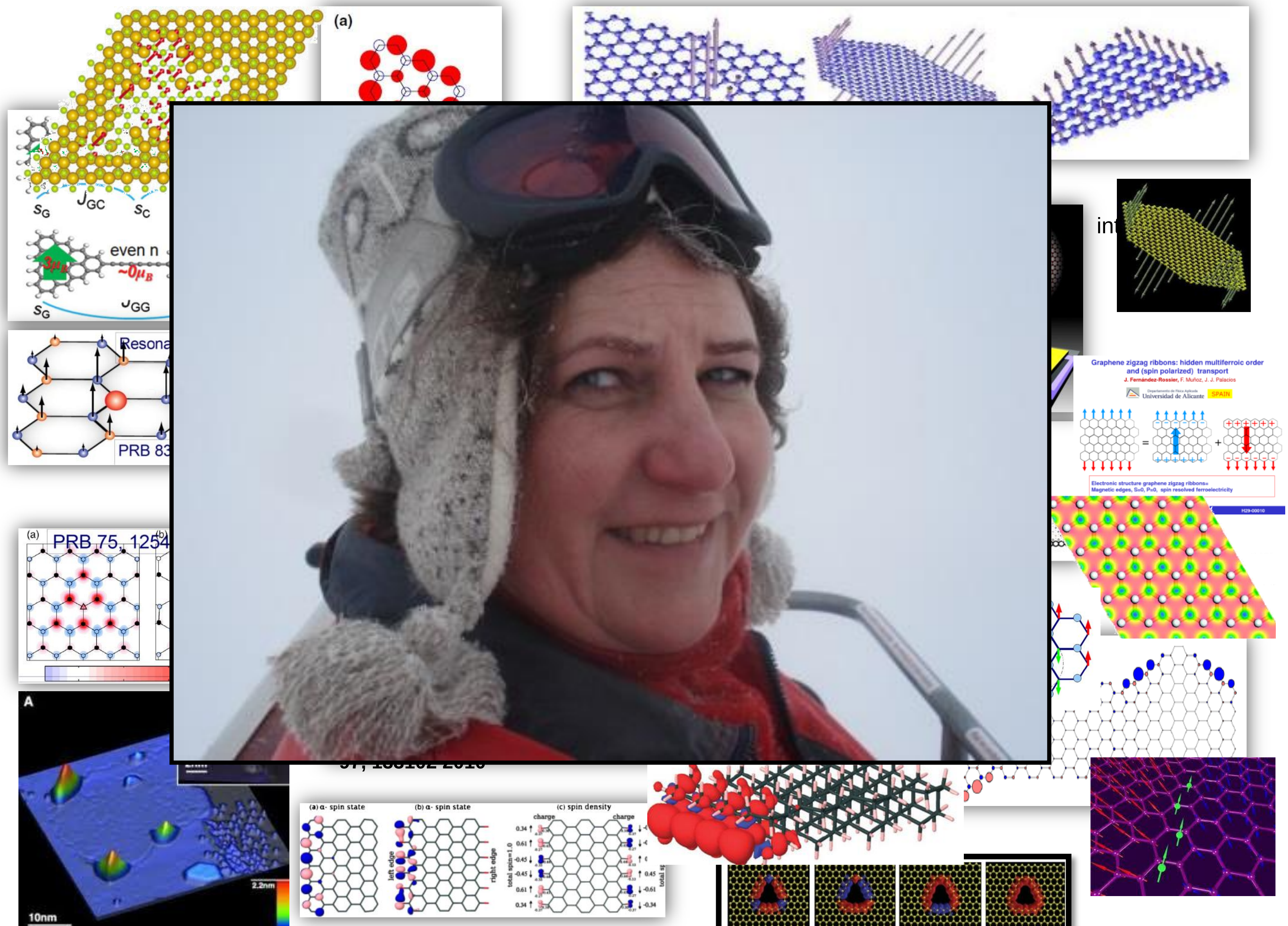
$C_2F_{0.94}$





$C_2F_{0.66}$

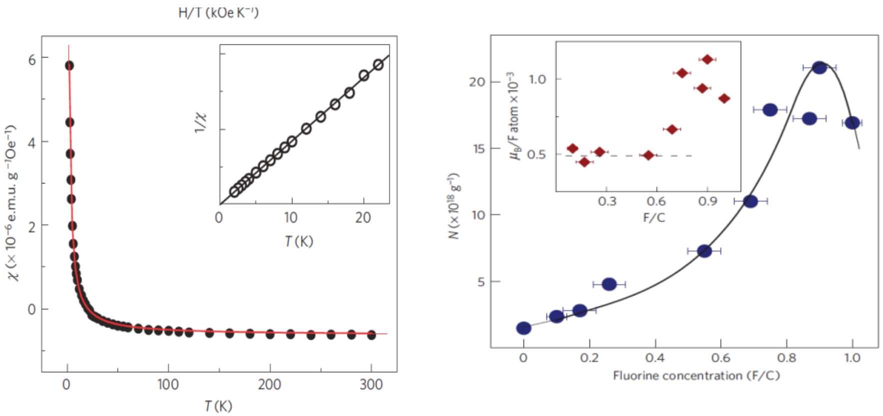



(a)
even n
Resona
PRB 83
PRB 75, 1254
(a)
A
10nm
2.2nm
0nm
Graphene zigzag ribbons: hidden multiferroic order and (spin polarized) transport
J. Fernández-Rossier, F. Muñoz, J. J. Palacios
Universidad de Alicante
SPAIN
(a) α- spin state
(b) α- spin state
(c) spin density
charge
left edge
right edge

nature physics
LETTERS
PUBLISHED ONLINE: 10 JANUARY 2012 | DOI: 10.1038/NPHYS2183

Spin-half paramagnetism in graphene induced by point defects

R. R. Nair[1], M. Sepioni[1], I-Ling Tsai[1], O. Lehtinen[2], J. Keinonen[2], A. V. Krasheninnikov[2,3], T. Thomson[1], A. K. Geim[1] and I. V. Grigorieva[1]*



J Supercond Nov Magn (2012) 25:79–83
DOI 10.1007/s10948-011-1209-2
ORIGINAL PAPER

Structural Evolution and Magnetic Properties of Underfluorinated C_2F

T.L. Makarova · V.S. Zagaynova · G. Inan · A.V. Okotrub · G.N. Chekhova · D.V. Pinakov · L.G. Bulusheva

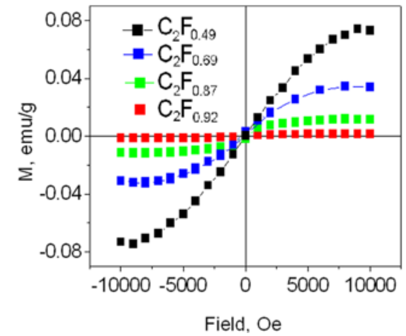
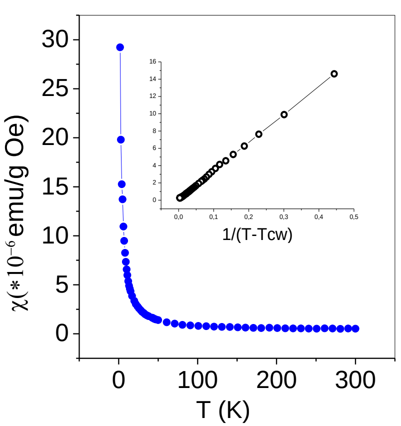
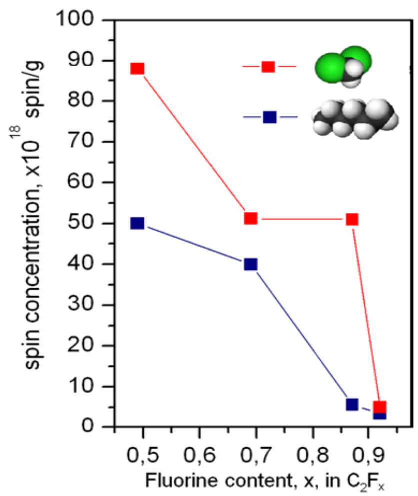
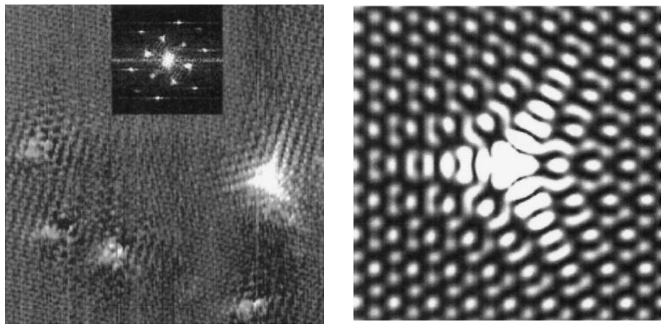


Figure 2 Paramagnetism due to fluorine adatoms





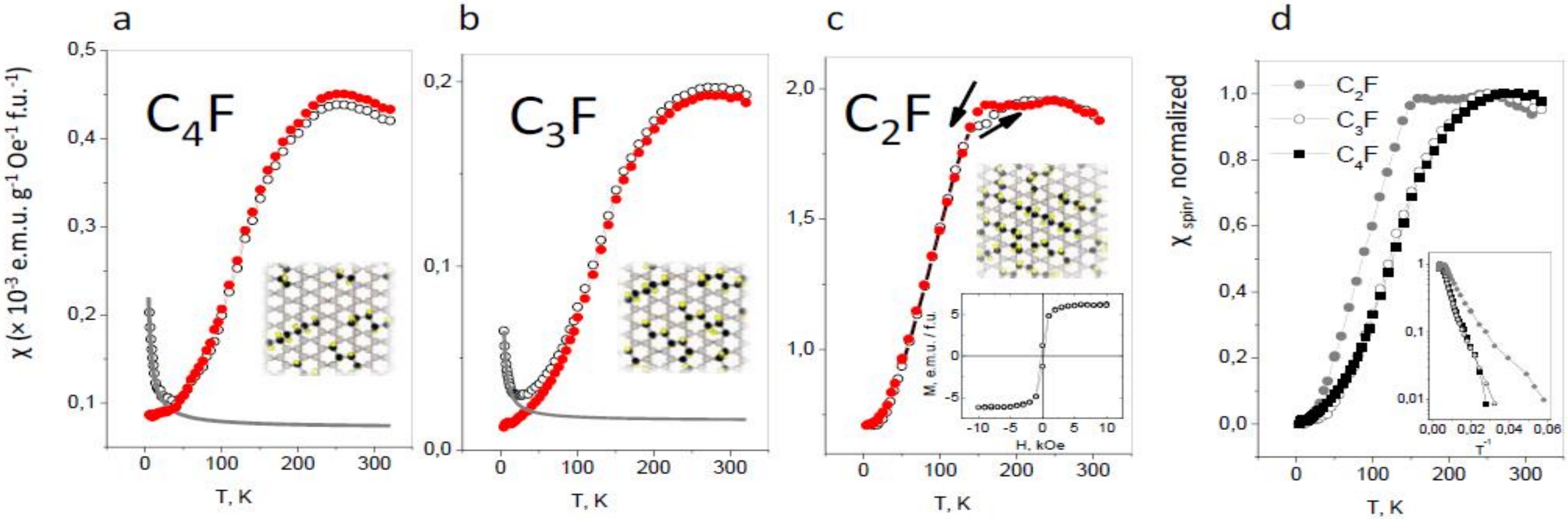


Nanoscale imaging of chemical interactions: Fluorine on graphite

Kevin F. Kelly*, Edward T. Mickelson†, Robert H. Hauge†, John L. Margrave†‡, and Naomi J. Halas*†‡

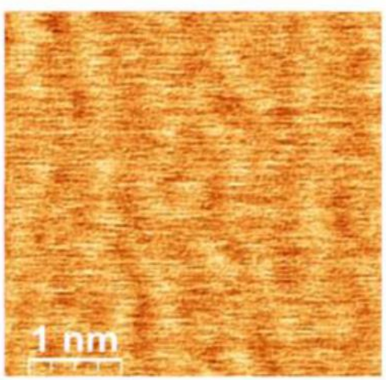
10318–10321 | PNAS | September 12, 2000 | vol. 97 | no. 19

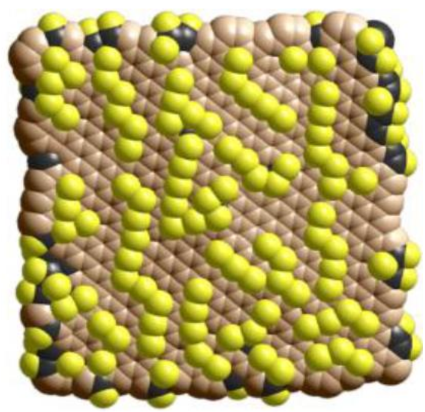
Magnetic susceptibility of the C_2F_x samples



$$\chi(T) = \chi_0 + \chi_{Curie} + \chi_{spin}$$

$$\chi_{spin} \sim \exp(-\Delta/T)$$



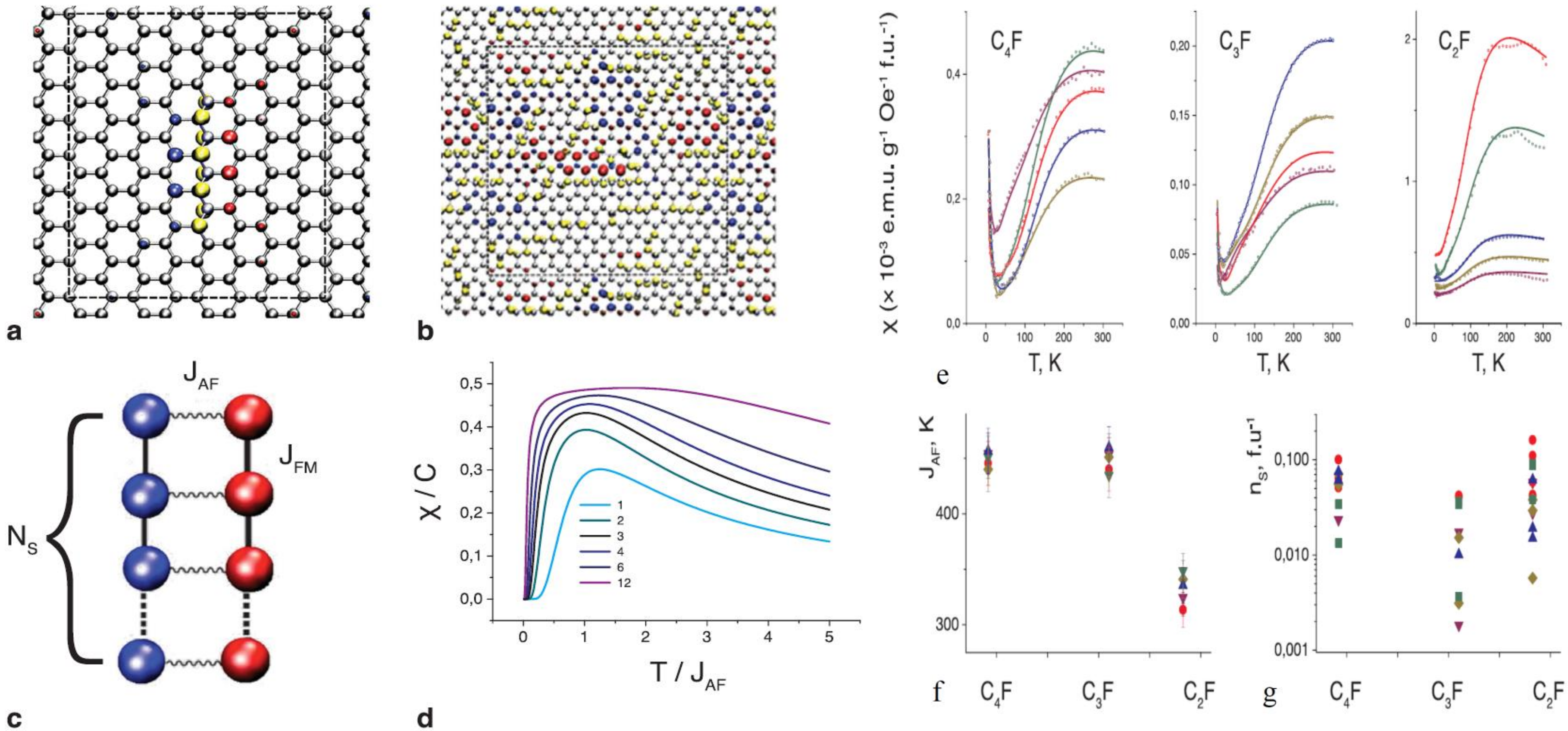


Edge state magnetism in zigzag-interfaced graphene via spin susceptibility measurements

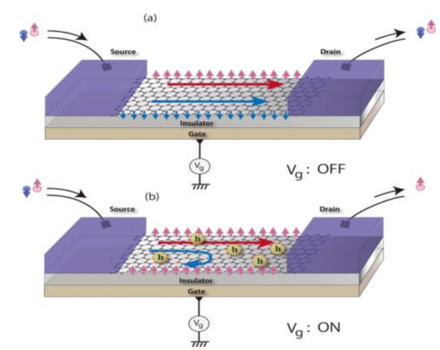
T. L. Makarova[1,2], A. L. Shelankov[2], A. A. Zyrianova[2], A. I. Veinger[2], T. V. Tisnek[2], E. Lähderanta[1], A. I. Shames[3], A. V. Okotrub[4], L. G. Bulusheva[4], G. N. Chekhova[4], D. V. Pinakov[4], I. P. Asanov[4] & Ž. Šljivančanin[5]

SCIENTIFIC REPORTS | 5:13382 | DOI: 10.1038/srep13382

Quantum chemical calculation of magnetic moment distribution

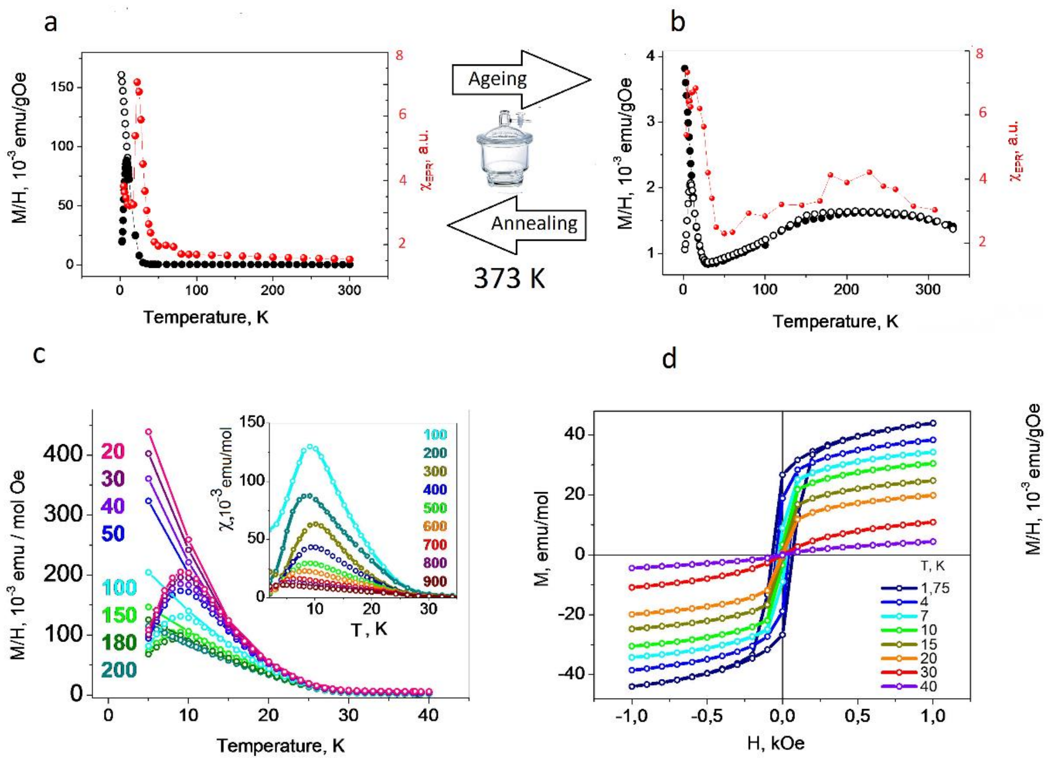


The scheme demonstrates the possibility for regulation of polarized the charge carriers by the electric field applied to the graphene ribbon



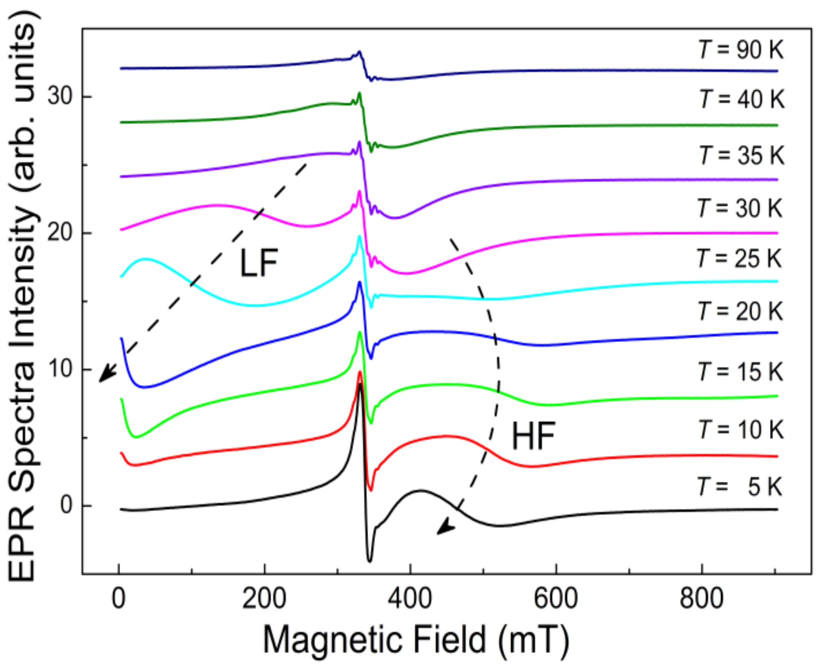
S. Dutta, K. Wakabayashi "Tuning Charge and Spin Excitations in Zigzag Edge Nanographene Ribbons" Scientific Reports, 2, 519 (2012)

Magnetic properties C_2F

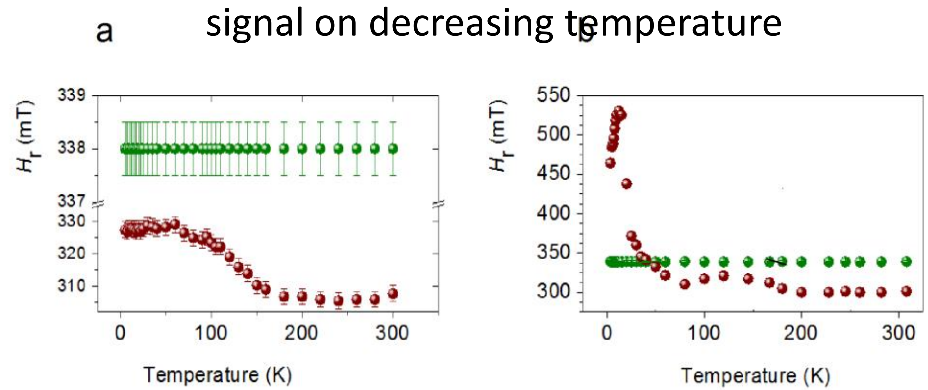


Temperature dependencies of magnetic susceptibility for *Tabby* graphenes, C_2F_x *x ~1*:
(a) pristine samples; **(b)** aged samples - open circles represent the ZFC, solid circles are the FC measurements, red symbols represent the double integrated intensity (the EPR susceptibility); **(c)** M(*T*) curves taken at different fields; **(d)** M(*H*) dependencies taken at different temperatures.

EPR study of C_2F



Temperature dependence of EPR spectra for the as prepared *Tabby* graphene, C_2F_x *(x » 1)* at $T < 100$ K. All spectra are recorded at the same experimental conditions: n = 9.469 GHz, incident microwave power 20 mW, 100 kHz magnetic field modulation amplitude 0.5 mT, receiver gain 10^4. Spectra are shifted vertically for better presentation. Dashed arrows indicate changes in H_r^{broad} for low- and high-field components of the FMR signal on decreasing temperature



Resonance field positions H_r of the EPR signal *vs* temperature for the *Tabby* graphene C_2F_x: (a) fluorine content *x < 1;* **(b)** aged sample with *x ~ 1*; and **(c)** the same sample with *x ~ 1* as prepared.

Tabby graphene: Dimensional magnetic crossover in fluorinated graphite

T. L. Makarova[1,2], A. L. Shelankov[2], A. I. Shames[3], A. A. Zyrianova[4], A. A. Komlev[1], G. N. Chekhova[5], D. V. Pinakov[5,6], L. G. Bulusheva[5,6], A. V. Okotrub[5,6] & E. Lähderanta[1]

SCIENTIFIC REPORTS | 7: 16544

Conclusion

The partially fluorinated graphite is perspective multifunctional material for application in electronics, optics, spintronics, sensors and many other.

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Dr. Alexander Shames (Ben-Gurion University of the Negev, Beersheba)

Dr. Tatyana Makarova (Lappeenranta University of Technology, Lappeenranta)

Thank you for attention!