DEFECT INDUCED MAGNETIC INTERACTIONS IN HIGHLY ORIENTED PYROLYTIC GRAPHITE (HOPG): A LOCAL INVESTIGATION USING TDPAD METHOD

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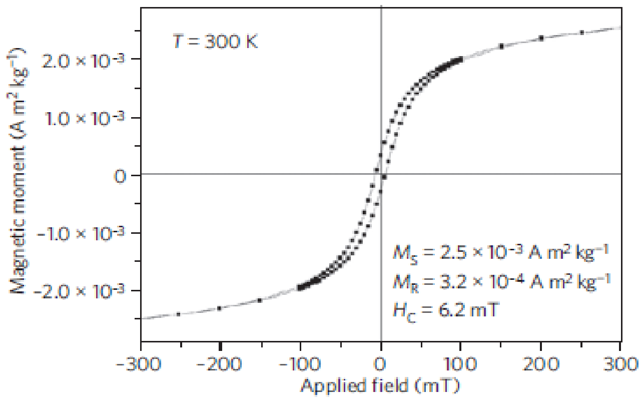
Magnetism in solids generally occur in alloys/compounds containing d/f ions.

Recently, some carbon based systems e.g., polymerized fullerenes and highly oriented pyrolytic graphite (HOPG) have been reported to show room temperature ferromagnetism. [Nature, 413, 716(2001); Nature Physics, 5, 840 (2009);PRL, 91, 227201 (2004)]



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- ❖ **Total magnetization quite small ~10^{-6} emu.**
- ❖ **Ferromagnetism in HOPG is believed to arise from dangling bonds associated with defects.**
- ❖ **Local magnetic studies are desirable**

Our Approach:

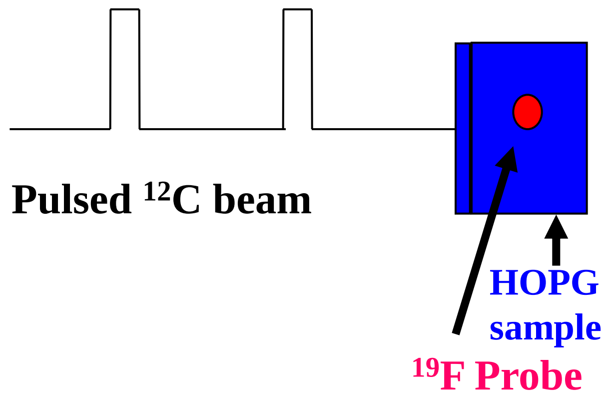
- ❑ Measure Hyperfine field for ^{19}F -- TDPAD method (TIFR-BARC Pelletron accelerator facility, Mumbai)

Why 19F?

$5/2^{+}$ isomer with $T_{1/2}$ = 89 ns,

$g_N = 1.44$; $Q_N = -0.12$ b

Well suited for magnetic studies



i. Production of ^{19}F

Via Heavy-ion reaction

$^{12}C(^{12}C,\alpha p)^{19}F$; E_{lab} = 40 MeV

ii) Recoil implantation of probe

Implantation depth ~ 10 μm

Concentration of ^{19}F in host << 1ppm

iii. The energetic ions also produce lots of defects

iv. Spin rotation of γ-rays from the $5/2^{+}$ isomeric state in ^{19}F and observation of spin rotation

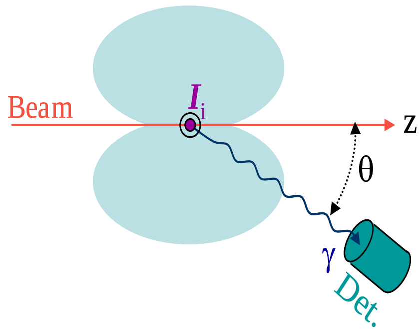
TDPAD setup at TIFR accelerator facility

7 Tesla Cryo-magnetic system --Temperature can be varied from 4~K to 500 K.

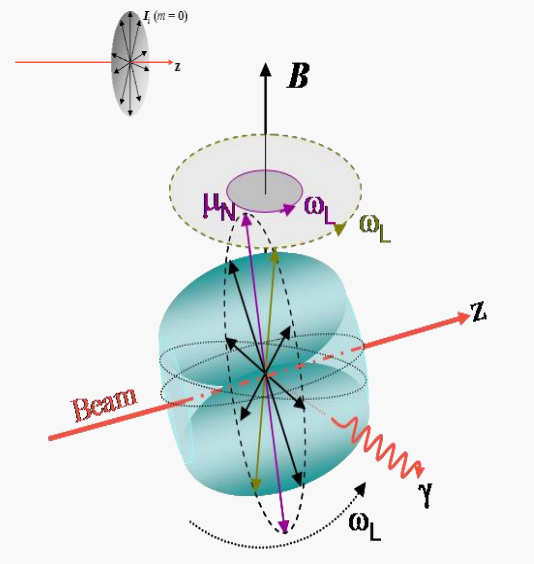
4 detectors (HPGe/La(Ce)Br_3) placed at 135^0 and 45^0

Angular Distribution of γ-Rays and its Perturbation

$$I_\gamma(\theta) = I_{0\gamma} e^{-\lambda t}\left[1 + A\,P_2(\cos\theta)\right]$$



The aligned probe nuclei precess in the "local" field. Emitting γ-rays are detected by one or more detectors placed in the reaction plane.

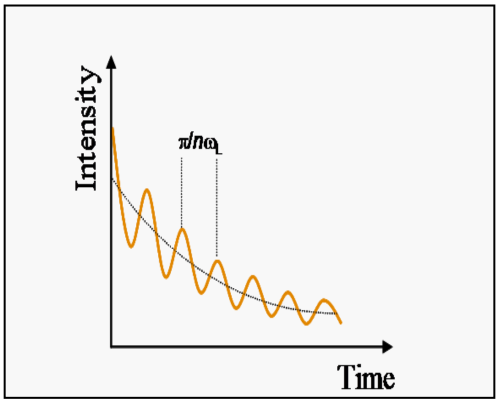


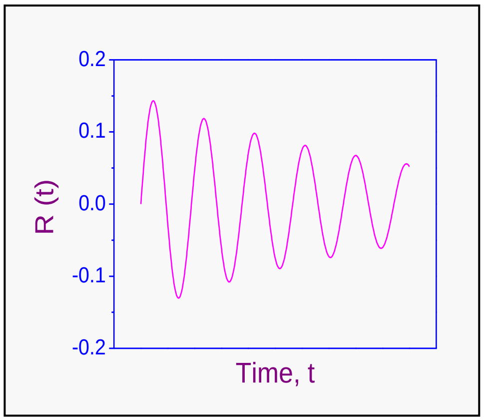
$$I_\gamma(\theta,t) = I_{0\gamma} e^{-\lambda t}\left[1 + G(t) P_2(\cos\theta)\right]$$

$$G(t)_{Magn} = A' \exp(-t/\tau_N)\cos(2\omega_L t - \varphi)$$

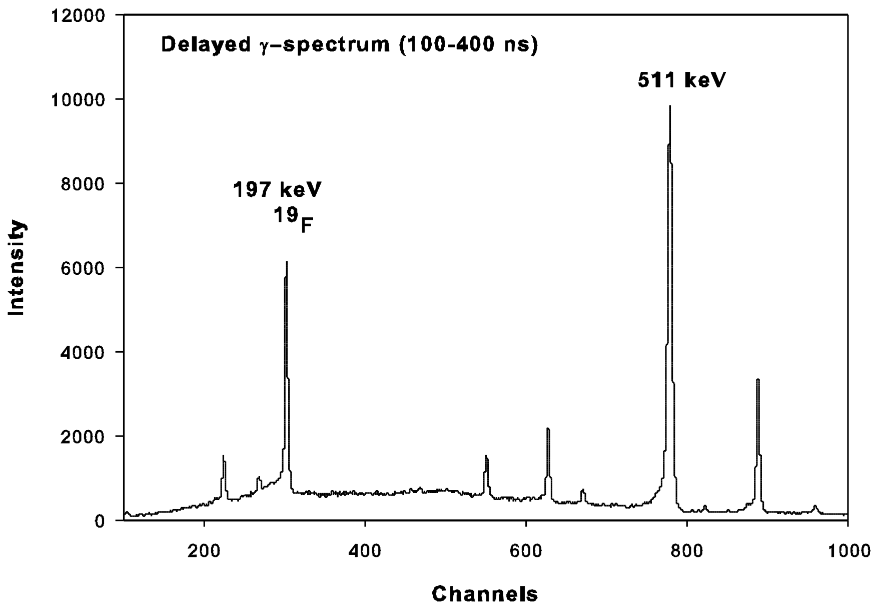
ω_L = Larmor frequency

τ_N ≡ relaxation time





- **Data collection: List mode**
- **Construct 2d spectra: (time vs energy)**
- **Projected energy spectrum show 197 keV line from $5/2^+$ state of ^{19}F**

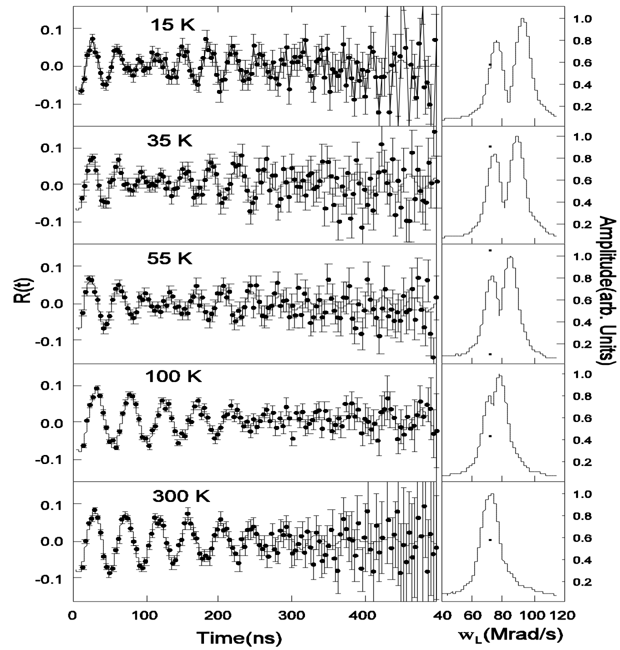


- **Life time spectra obtained by taking energy gated time projection**

- **Spin rotation spectra constructed from ratio**
  $R(t) = (N_1-N_2)/(N_1+N_2)$

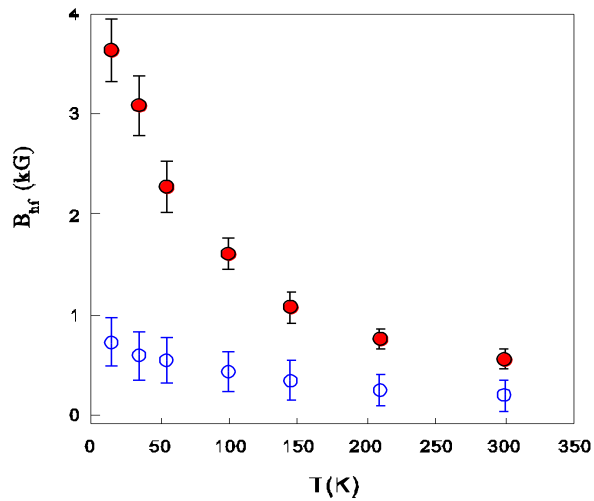
Results

- R(t) (measured in 1 T) show two frequencies



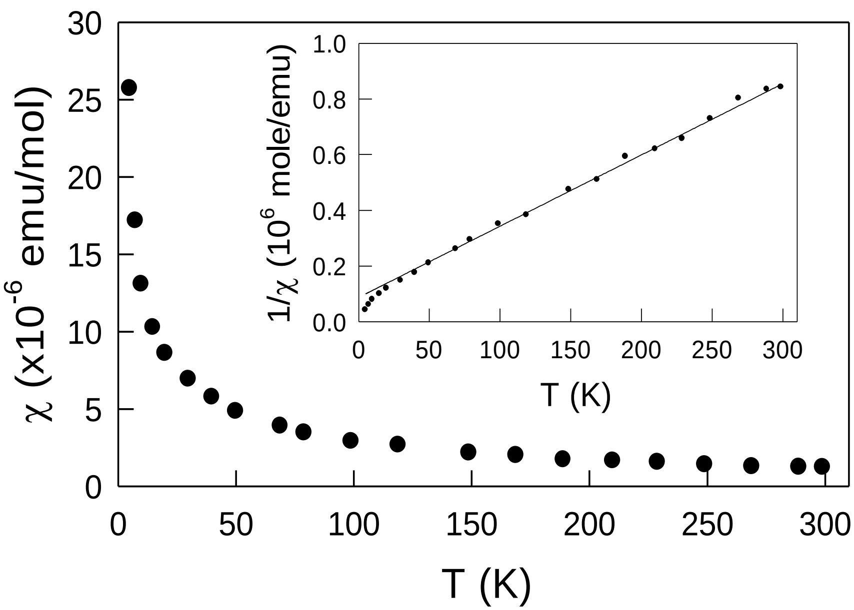
- @15 K
- $\omega_L(1)$ = 64 MHz (Bhf = 0.8 kG); Rel. Int. 45%
- $\omega_L(2)$ = 93 MHz (Bhf = 3.6 kG); Rel. Int. 55%

- ^{19}F comes to rest at two lattice sites
- $B_{hf}(T)$ Curie-Weiss type
- => Strong Paramagnetism



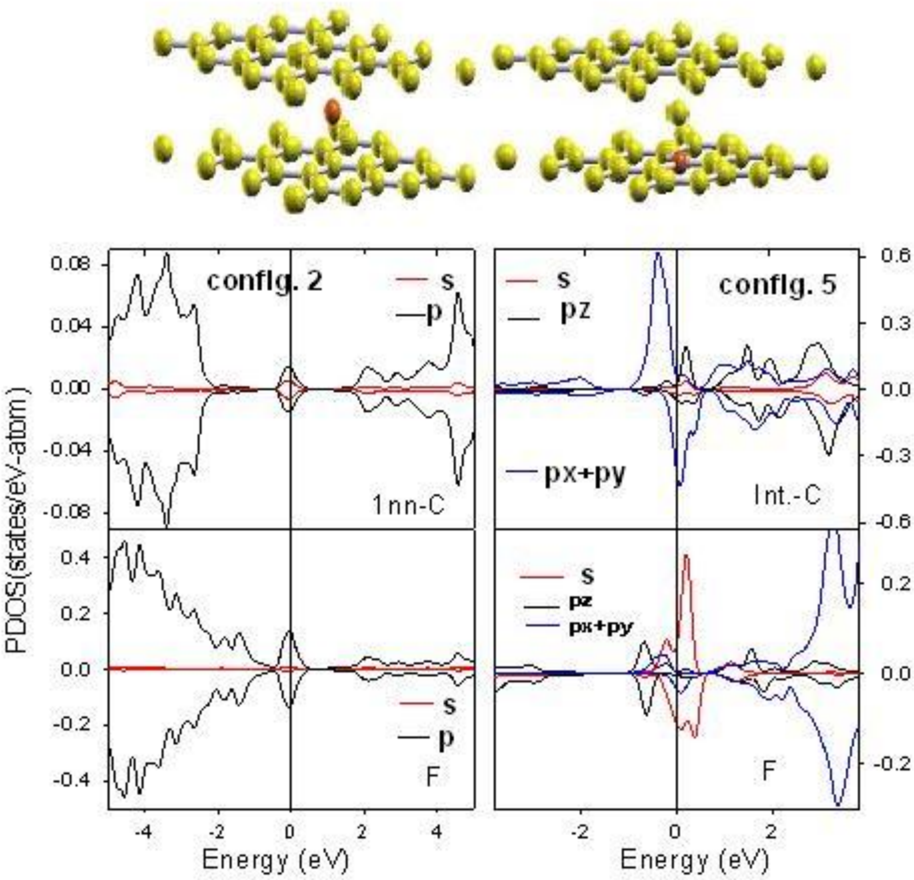
- No clear signature of ferromagnetic ordering

Absence of ferromagnetism confirmed by SQUID measurement of bulk susceptibility.



Density of states

magnetic moment on interstitial C atoms (right panel) mainly due to π electrons



How do we understand the results?

ab-initio density functional calculations using WIEN2K

- **Calculations made for many Configurations**
- **(i) F @ subst sites**
- **(ii)F @ interstitial sites**
- **(iii) subst. F + 1 vac**
- **(iv) Inters. F + 1 vac**
- **(v) Subst. F + 1 int. C**

Conf.	μ_{tot}	μ_F	$\mu_{1nn\text{-}C}$	$\mu_{2nn\text{-}C}$	B_{hf}(kG)
(i)	$1x10^{-4}$	0	0	0	-.001
(ii)	$5x10^{-3}$	$5x10^{-4}$	0	0	-0.271
(iii)	0.64	$3x10^{-2}$	-.011	0.017	-1.12
(iv)	1.0	0.067	0.005	-0.01	93.08
(v)	1.32	0.02	-0.007	0.16	9.4

B_{hf} observed for the majority fraction is close to the value calculated for configurations-v.

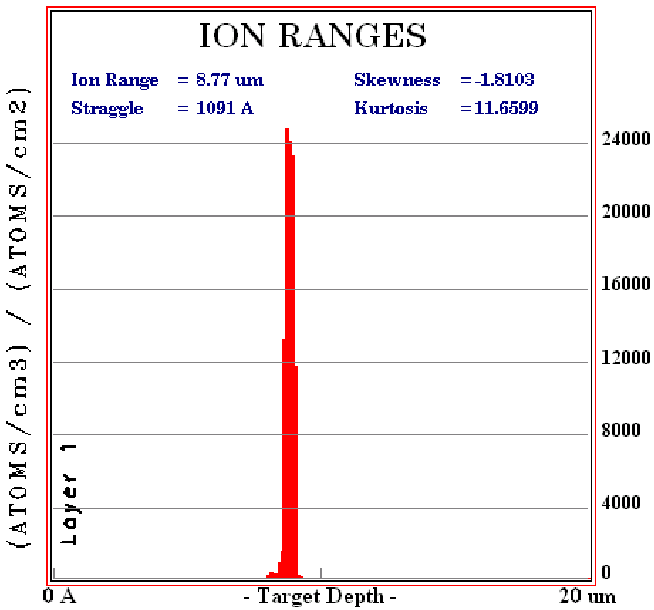
We therefore attribute it to F @ substitutional sites associated with one C atom at interstitial position.

The small B_{hf} of the minority fraction agrees with the value calculated for substitution F with one vacancy.

Conclusion:

Local measurements of 19F hyperfine field in HOPG by TDPAD technique does not show evidence of ferromagnetism. The results, however, reveal strong paramagnetism, due to defects induced by heavy-ion irradiation.

Thanks for your attention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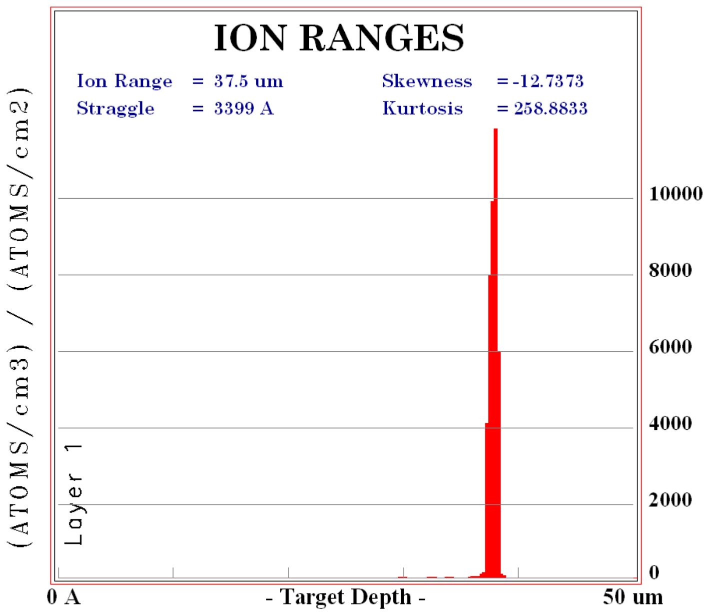
Ion Range = 8.77 um
Skewness = -1.8103
Straggle = 1091 A
Kurtosis = 11.6599
24000
20000
16000
12000
8000
4000
0
Layer 1
(ATOMS/cm3) / (ATOMS/cm2)
0 A
- Target Depth -
20 um


ION RANGES
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Skewness = -12.7373
Straggle = 3399 A
Kurtosis = 258.8833
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8000
6000
4000
2000
0
Layer 1
(ATOMS/cm3) / (ATOMS/cm2)
0 A
- Target Depth -
50 um