Graphite is a narrow band semiconductor

Searching for its intrinsic carrier density and mobility

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In Collabaoration with:U. Leipzig

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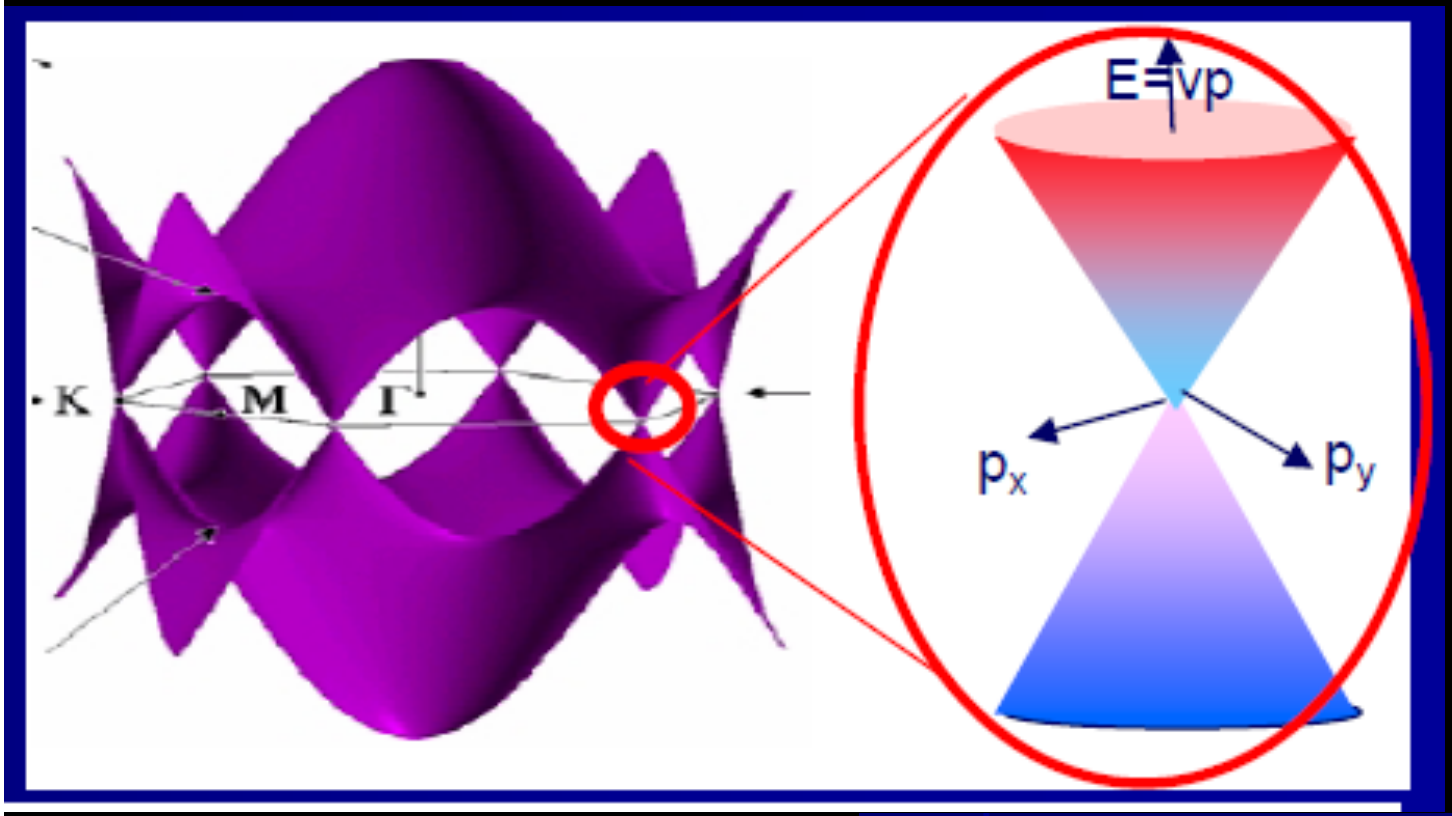
Content

- . The quasi-2D behavior of graphite and graphene (thin layers)
- Carrier density and mobility
- Comparison with graphene and
- Consequences

2D perfect graphene plane: Dirac Fermions of "zero mass"



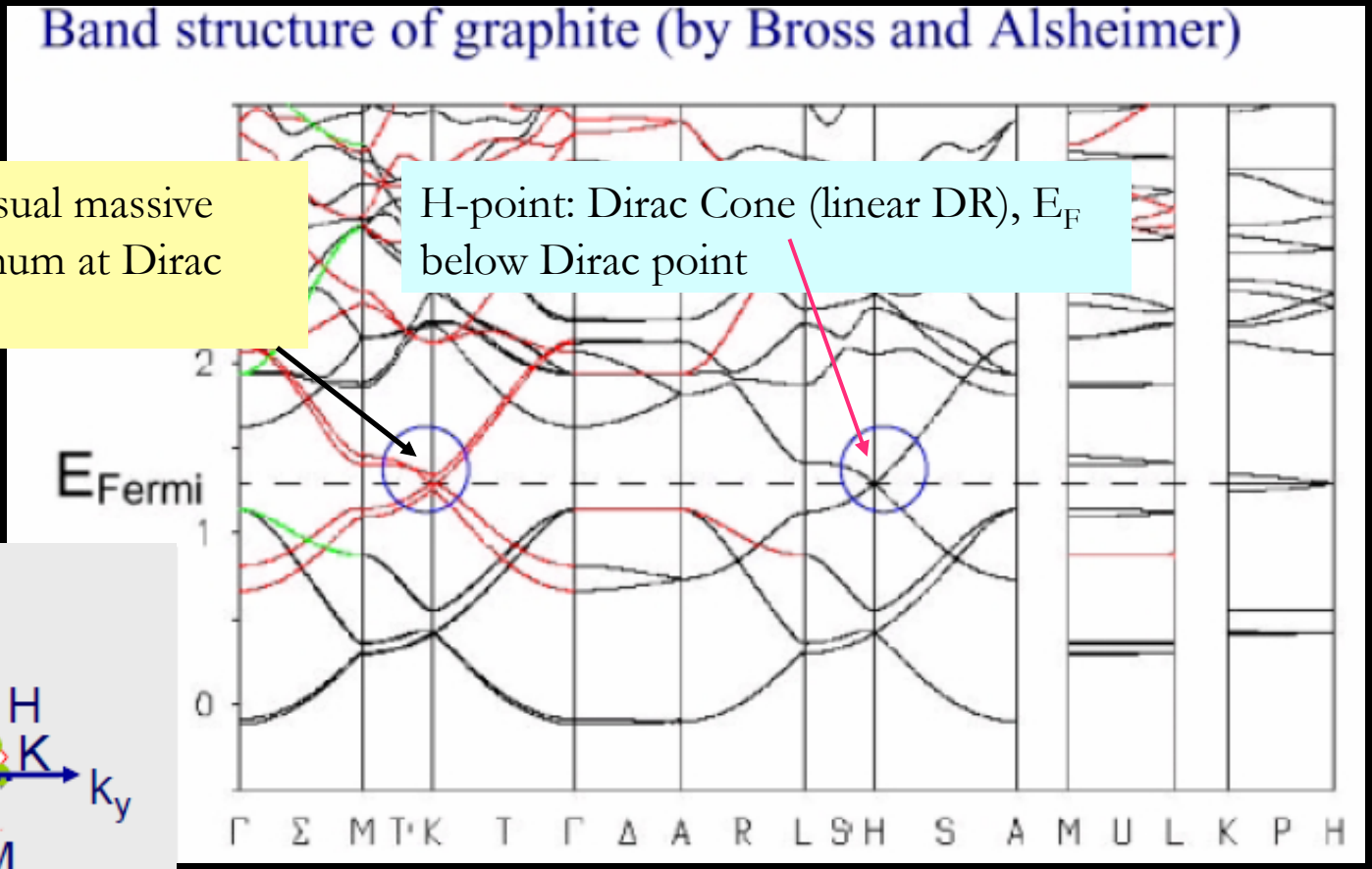
- *linear dispersion*

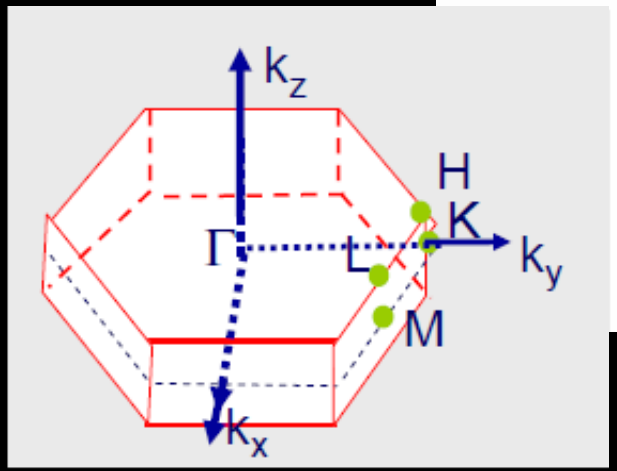
$$E(\vec{q}) = \pm v_F \hbar |\vec{q}|,$$

$$\vec{q} = \vec{k} - \vec{K}_F, \quad v_F \approx 10^6 \,\mathrm{m/s} \sim \mathrm{c}/300$$

- *Zero band mass*

Band structure of graphite





The details of this band structure depends on the assumed coupling between graphene layers !

Interlayer coupling or Binding energy per Carbon Atom: „an old and never-end story“

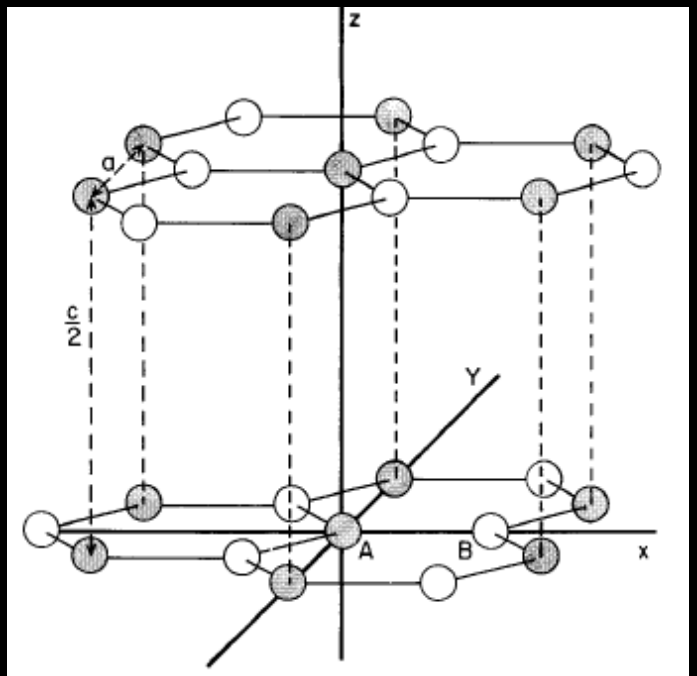


Figure 1 **The graphite crystal lattice.** *The distances between atoms are shown to scale. The distance a is 2.46 Å (the distance between nearest neighbors in a plane is 1.42 Å), and the c spacing is 6.74 Å (the distance between planes is 3.37Å).*

γ_1

The coupling γ_1 dramatically modifies all properties of the electron gas in Graphite →

Dispersion in perpendicular direction to the graphene planes

In other words, how large is the intrinsic carrier density ?

The energy band structure of graphite
A never-end story?

- 1937: first calculations, **Hund and Mrowka** (Akad.Wiss.Leipzig 87,185)
- 1947: first attempts to relate calculations with measured properties, **Wallace and Coulson**: zero energy gap and effective carrier density (per C-atom) 2D result:

$$n_{eff} = 0.3\,(k_B T/\gamma_0)^2$$

where $\gamma_0 \sim 3$eV is the overlap integral between nearest in-plane neighbors.

→ experimental results showed $n >> n_{eff}$

3D TB calculations introduce the overlap between atoms of one type in adjacent layers through a new integral $\gamma_1 \sim 0.3$ eV

$$n_{eff} = \frac{4}{\sqrt{3}\pi} k_B T \frac{\gamma_1}{\gamma_0^2} \left[S_1 + \frac{\pi k_B T}{2\gamma_1} S_2 + \frac{3}{2} \left(\frac{k_B T}{\gamma_1} \right)^2 S_3 + \ldots \right]$$

$n \rightarrow 0$ cm^{-2} for T → 0K

- … (new γ's)
- 1952: Coulson and Taylor studied the effect of the distance between adjacent planes
- … (new γ's)
- 1958: Slonczweski and Weiss, TB 3D full perturbative calculation
- … (new γ's)

Energy Band Structure of Graphite*

IBM JOURNAL • JULY 1964

J. W. McClure †

Abstract: The energy band structure of graphite is described in the region of the Fermi surfaces by the Slonczewski-Weiss model. The electron and hole Fermi surfaces are highly elongated and are aligned along the six Brillouin zone edges which are parallel to the trigonal axis of the crystal. The energy is a non-parabolic function of wavenumber and the Fermi surfaces are not ellipsoids. Galvanomagnetic, de Haas-van Alphen, and other experiments have established that: the band overlap is about 0.03 to 0.04 eV, the carrier densities of electrons and holes are each about 3×10^{18} cm^{-3} at low temperatures, the effective masses perpendicular to the trigonal axis are about 0.04 m_0 for electrons and 0.06 m_0 for holes, and the

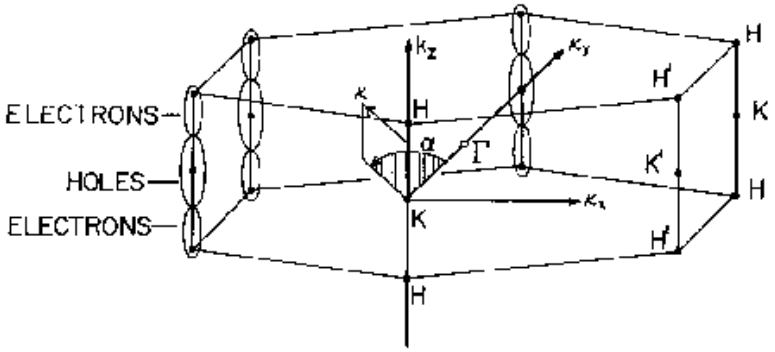


Figure 2 **The Brillouin zone for graphite, showing the positions of the Fermi surfaces.** *The Fermi surfaces are magnified in the horizontal direction by about a factor four. The surfaces are not drawn about all of the zone edges, in order to show the coordinate system more clearly.*

$n(0) \sim 10^{10}$ cm^{-2}

- γ_0
- γ_1
- γ_2 : Overlap integral between other C-atoms site
- γ_3 : Overlap integral between C-atoms of different sites
- γ_4 : Overlap integral between layers
- γ_5 : Overlap integral between layers
- Δ : Energy shift

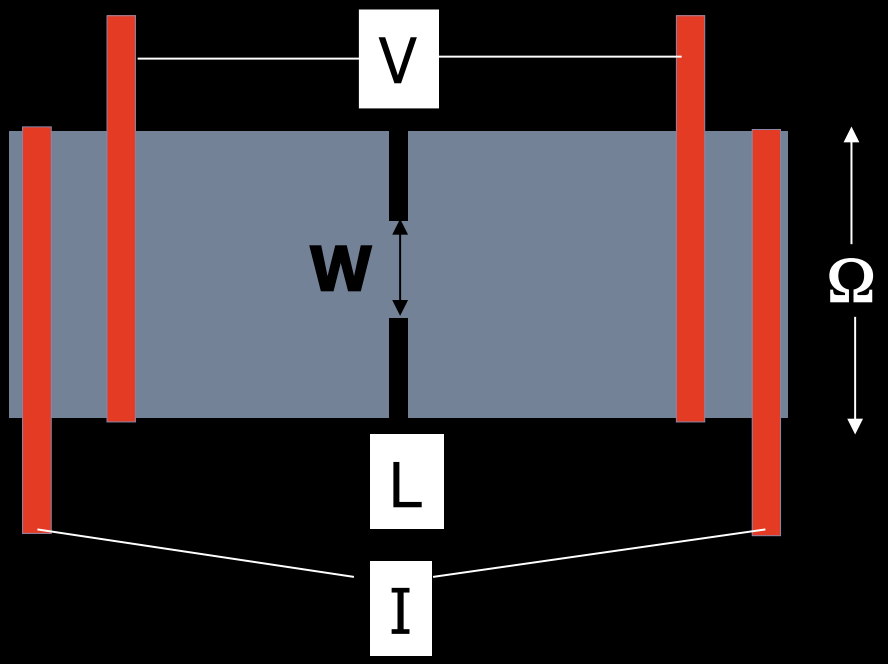
But …

How large is the “intrinsic” carrier density in graphite ?

and the carrier mean free path ?

How can we measure them without introducing too many unknown parameters ?

Use Constrictions and check whether there is a crossing to ballistic regime



Transport of carriers shifts from Ohmic to ballistic when $\ell > W$, the constriction width.

The difference between the resistance of the samples with and without constriction gives $\ell(T)$

L ~ 0.5 … 5 μm
W ~ 1 μm to 1000 μm

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Simple ballistic model for 2-dimensional systems

ℓ < sample dimensions

λ_F < sample dimensions and constriction width **W**

$$R_{2D} = \frac{\rho(T)}{t}\left[\ \frac{\ell(T)a\pi}{4W} + \frac{2a}{\pi}\gamma\left(\frac{W}{\ell(T)}\right)\ln\left(\frac{\Omega}{W}\right)\Big|_{W<<\Omega} + \frac{L}{W}\ \right]$$

Ballistic

Ohmic

Ohmic at Constriction

γ – geometrical function depends on $\frac{W}{\ell(T)}$, γ ~ 0.7.....1.

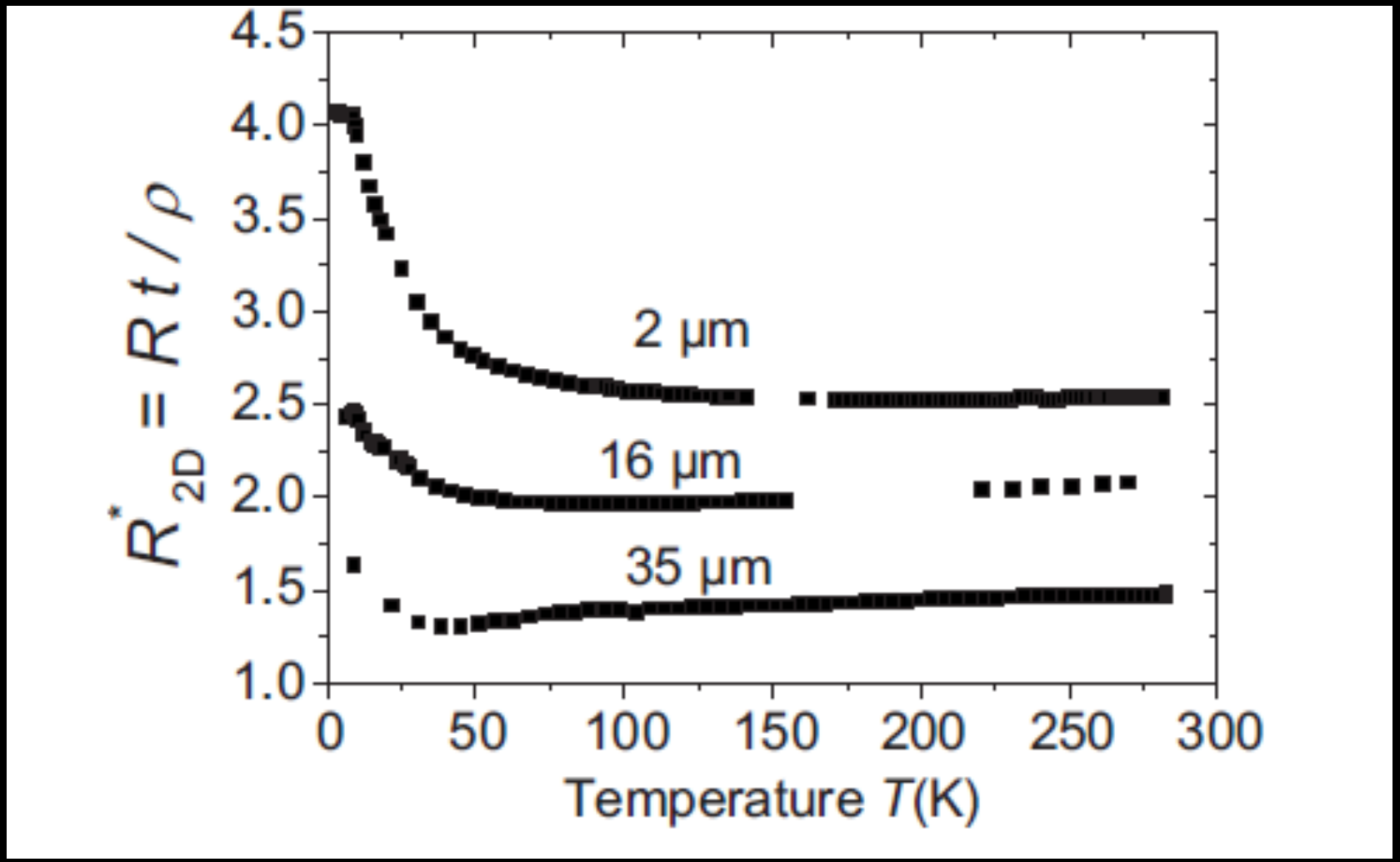
t – thickness

a ~ $\frac{1}{2}$

$$\frac{\pi\rho(T)\ell(T)}{4Wt} = \frac{h}{4e^2}\frac{1}{N_s}\frac{\lambda(T)}{2W}$$

$$\mu = (e/h)\lambda(T)\ell(T)$$

Macroscopic HOPG sample results



GARCÍA *et al.* PHYSICAL REVIEW B **78**, 035413 (2008)

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Transition from Ohmic to ballistic transport in oriented graphite: Measurements and numerical simulations

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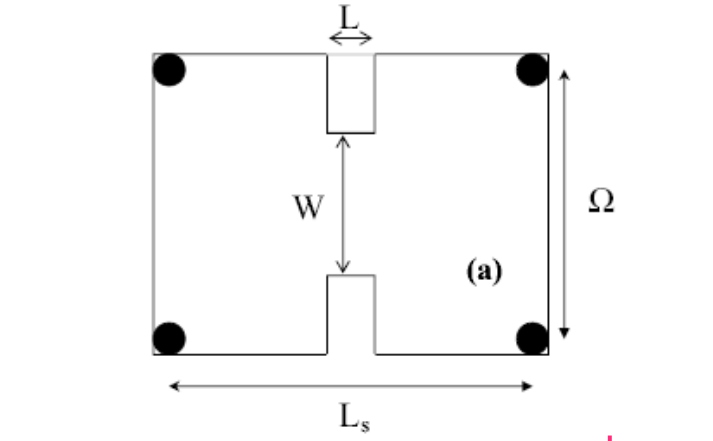
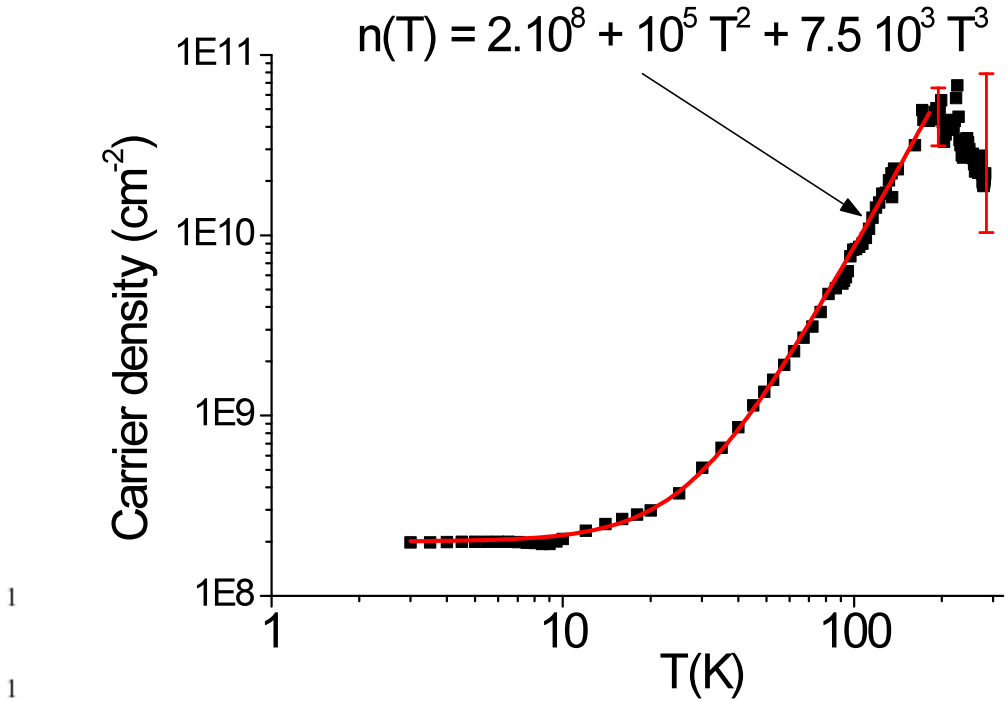
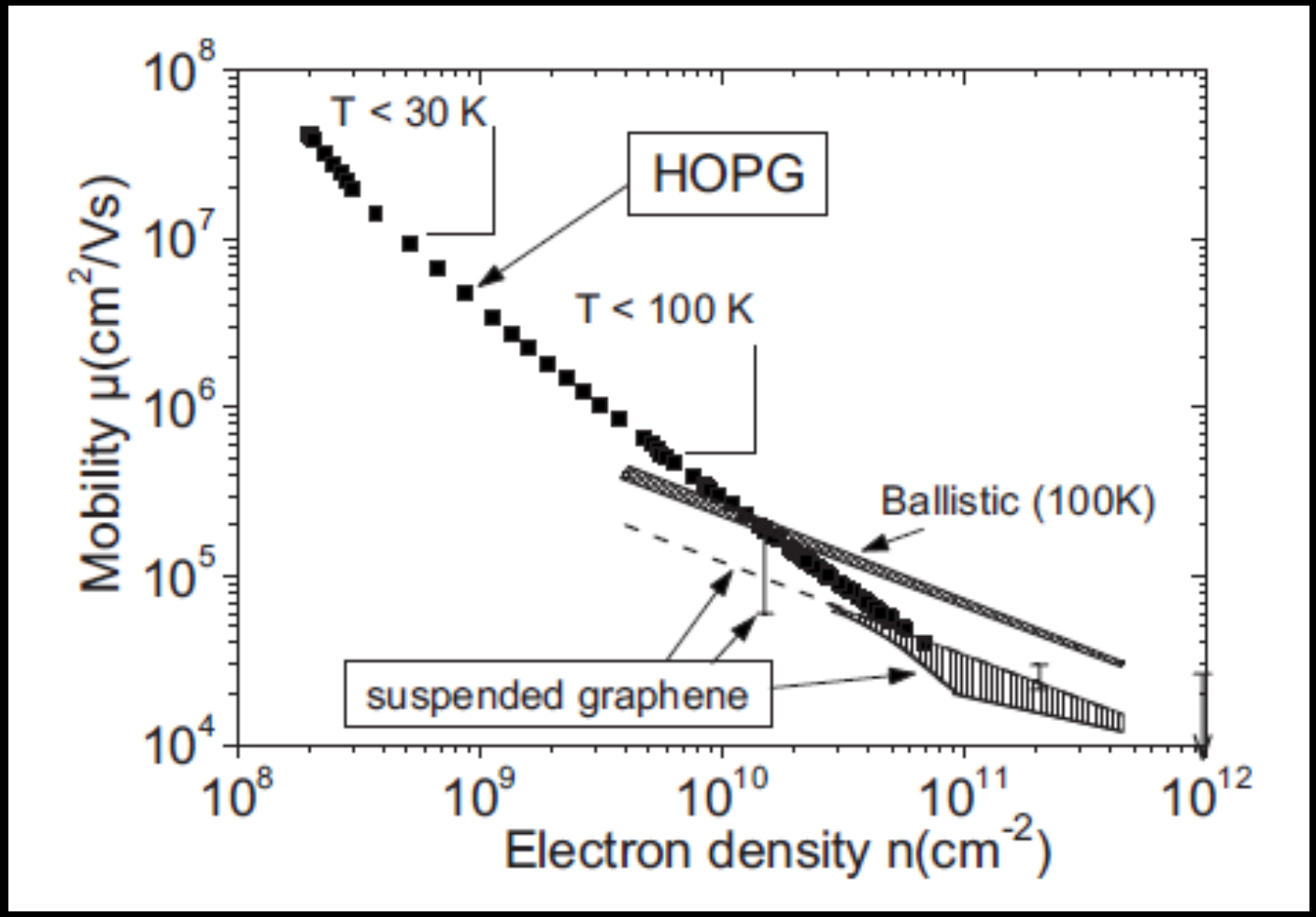
Parameter free determination of **n** and mobility **μ** in oriented graphite





Comparison between graphite and graphene



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Evidence for a narrow band gap in Bernal graphite

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Abstract.

We have studied the resistance of a large number of highly oriented graphite samples with areas ranging from several mm^2 to a few μm^2 and thickness from $\sim$ 10 nm to several tens of micrometers. The measured resistance can be explained by the parallel contribution of semiconducting graphene layers with low carrier density $< 10^9$ cm^{-2} and the one from metalliclike internal interfaces. The results indicate that ideal graphite with Bernal stacking structure is a narrow-gap semiconductor with an energy gap $E_g \sim 40$ meV.

PACS numbers: 73.90.+f,61.80.-x,81.05.Uw

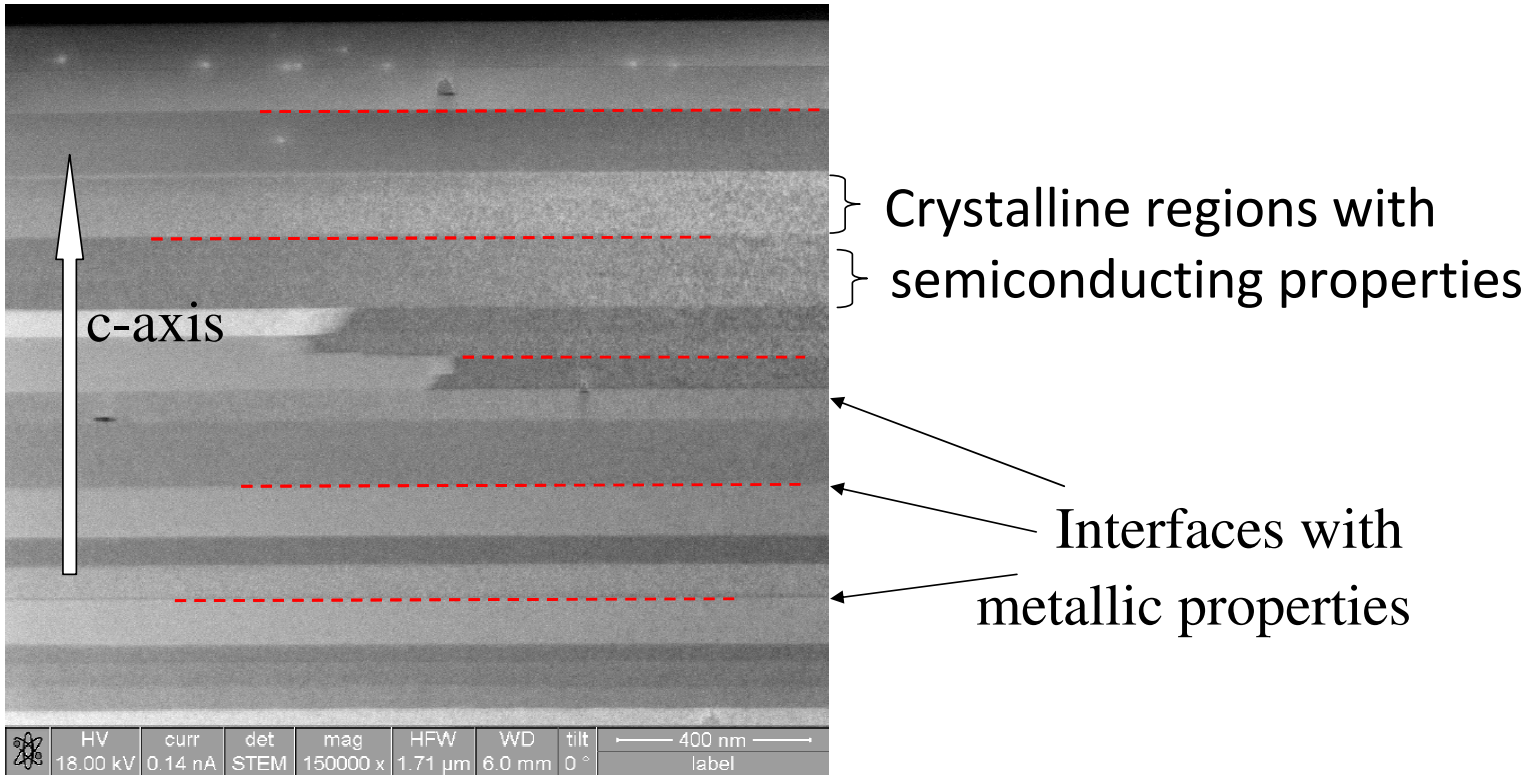


Figure 1. Transmission electron microscope picture of the internal microstructure of a highly oriented pyrolytic graphite sample as shown in Ref.[19] and similar to those used in this study. The dashed red lines indicate some of the interface regions between the single crystalline graphite parts. These interfaces run parallel to the graphene layers up to several micrometers till a larger defect is encountered (see the defective region in the middle of the picture). Regions with different gray colors indicate slightly different orientation of the graphite structure. From measurements with EBSD we know that the usual size of these single crystalline regions in the a, b plane is less than 10 μm [17, 18].

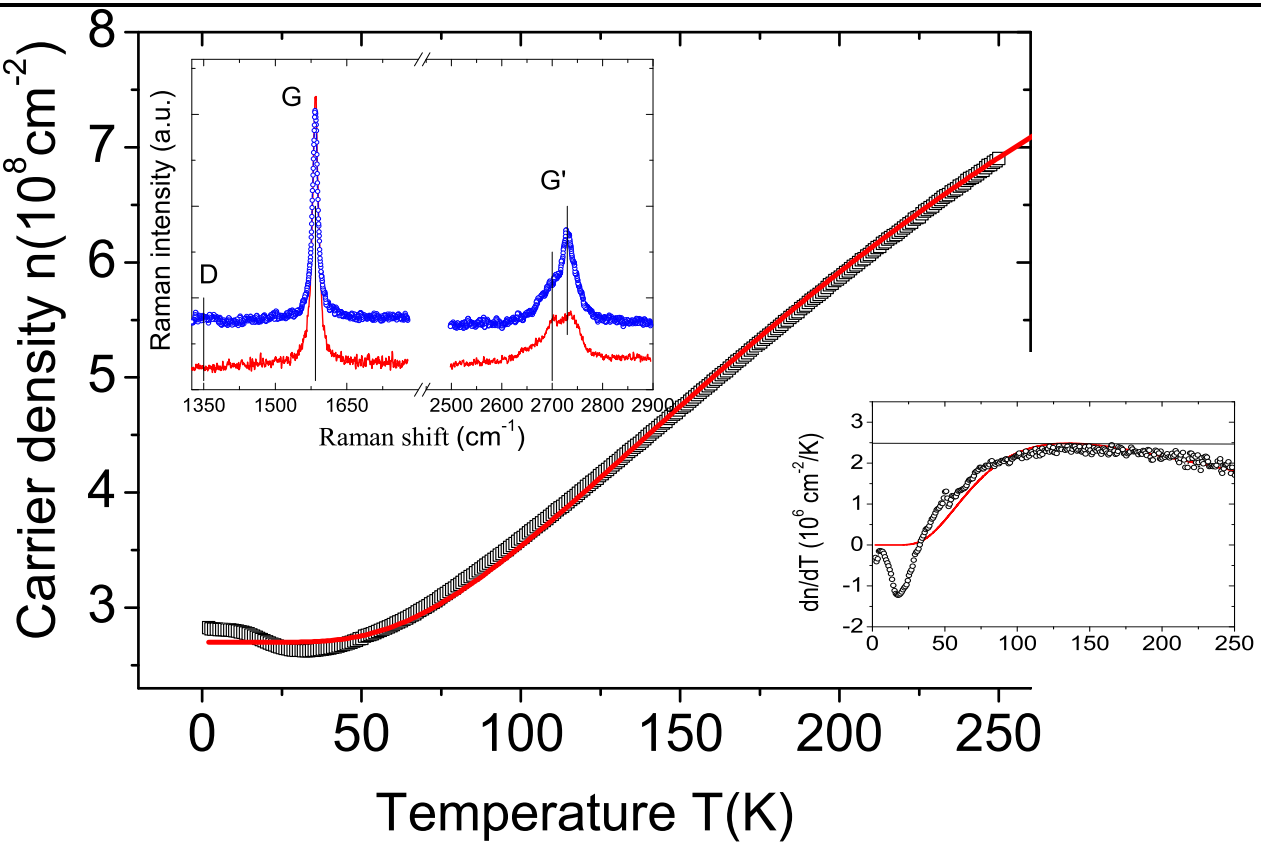


Figure 2. Carrier density per graphene layer obtained using the constriction method [18] for a graphite sample of size $9 \times 3 \times 0.040$ μm^3. The continuous line is a fit to the data and follows $n(T)[10^8\mathrm{cm}^{-2}] = 2.7 + 12.4\exp(-540/2T[\mathrm{K}])$. We estimate a $\sim 30\%$ error in the absolute value of the carrier density, mainly due sample geometry errors as well as in the constriction widths. The upper left inset shows the Raman (514 nm) spectra of: ($\circ$) bulk graphite (Fig.2(a)) and a (red line) multigraphene sample (similar to that of Fig.3(a)). The absence of a D-peak indicates the absence of a significant number of defects. The bottom right inset shows the temperature dependent derivative of the carrier density (circles) and of the fitting curve shown in the main panel. Note the maximum in the derivative at $\sim$ 125 K present in both derivatives. The horizontal straight line is only a guide to the eye.

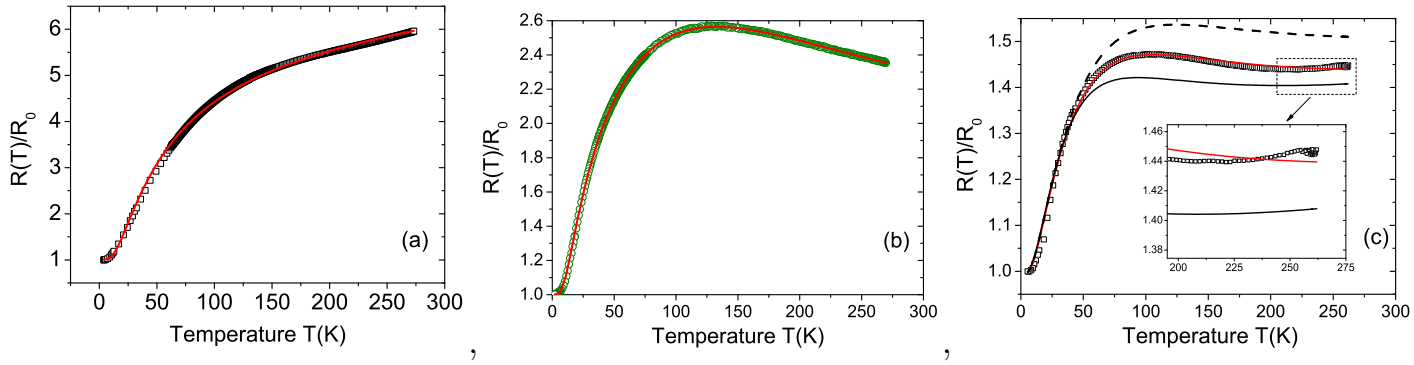


Figure 3. Normalized resistance R/R_0 vs. temperature for three HOPG samples with thickness, length (between voltage electrodes), width and R_0: (a) $\simeq$ 20 μm,

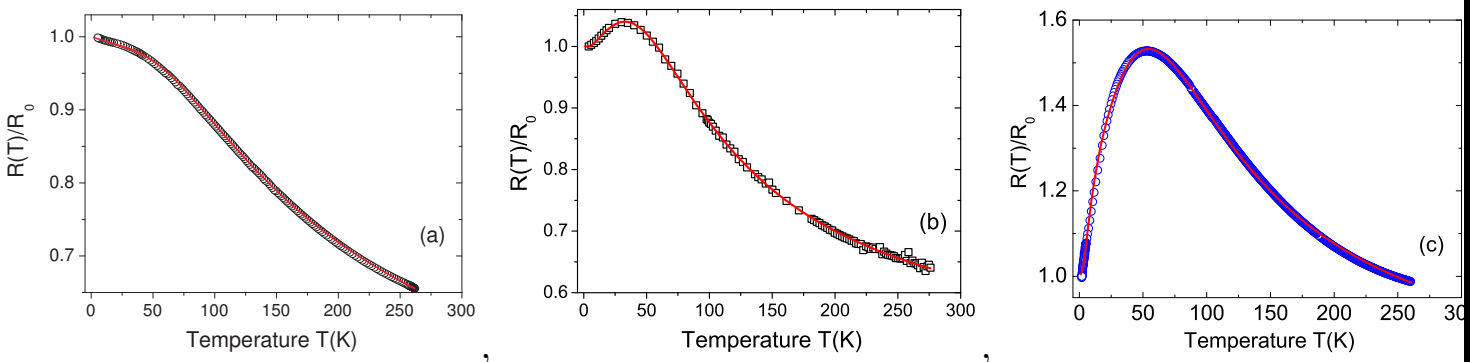


Figure 4. Similar to Fig. 3 but for samples with geometry and R_0: (a) $\simeq$ 13 14 μm , 10 μm, 490 Ω; (b) $\simeq$ 20 nm, 5 μm , 10 μm, 32 Ω; (c) $\simeq$ 37 nm, 27 6 μm, 69 Ω. The lines through the experimental data follow: (a) $R_i(T)/R$

However, a main issue remains still open

- Is the “measured” carrier concentration in graphite intrinsic or is affected by defects and impurities? Note: 10^{10} cm^{-2} ~ 10 ppm !

→ We can measure nowadays impurities in carbon to 0.1 ppm, but we cannot measure the C-vacancies and C-interstitials concentration with such a precision!

Since there are no defect-free graphite samples, let us answer the main question by

- Inducing a small amount of defects (vacancies and interstitials), e.g. between 0.1 … 100 ppm, and
- measure the change in the electrical resistivity induced by those defect concentrations

Simple estimate

In the virgin state and at 300 K, within a factor of two, the carrier density is:

$$n_0 \sim 6 \times 10^{10}\ \mathrm{cm}^{-2}$$

For a fluence of 10^{13} H^+/ cm^2 one would produce:

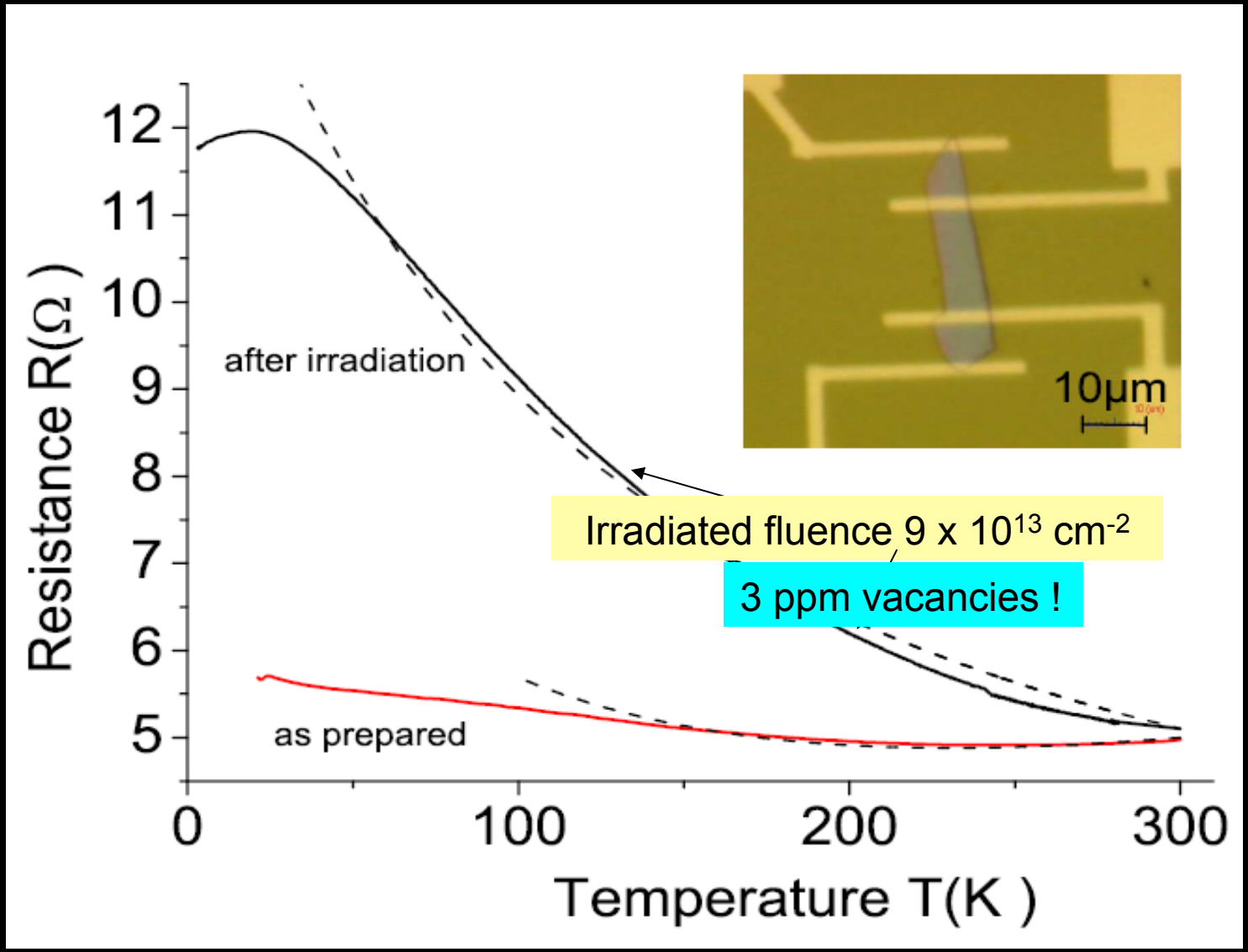
$$n_V \sim 10^9\ \mathrm{cm}^{-2} \sim 0.01\ n_0$$

assuming that each vacancy produces 1 carrier

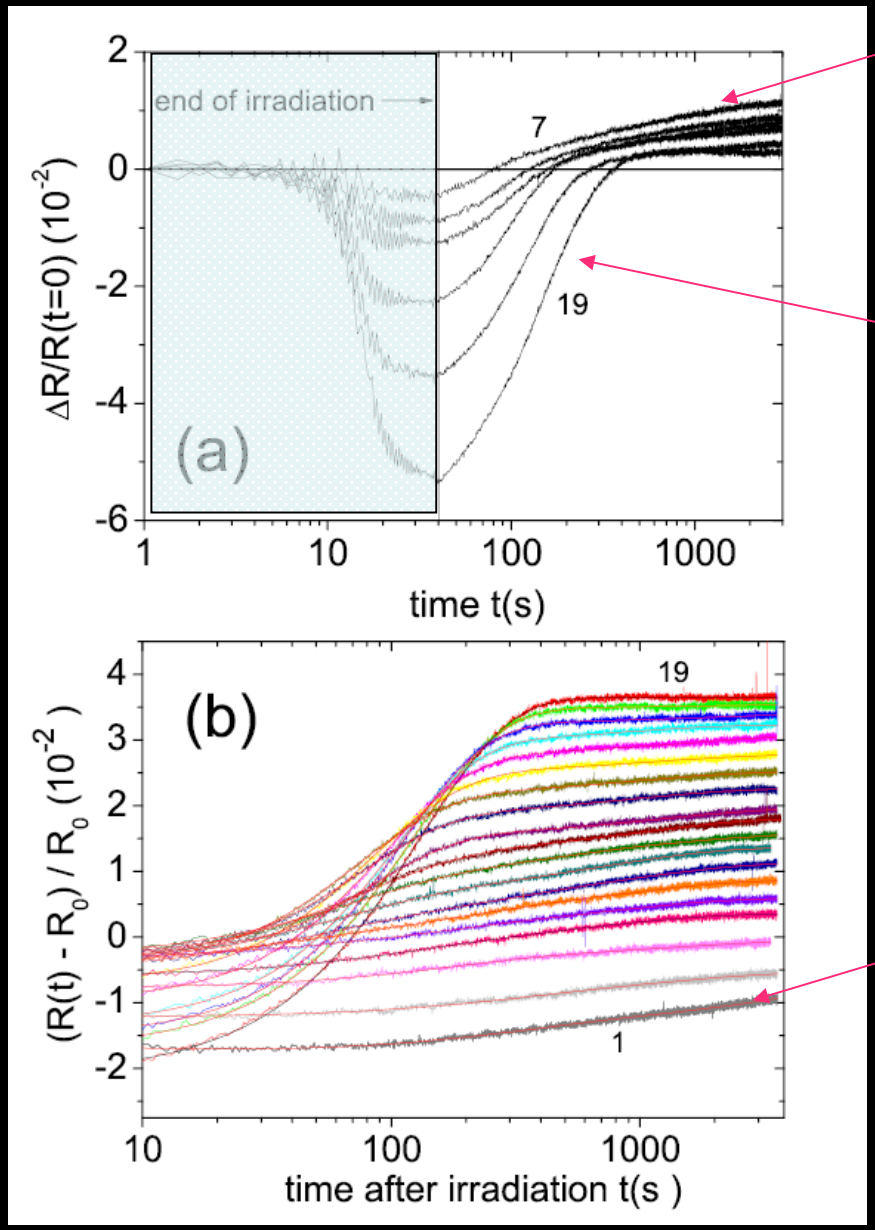
The related wave-vector $k_V = (\pi n_V)^{1/2} \sim 0.1\ k_F$

This estimate reveals that a small concentration of defects can be relevant to the transport

Experimental results
Temperature dependence R(T)



Change of R during and after proton irradiation



3 x 10^9 cm^{-2}

R(t=0) resistance in relaxed state after irradiation

9 x 10^9 cm^{-2}

T = 297 K

R_0 resistance in virgin state

1 x 10^9 cm^{-2}