



Carbonio, suoi stati allotropici e Grafite

M. Riccò



PERIODIC TABLE

Atomic Properties of the Elements

	Group 1 IA	Group 2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIII	9 VIII	10 VIII	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA	
1	H Hydrogen 1.00794 1s																	He Helium 4.002602 1s ²	
2	Li Lithium 6.941 1s ² 2s ¹	Be Beryllium 9.012182 1s ² 2s ²																B Boron 10.811 1s ² 2s ² 2p ¹	Ne Neon 20.1797 1s ² 2s ² 2p ⁶
3	Na Sodium 22.989770 [Ne]3s ¹	Mg Magnesium 24.3050 [Ne]3s ²																Ar Argon 39.948 [Ne]3s ² 3p ⁶	
4	K Potassium 39.0983 [Ar]4s ¹	Ca Calcium 40.078 [Ar]4s ²	Sc Scandium 44.955910 [Ar]3d ¹ 4s ²	Ti Titanium 47.88 [Ar]3d ² 4s ²	V Vanadium 50.9415 [Ar]3d ³ 4s ²	Cr Chromium 51.9961 [Ar]3d ⁵ 4s ¹	Mn Manganese 54.938049 [Ar]3d ⁵ 4s ²	Fe Iron 55.845 [Ar]3d ⁶ 4s ²	Co Cobalt 58.933200 [Ar]3d ⁷ 4s ²	Ni Nickel 58.6934 [Ar]3d ⁸ 4s ²	Cu Copper 63.546 [Ar]3d ¹⁰ 4s ¹	Zn Zinc 65.38 [Ar]3d ¹⁰ 4s ²	Ga Gallium 69.723 [Ar]3d ¹⁰ 4s ² 4p ¹	Ge Germanium 72.64 [Ar]3d ¹⁰ 4s ² 4p ²	As Arsenic 74.9216 [Ar]3d ¹⁰ 4s ² 4p ³	Se Selenium 78.96 [Ar]3d ¹⁰ 4s ² 4p ⁴	Br Bromine 79.904 [Ar]3d ¹⁰ 4s ² 4p ⁵	Kr Krypton 83.798 [Ar]3d ¹⁰ 4s ² 4p ⁶	
5	Rb Rubidium 85.4678 [Kr]5s ¹	Sr Strontium 87.62 [Kr]5s ²	Y Yttrium 88.90585 [Kr]4d ¹ 5s ²	Zr Zirconium 91.224 [Kr]4d ² 5s ²	Nb Niobium 92.90638 [Kr]4d ⁴ 5s ¹	Mo Molybdenum 95.94 [Kr]4d ⁵ 5s ¹	Tc Technetium (98) [Kr]4d ⁵ 5s ²	Ru Ruthenium 101.07 [Kr]4d ⁷ 5s ¹	Rh Rhodium 102.90550 [Kr]4d ⁸ 5s ¹	Pd Palladium 106.42 [Kr]4d ¹⁰	Ag Silver 107.8682 [Kr]4d ¹⁰ 5s ¹	Cd Cadmium 112.411 [Kr]4d ¹⁰ 5s ²	In Indium 114.818 [Kr]4d ¹⁰ 5s ² 5p ¹	Tl Thallium 118.710 [Kr]4d ¹⁰ 5s ² 5p ²	Pb Lead 127.603 [Kr]4d ¹⁰ 5s ² 5p ²	Bi Bismuth 127.603 [Kr]4d ¹⁰ 5s ² 5p ³	Po Polonium (209) [Kr]4d ¹⁰ 5s ² 5p ⁴	At Astatine (210) [Kr]4d ¹⁰ 5s ² 5p ⁵	Xe Xenon 131.293 [Kr]4d ¹⁰ 5s ² 5p ⁶
6	Cs Cesium 132.90545 [Xe]6s ¹	Ba Barium 137.327 [Xe]6s ²	La Lanthanum 138.9055 [Xe]5d ¹ 6s ²	Ce Cerium 140.116 [Xe]4f ¹ 5d ¹ 6s ²	Pr Praseodymium 140.90765 [Xe]4f ³ 6s ²	Nd Neodymium 144.24 [Xe]4f ⁴ 6s ²	Pm Promethium (145) [Xe]4f ⁵ 6s ²	Sm Samarium 150.36 [Xe]4f ⁶ 6s ²	Eu Europium 151.964 [Xe]4f ⁷ 6s ²	Gd Gadolinium 157.25 [Xe]4f ⁷ 5d ¹ 6s ²	Tb Terbium 158.92534 [Xe]4f ⁹ 6s ²	Dy Dysprosium 162.500 [Xe]4f ¹⁰ 6s ²	Ho Holmium 164.93032 [Xe]4f ¹¹ 6s ²	Er Erbium 167.259 [Xe]4f ¹² 6s ²	Tm Thulium 168.93421 [Xe]4f ¹³ 6s ²	Yb Ytterbium 173.04 [Xe]4f ¹⁴ 6s ²	Lu Lutetium 174.967 [Xe]4f ¹⁴ 5d ¹ 6s ²		
7	Fr Francium (223) [Rn]7s ¹	Ra Radium (226) [Rn]7s ²	Ac Actinium (227) [Rn]5f ¹ 7s ²	Th Thorium 232.0381 [Rn]5f ¹ 6d ² 7s ²	Pa Protactinium 231.03688 [Rn]5f ² 6d ¹ 7s ²	U Uranium 238.02891 [Rn]5f ³ 6d ¹ 7s ²	Np Neptunium (237) [Rn]5f ⁴ 6d ¹ 7s ²	Pu Plutonium (244) [Rn]5f ⁶ 7s ²	Am Americium (243) [Rn]5f ⁷ 7s ²	Cm Curium (247) [Rn]5f ⁸ 6d ¹ 7s ²	Bk Berkelium (247) [Rn]5f ⁹ 6d ¹ 7s ²	Cf Californium (251) [Rn]5f ¹⁰ 7s ²	Es Einsteinium (252) [Rn]5f ¹¹ 7s ²	Fm Fermium (257) [Rn]5f ¹² 7s ²	Md Mendelevium (258) [Rn]5f ¹³ 7s ²	No Nobelium (259) [Rn]5f ¹⁴ 7s ²	Lr Lawrencium (262) [Rn]5f ¹⁴ 6d ¹ 7s ²		

Frequently used fundamental physical constants

For the most accurate values of these and other constants, visit physics.nist.gov/constants

1 second = 9 192 631 770 periods of radiation corresponding to the transition between the two hyperfine levels of the ground state of ¹³³Cs

speed of light in vacuum	<i>c</i>	299 792 458 m s ⁻¹ (exact)
Planck constant	<i>h</i>	6.6261 × 10 ⁻³⁴ J s (<i>h</i> = <i>h</i> 2π)
elementary charge	<i>e</i>	1.6022 × 10 ⁻¹⁹ C
electron mass	<i>m_e</i>	9.1094 × 10 ⁻³¹ kg
	<i>m_ec²</i>	0.5110 MeV
proton mass	<i>m_p</i>	1.6726 × 10 ⁻²⁷ kg
fine-structure constant	<i>α</i>	1/137.036
Rydberg constant	<i>R_∞</i>	10 973 732 m ⁻¹
	<i>R_{H,C}</i>	3.289 842 × 10 ¹⁵ Hz
	<i>R_∞hc</i>	13.6057 eV
Boltzmann constant	<i>k</i>	1.3807 × 10 ⁻²³ J K ⁻¹

- Solids
- Liquids
- Gases
- Artificially Prepared

Atomic Number: 58

Ground-state Level: 1G₄

Symbol: **Ce**

Name: Cerium

Atomic Weight: 140.116

Ground-state Configuration: [Xe]4f¹5d¹6s²

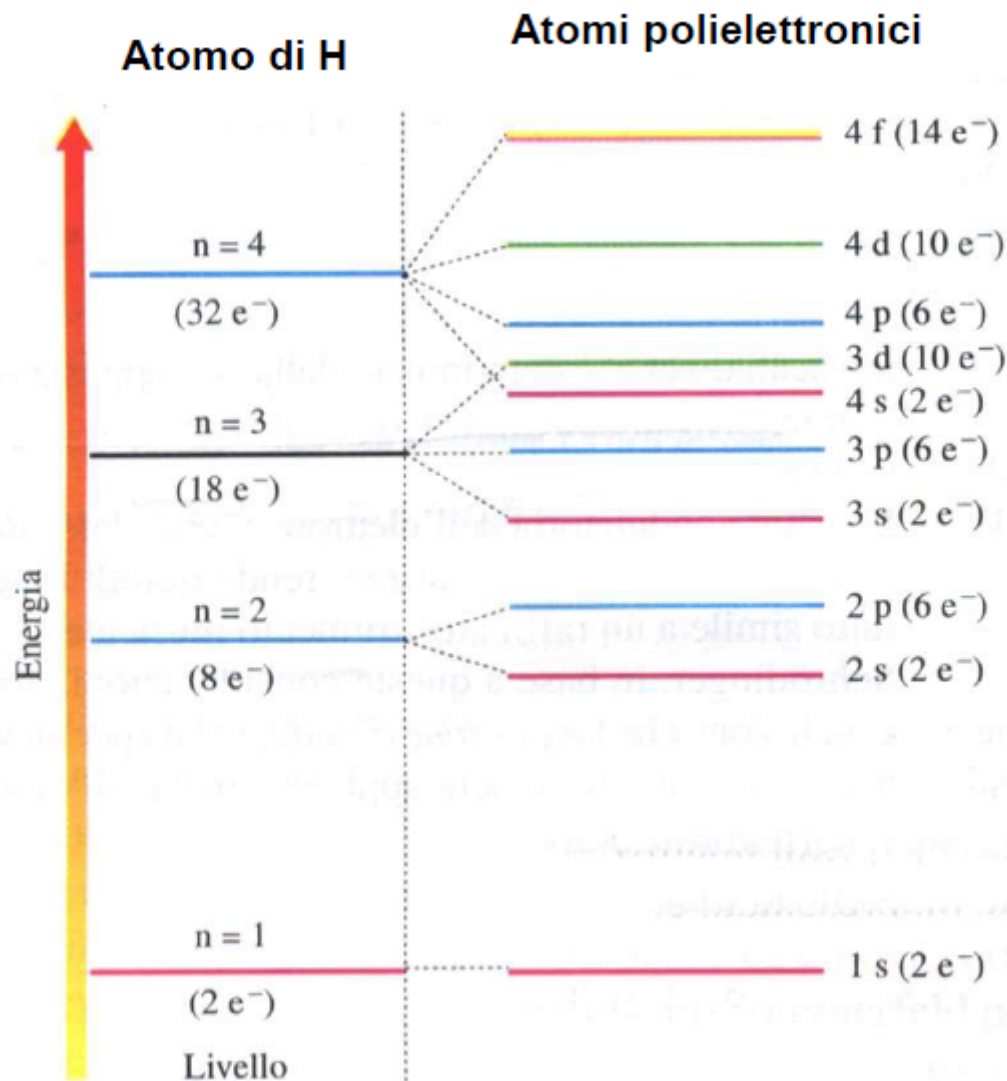
Ionization Energy (eV): 5.5387

[†]Based upon ¹²C. () indicates the mass number of the most stable isotope.

For a description of the data, visit physics.nist.gov/data



- Isotopo ^{12}C \rightarrow abbondanza naturale (98.93%, $S=0$)
- Isotopo ^{13}C \rightarrow importante per l'NMR (1.07%, $S=1/2$)
- Isotopo ^{14}C \rightarrow importante per la datazione archeologica (vita media 5730 anni)



L'energia di ogni elettrone negli atomi polielettronici dipende non solo da n , ma anche da l ; conseguenza fondamentale delle interazioni interelettroniche

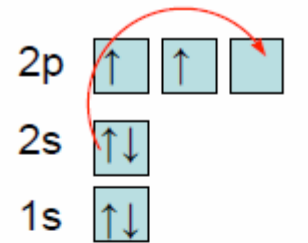
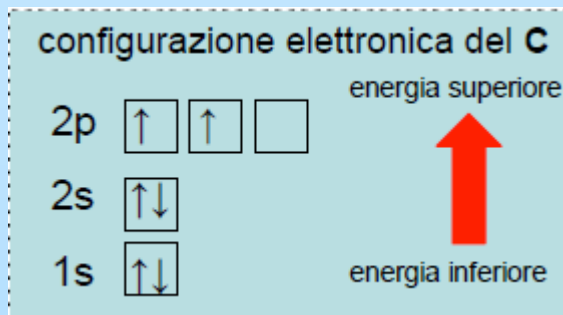
Scissione dei livelli energetici in più sottolivelli distinti di energia crescente, per un dato valore di n , con il crescere di l .

Tra il livello 3 ed il livello 4 vi è una sovrapposizione dei livelli energetici

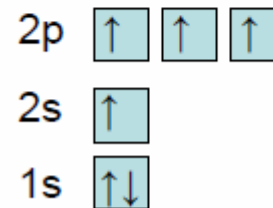


Ibridizzazione sp^3

Configurazione: $[\text{He}] 2s^2 2p^2$



stato fondamentale



stato eccitato



orbitale s



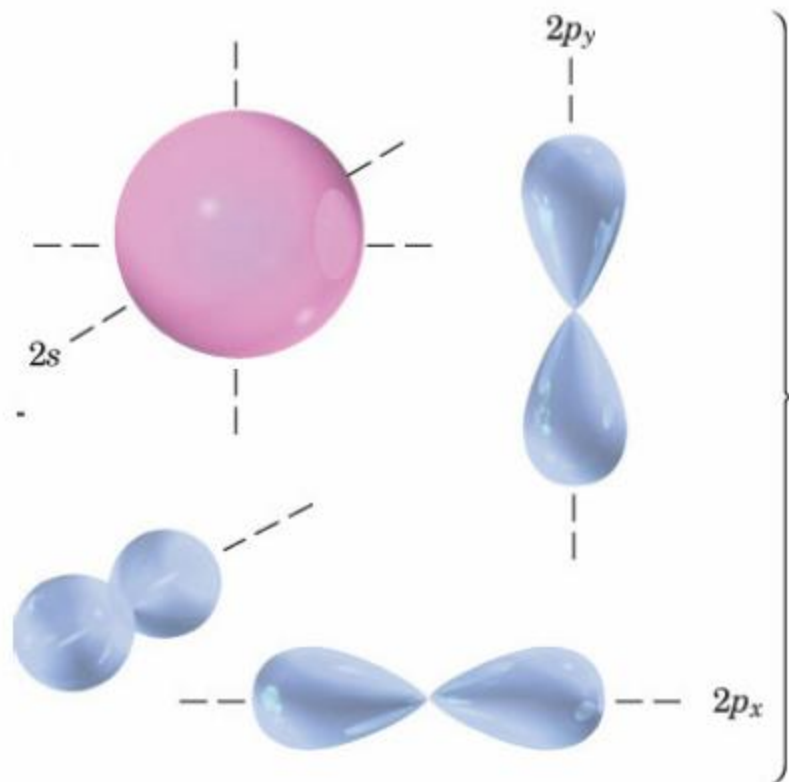
orbitale p



orbitale sp^3



Ibridizzazione sp^3



Ibridizzazione →



Quattro orbitali sp^3 tetraedrici



Orbitale sp^3

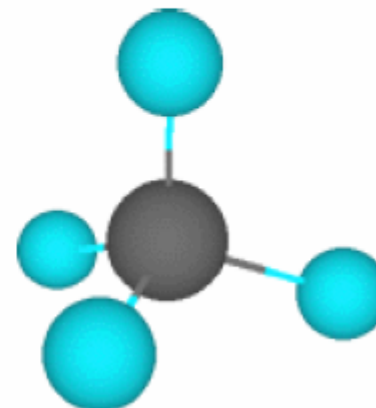


Ibridizzazione sp^3

Metano

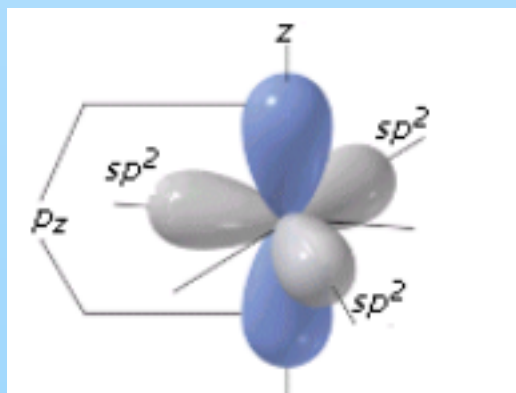
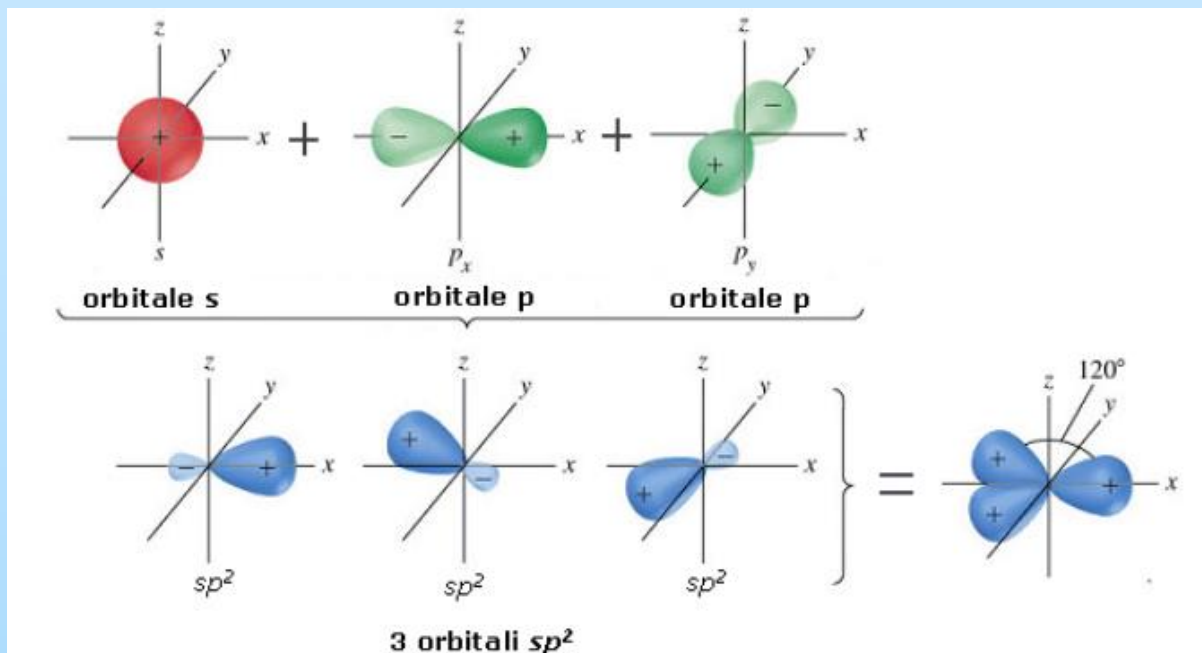


L'angolo di legame formato da ciascun H-C-H vale esattamente $109,5^\circ$ (angolo tetraedrico)



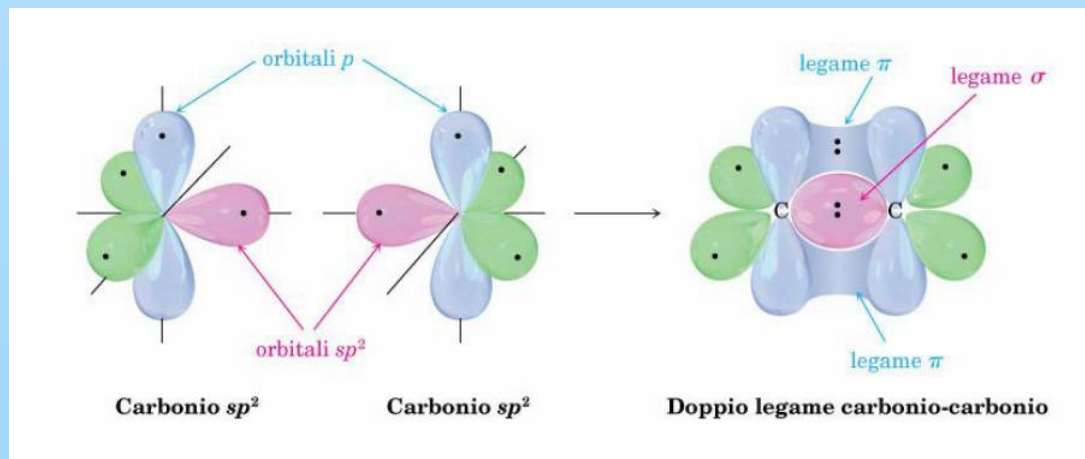
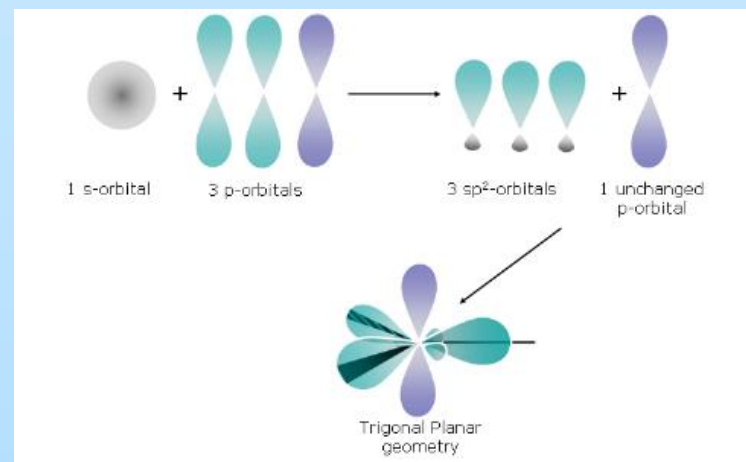
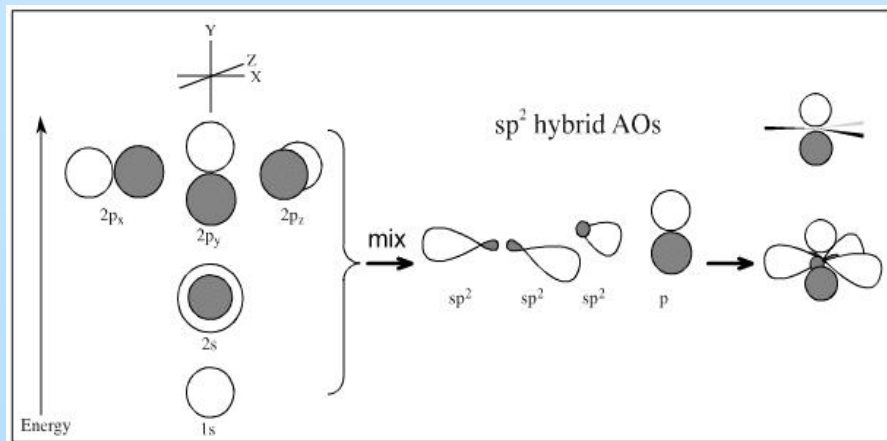


Ibridizzazione sp^2





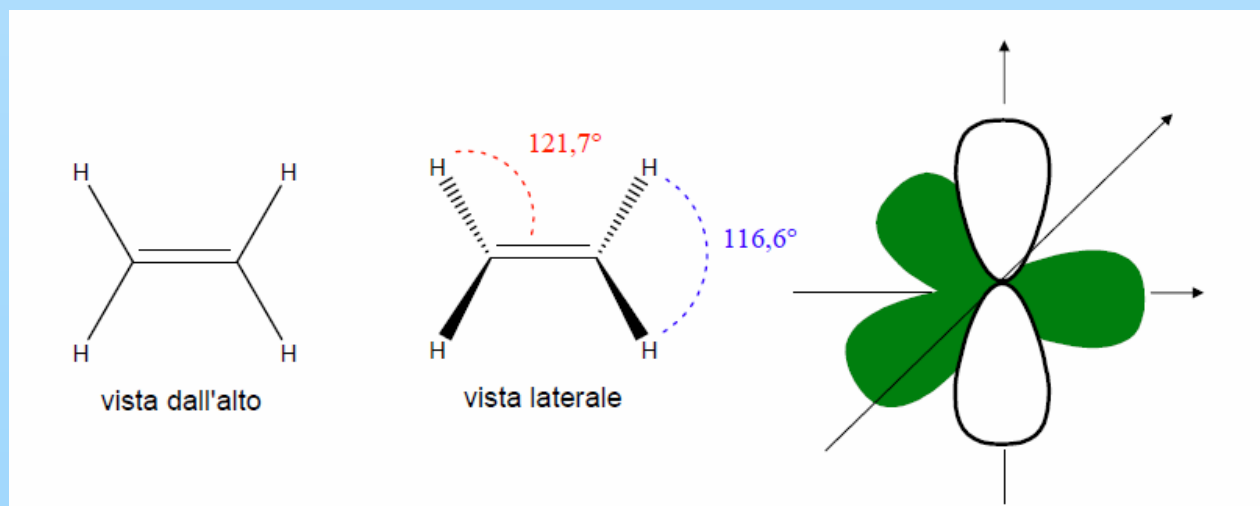
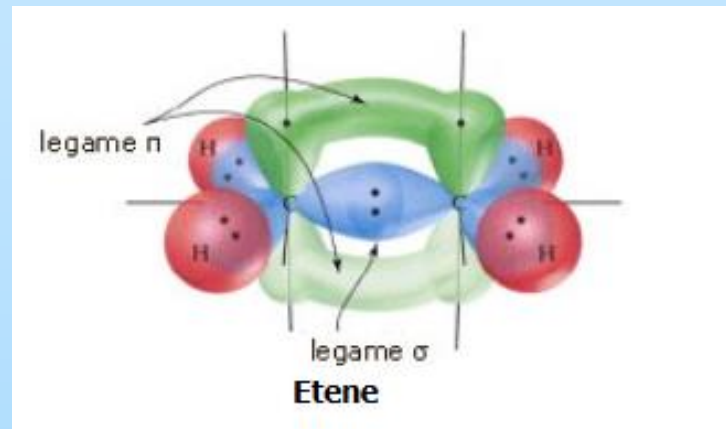
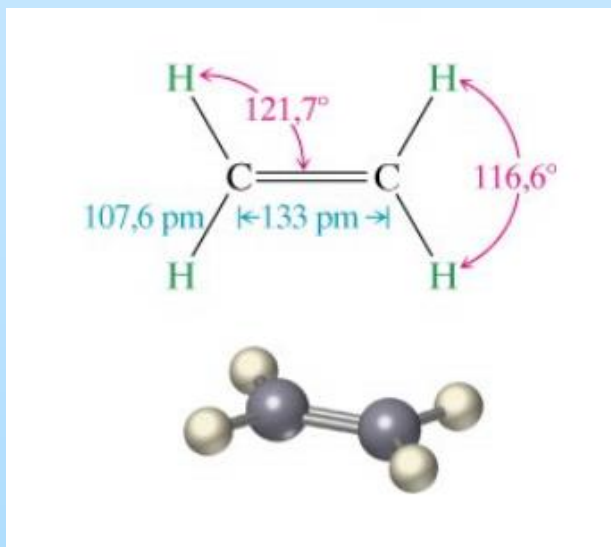
Ibridizzazione sp^2





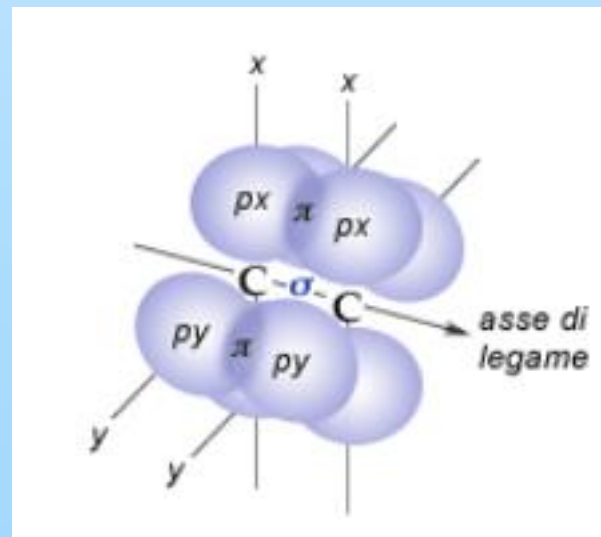
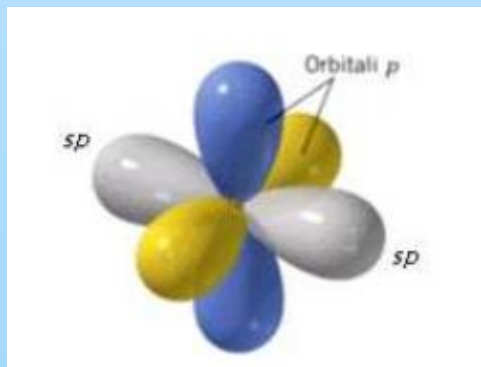
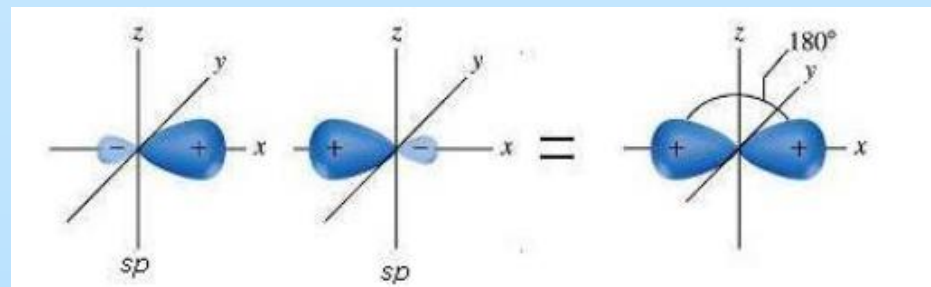
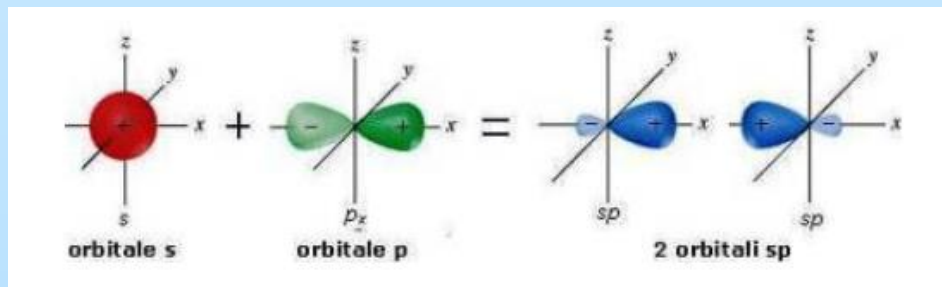
Ibridizzazione sp^2

Etilene





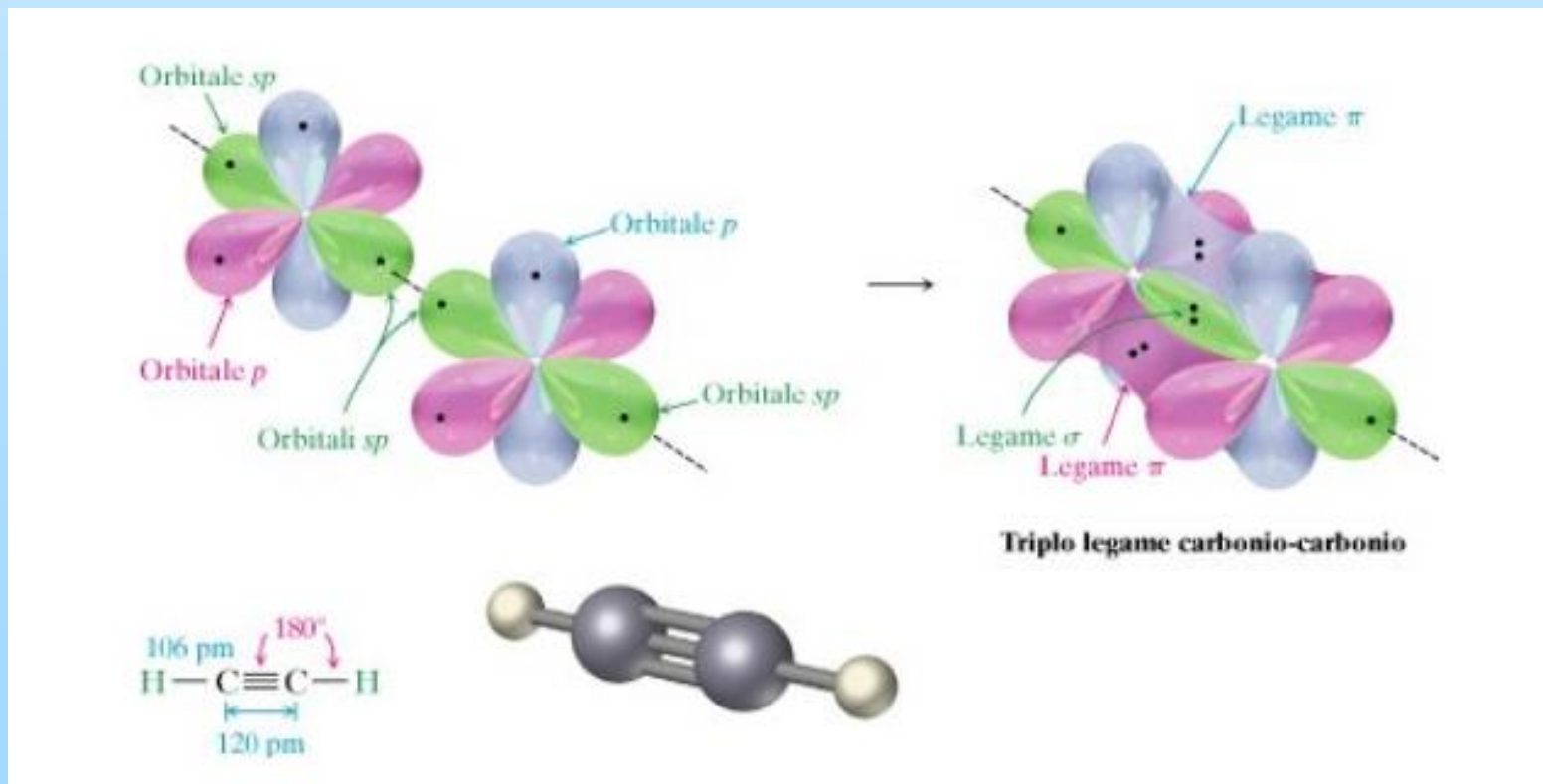
Ibridizzazione sp





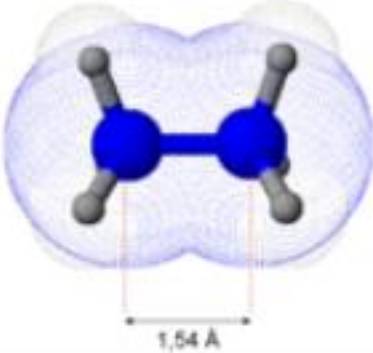
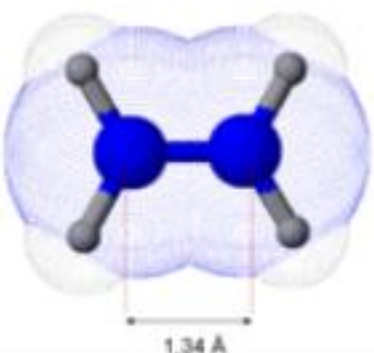
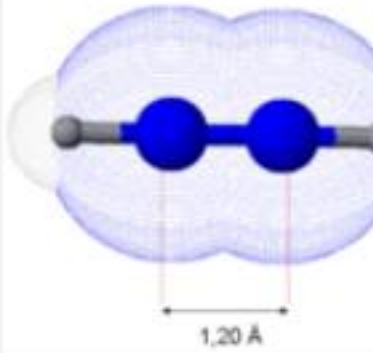
Ibridizzazione sp

Acetilene



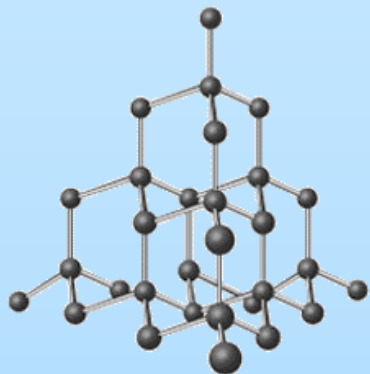


Ibridizzazione sp^n

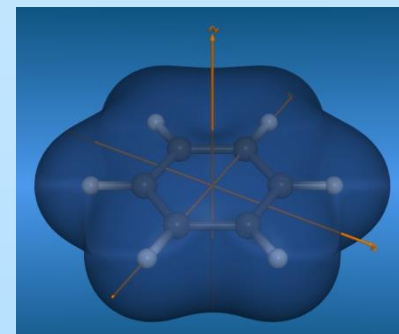
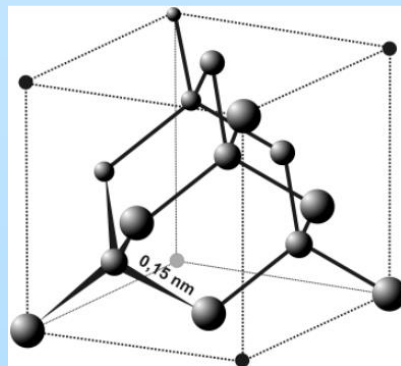
		
1,54 Å	1,34 Å	1,20 Å
Legame singolo Carbonio-Carbonio	Legame doppio Carbonio-Carbonio	Legame triplo Carbonio-Carbonio
Ibridizzazione sp^3	Ibridizzazione sp^2	Ibridizzazione sp



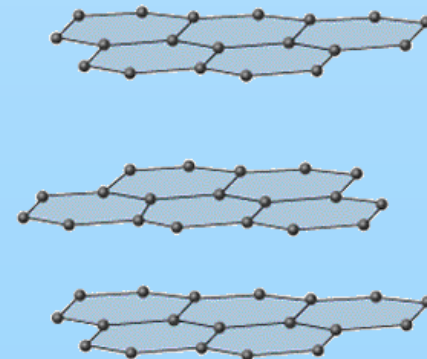
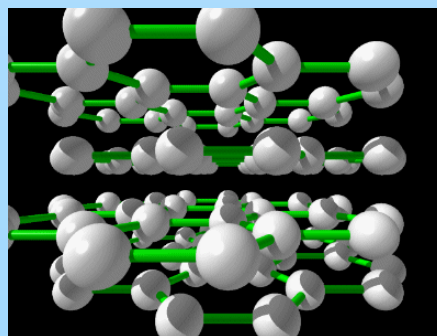
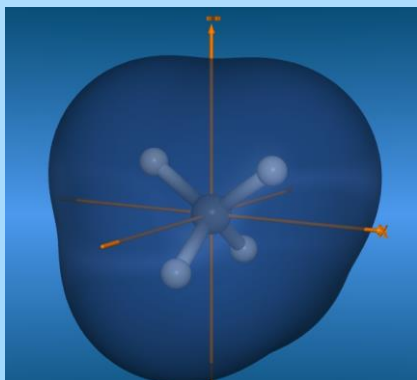
Stati allotropici del carbonio



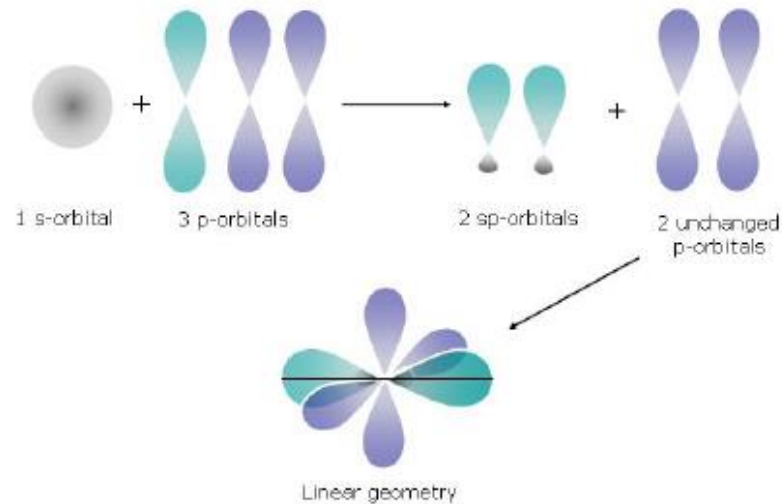
Diamante



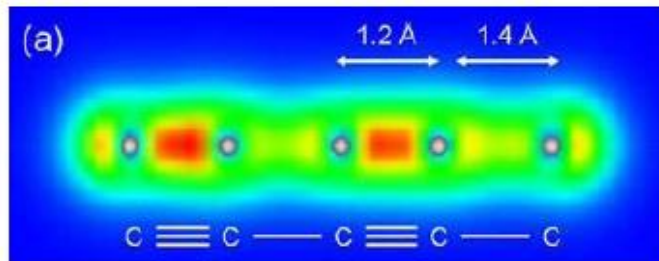
Grafite



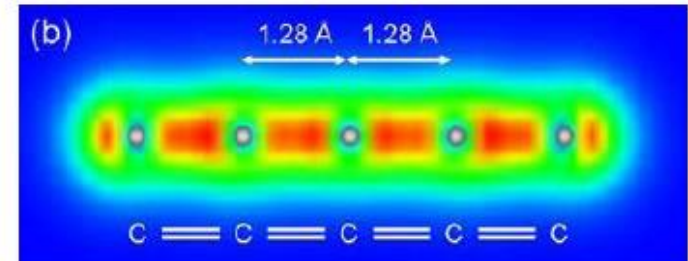
Ibridizzazione sp



Due possibilità: (a) **poliini**, alternanza legami tripli e doppi



(b) **cumuleni**, catena di legami doppi



Problema: i sistemi di carbonio sp sono instabili

- reattività delle catene insature (es. O_2);
- tendenza a formare *cross-links* fra le catene, favorendo l'evoluzione verso la più stabile fase sp^2 .

Catene sp isolate sono state osservate solo in fase gassosa o in matrici di gas inerti a basse temperature.



Chaoite

REPORTS

A New Allotropic Form of Carbon from the Ries Crater

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+ See all authors and affiliations

Science 26 Jul 1968:
Vol. 161, Issue 3839, pp. 363-364
DOI: 10.1126/science.161.3839.363

Article

Info & Metrics

eLetters

PDF

Abstract

A new allotropic form of carbon occurs in shock-fused graphite gneisses in the Ries Crater, Bavaria. The assemblage in which it occurs consists of hexagonal graphite, rutile, pseudobrookite, magnetite, nickeliferous pyrrhotite, and baddeleyite. Electron-probe analyses indicate that the new phase is pure carbon. It is opaque and much more strongly reflecting than hexagonal graphite. Measurement of x-ray diffraction powder patterns leads to cell dimensions $a = 8.948 \pm 0.009$, $c = 14.078 \pm 0.017$ angstroms, with a primitive hexagonal lattice.



Science

Vol 161, Issue 3839
26 July 1968

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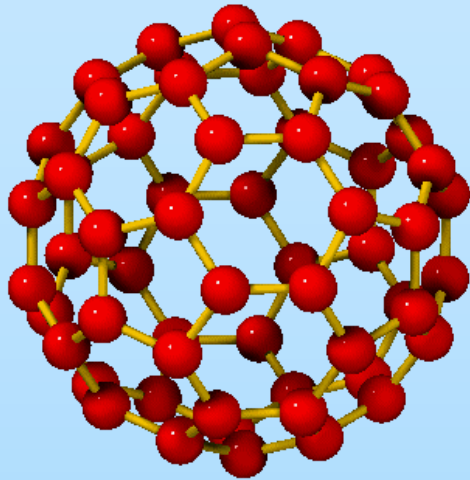
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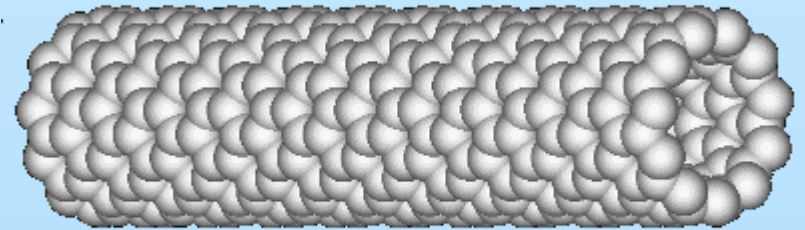


Stati allotropici del carbonio



Fullerene (C₆₀)

Curl, Kroto e Smalley,
premio Nobel per la Chimica 1996



Nanotubi

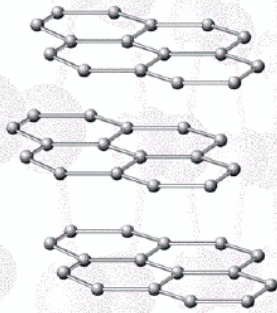
(Iijima 1991)

Nanostrutture.....



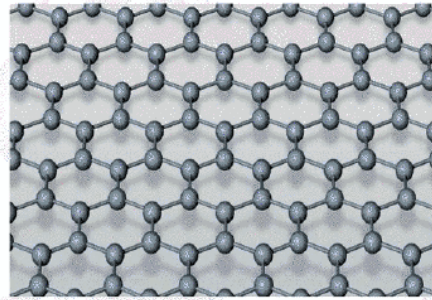
GRAPHENE ALLOTROPES

3D



Graphite

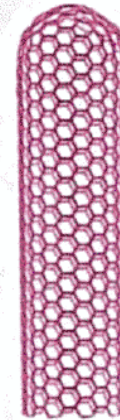
2D



graphene

PRESUMED
NOT TO EXIST
IN THE FREE STATE

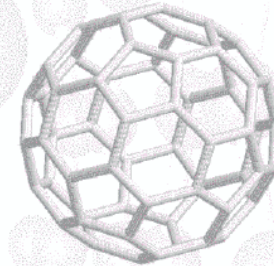
1D



**Carbon
Nanotube**

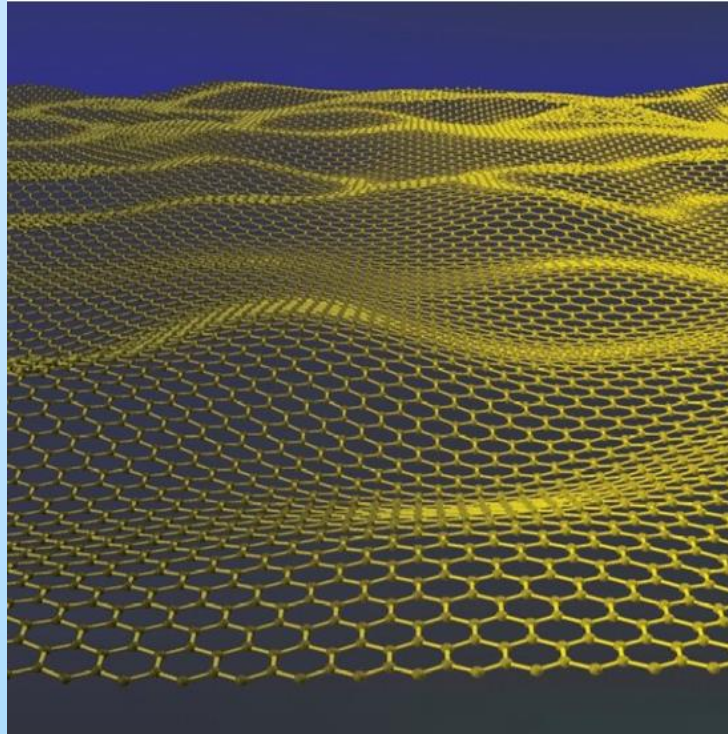
multi-wall:
1952 to *Iijima* 1991
single-wall: 1993

0D



Buckyballs

Kroto et al 1985



Grafene

K. Novoselov, A. Geim

Premio Nobel per la Fisica 2010



Diamante ↔ Grafite

Table 2.1
Properties of graphite and diamond

Property	Graphite ^a		Diamond
Lattice structure	Hexagonal		Cubic
Space group	$P6_3/mmc (D_{6h}^{19})$		$Fd\bar{3}m (O_h^7)$
Lattice constant ^b (Å)	2.462	6.708	3.567
Atomic density (C atoms/cm ³)	1.14×10^{23}		1.77×10^{23}
Specific gravity (g/cm ³)	2.26		3.515
Specific heat (cal/g·K)	0.17		0.12
Thermal conductivity ^b (W/cm·K) ^c	30	0.06	~25
Binding energy (eV/C atom)	7.4		7.2
Debye temperature (K)	2500	950	1860
Bulk modulus (GPa)	286		42.2
Elastic moduli (GPa)	1060 ^d	36.5 ^d	107.6 ^e
Compressibility (cm ² /dyn)	2.98×10^{-12}		2.26×10^{-13}
Mohs hardness ^f	9		10
Band gap (eV)	-0.04 ^g		5.47
Carrier density (10 ¹⁸ /cm ³ at 4 K)	5		0
Electron mobility ^b (cm ² /Vsec)	20,000	100	1800
Hole mobility ^b (cm ² /Vsec)	15,000	90	1500
Resistivity (Ωcm)	50×10^{-6}	1	~10 ²⁰
Dielectric constant ^b (low ω)	3.0	5.0	5.58
Breakdown field (V/cm)	0		10 ⁷ (highest)
Magnetic susceptibility (10 ⁻⁶ cm ³ /g)	-0.5	-21	—
Refractive index (visible)			2.4
Melting point (K)	4450		4500
Thermal expansion ^b (/K)	-1×10^{-6}	$.29 \times 10^{-6}$	$\sim 1 \times 10^{-6}$
Velocity of sound (cm/sec)	$\sim 2.63 \times 10^5$	$\sim 1 \times 10^5$	$\sim 1.96 \times 10^5$
Highest Raman mode (cm ⁻¹)	1582		1332

^aFor anisotropic properties, the in-plane (*ab* plane or *a*-axis) value is given on the left and the *c*-axis value on the right.

^bMeasurements at room temperature (300 K).

^cHighest reported thermal conductivity values are listed.

^dIn-plane elastic constant is C_{11} and *c*-axis value is C_{33} . Other elastic constants for graphite are $C_{12} = 180$, $C_{13} = 15$, $C_{44} = 4.5$ GPa.

^eFor diamond, there are three elastic constants, $C_{11} = 1040$, $C_{12} = 170$, $C_{44} = 550$ GPa.

^fA scale based on values from 0 to 10, where 10 is the hardest material (diamond) and 1 is talc [2.8].

^gA negative band gap implies a band overlap, i.e., semimetallic behavior.



Diagramma di Fase

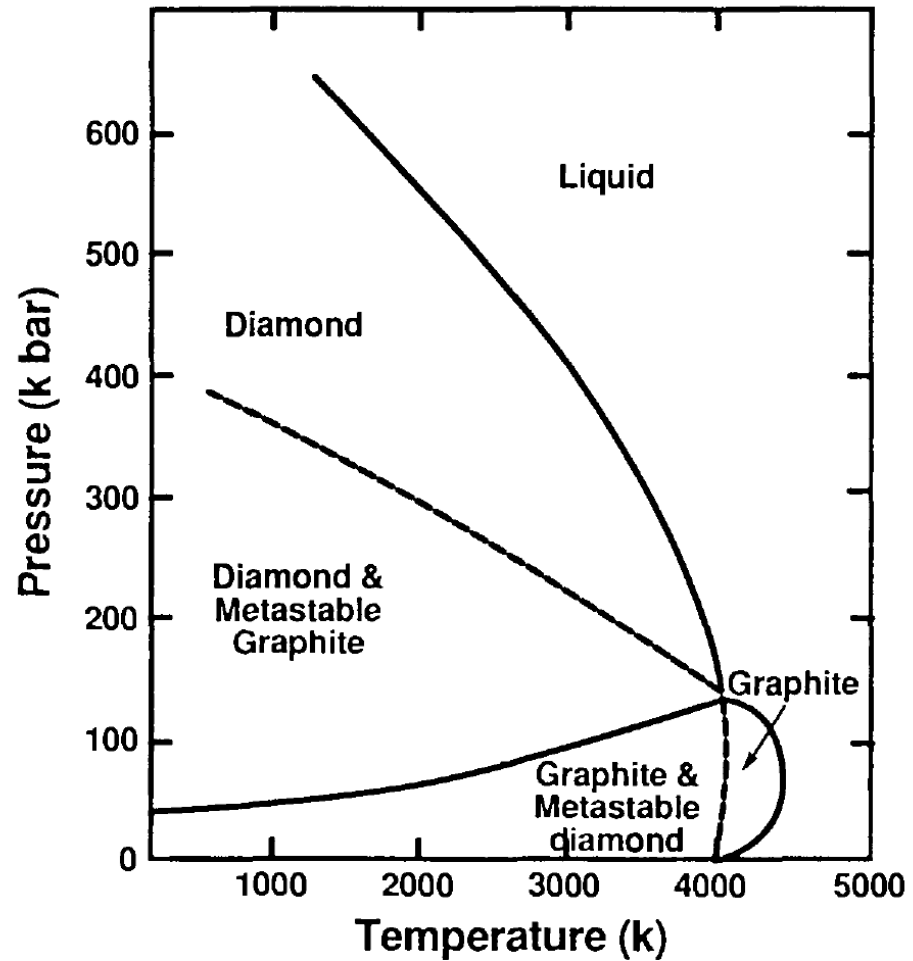
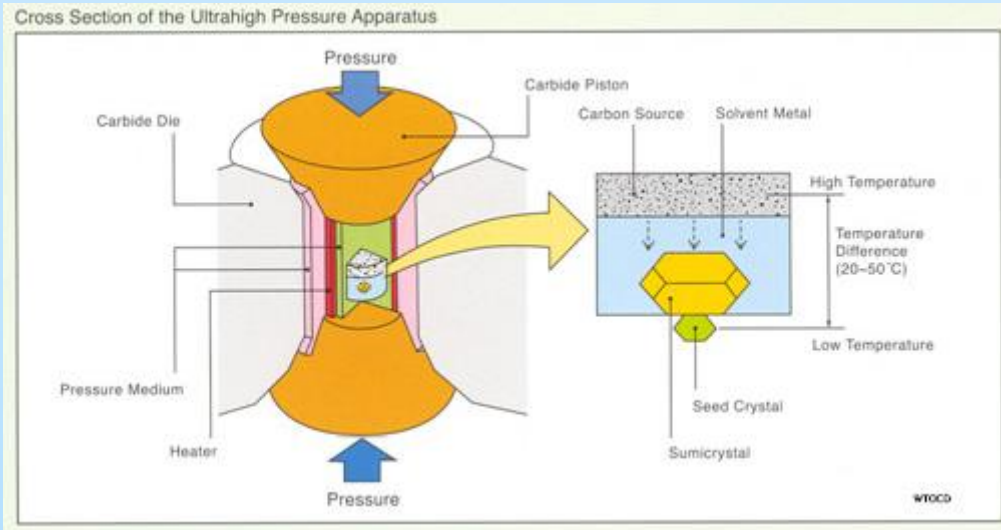


Figure 2.20. Carbon phase diagram.

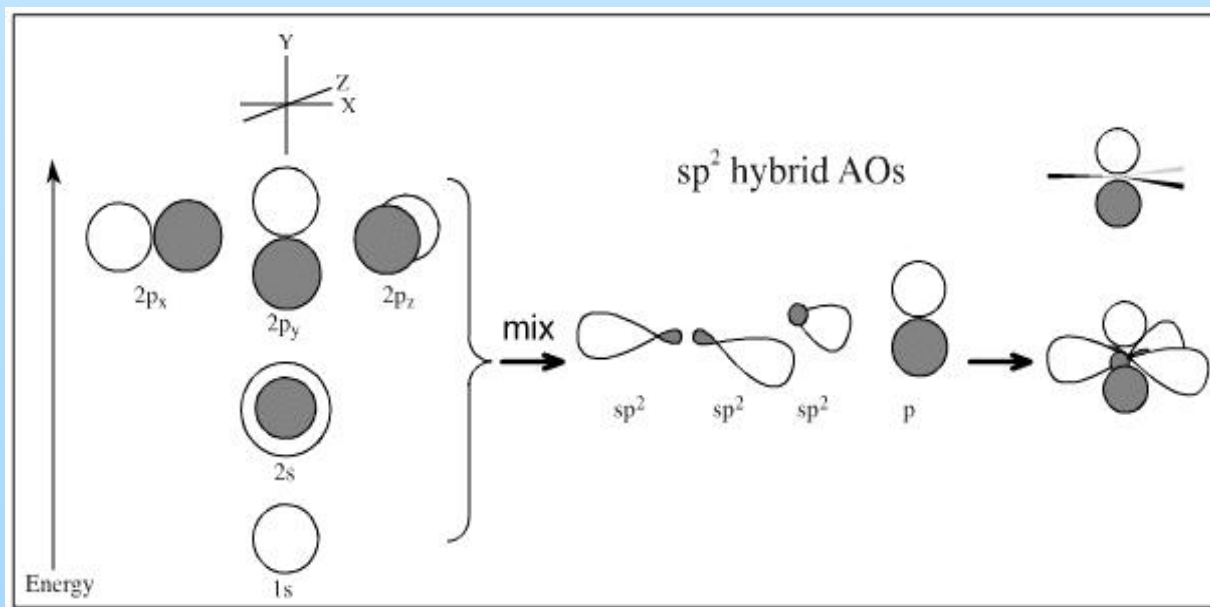
Sintesi dei diamanti





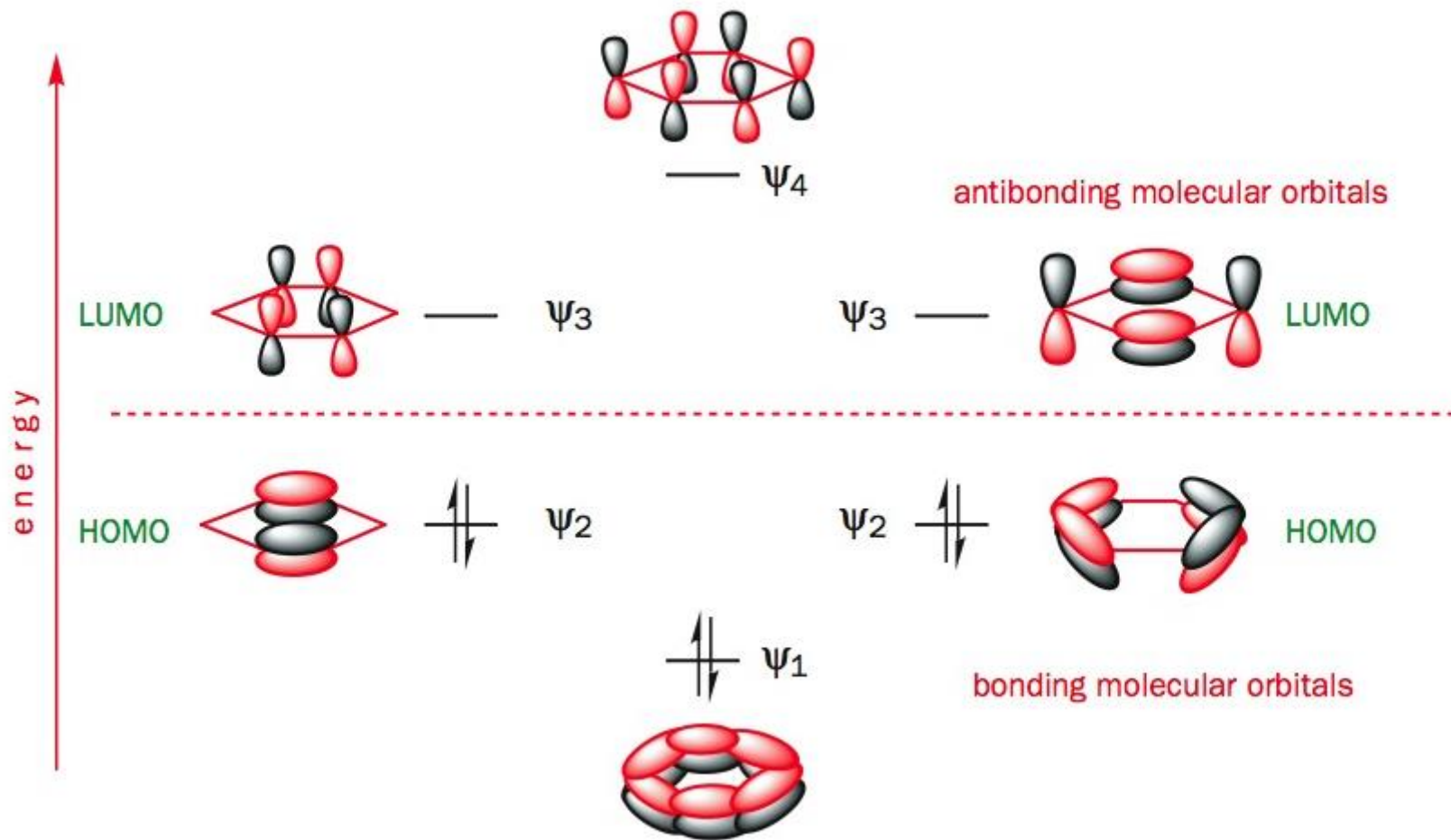
Ibridizzazione sp^2

Configurazione: $[\text{He}] 2s^2 2p^2$



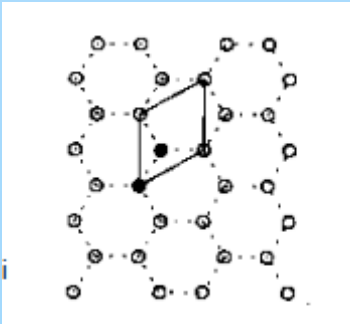
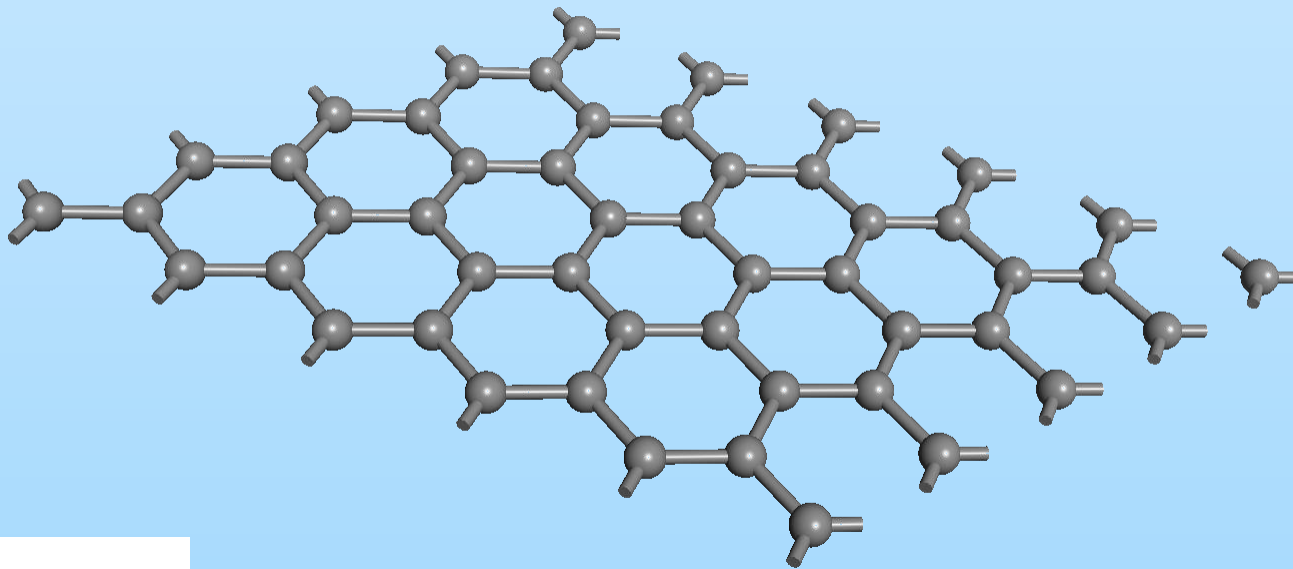


Ibridizzazione sp^2 : benzene





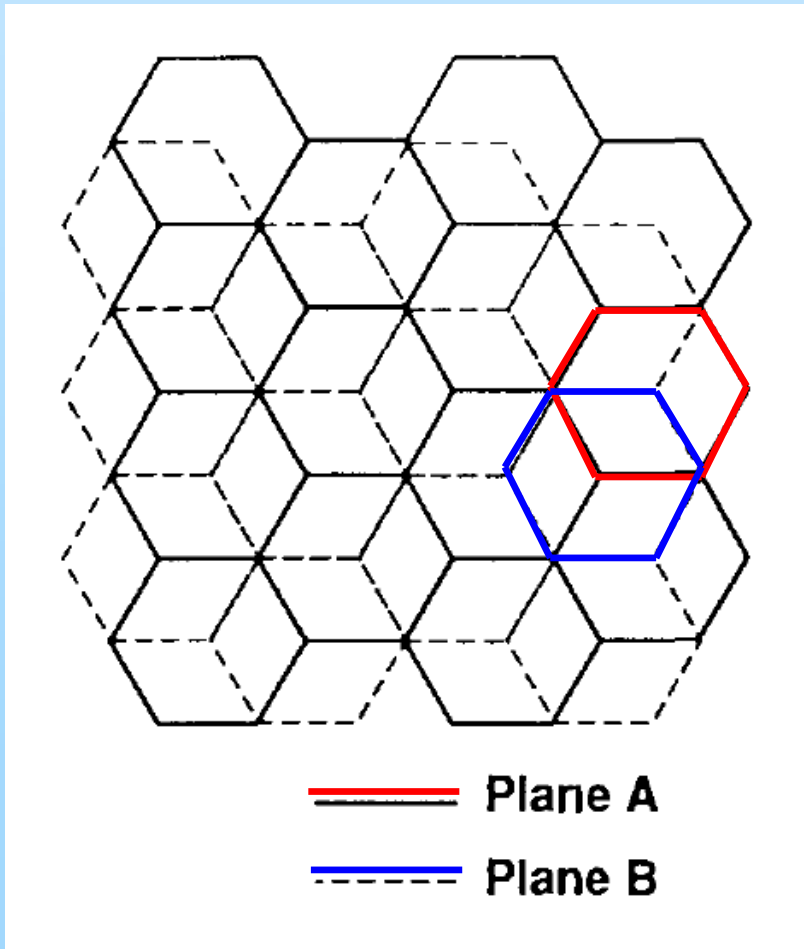
Ibridizzazione sp^2 : grafene



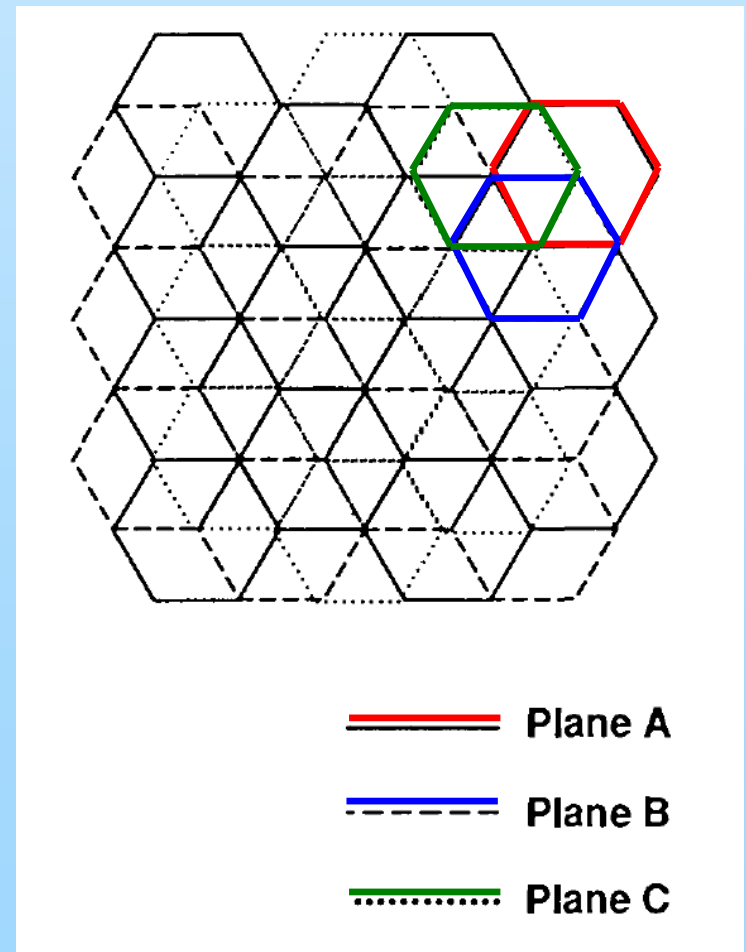


Grafite Struttura

grafite esagonale

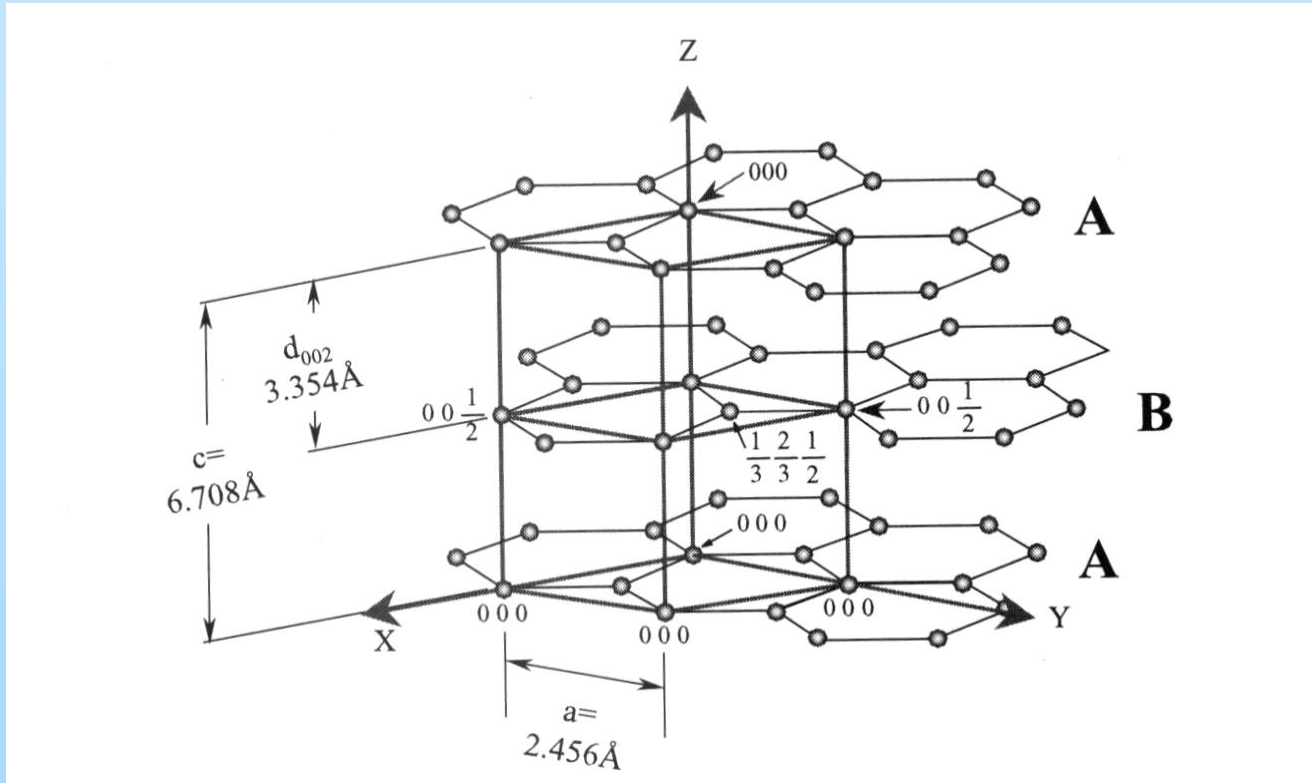


grafite romboedrica





Grafite esagonale: cella unitaria

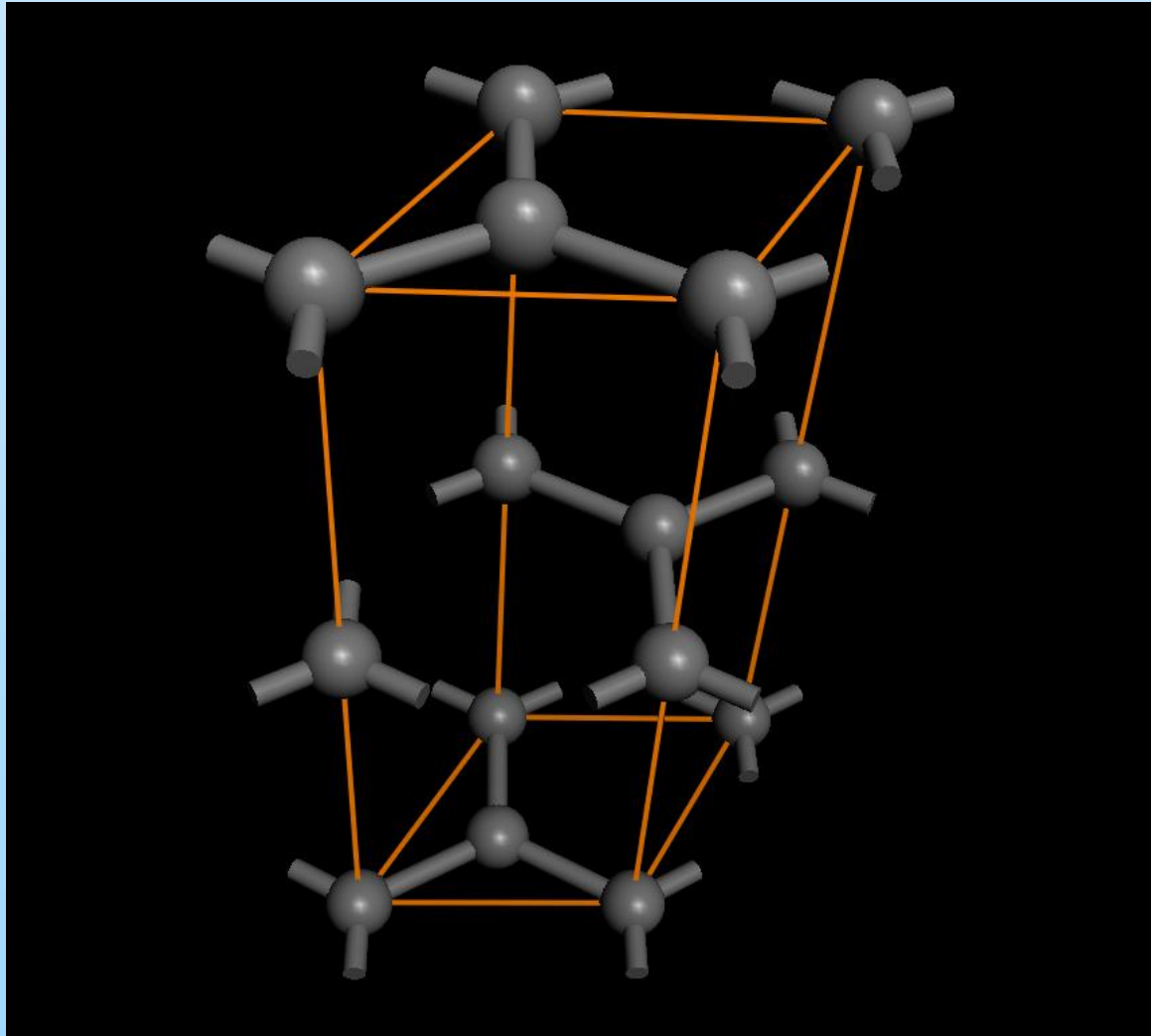


$$d(\text{C}=\text{C}) = 1.42 \text{ \AA}$$



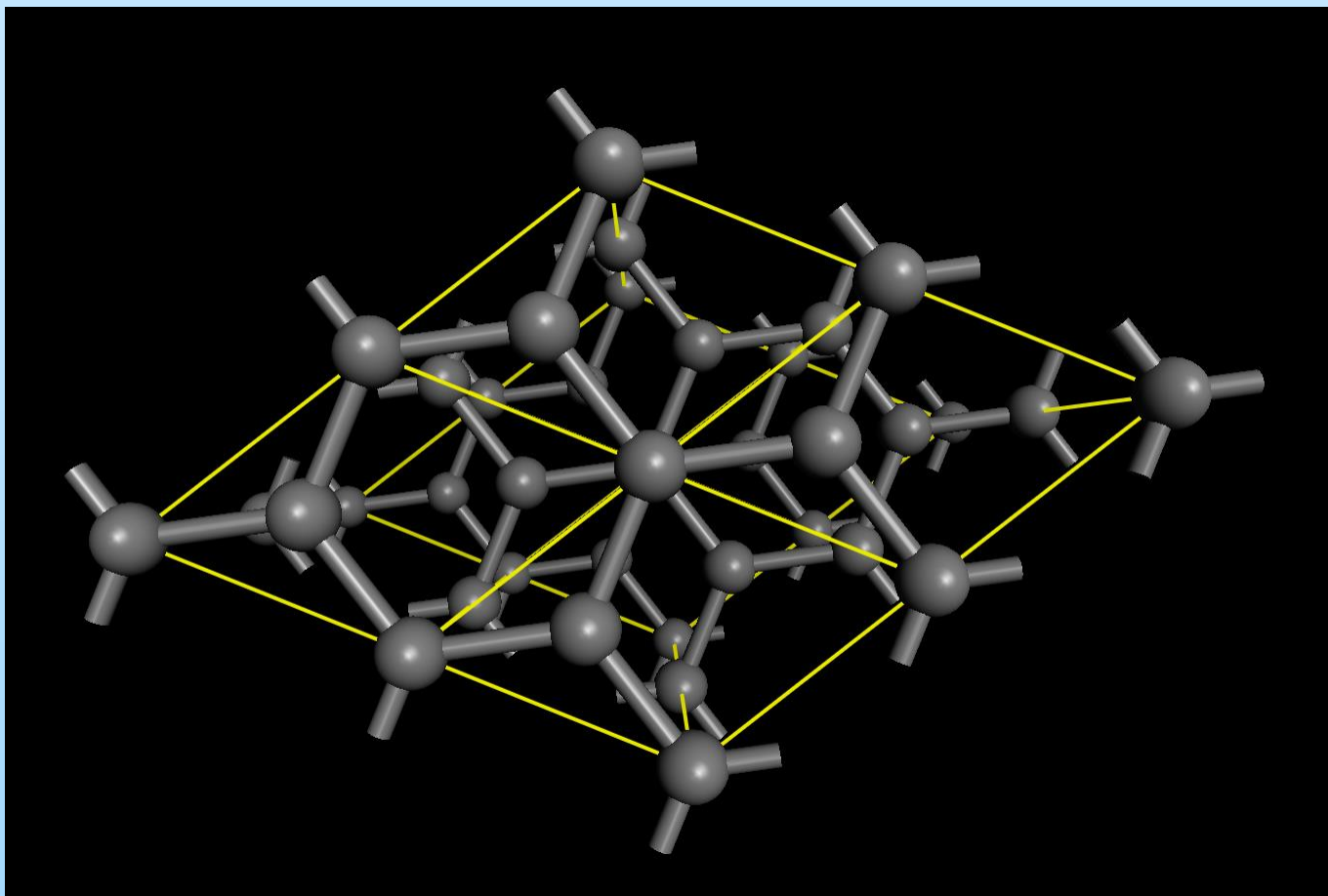
Grafite cella unitaria

Gruppo esagonale P 63 MMC #194





Grafite cella unitaria



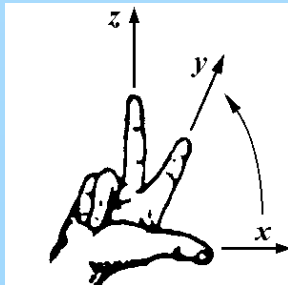


Reticolo reciproco 2D

$$\mathbf{A} = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}; \quad \mathbf{B} = 2\pi \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}; \quad \mathbf{C} = 2\pi \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}}.$$

ESEMPIO

Reticolo reciproco in due dimensioni. Un reticolo a due dimensioni (fig. 21) ha i vettori base $\mathbf{a} = 2\hat{x}$; $\mathbf{b} = \hat{x} + 2\hat{y}$. Trovare i vettori base del reticolo reciproco.



Possiamo usare le nostre definizioni per il caso tridimensionale in questo problema in due dimensioni se supponiamo che \mathbf{c} sia parallelo all'asse z , per cui il piano dei vettori \mathbf{A} e \mathbf{B} del reticolo reciproco sarà nel piano di \mathbf{a} e \mathbf{b} . Prendiamo $\mathbf{c} = \hat{z}$. Ora

$$\mathbf{c} \times \mathbf{a} = \hat{z} \times (2\hat{x}) = 2\hat{y};$$

$$\mathbf{b} \times \mathbf{c} = \hat{x} \times \hat{z} + 2\hat{y} \times \hat{z} = -\hat{y} + 2\hat{x}; \quad \mathbf{a} \cdot \mathbf{b} \times \mathbf{c} = 4.$$

Questi risultati sostituiti nelle (33) danno

$$\mathbf{A} = \pi\hat{x} - \frac{1}{2}\pi\hat{y}; \quad \mathbf{B} = \pi\hat{y},$$

come indicato in figura 21.

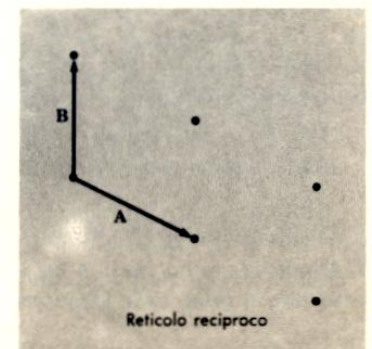
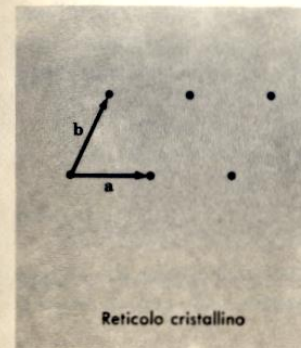
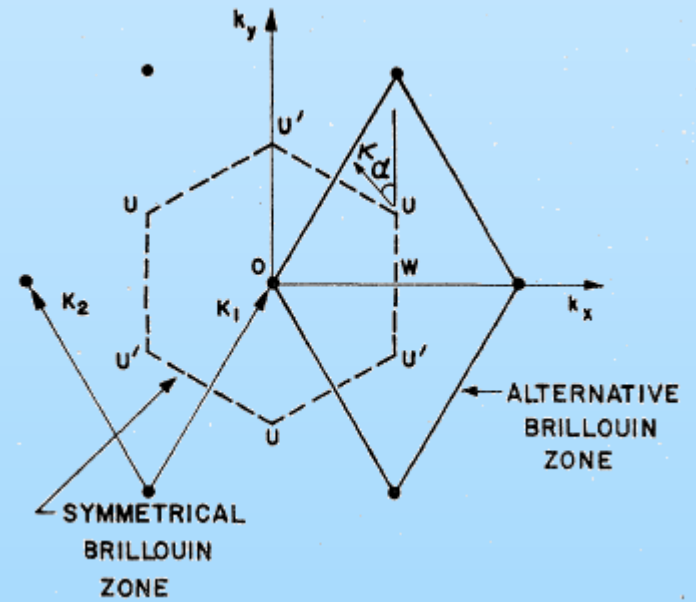
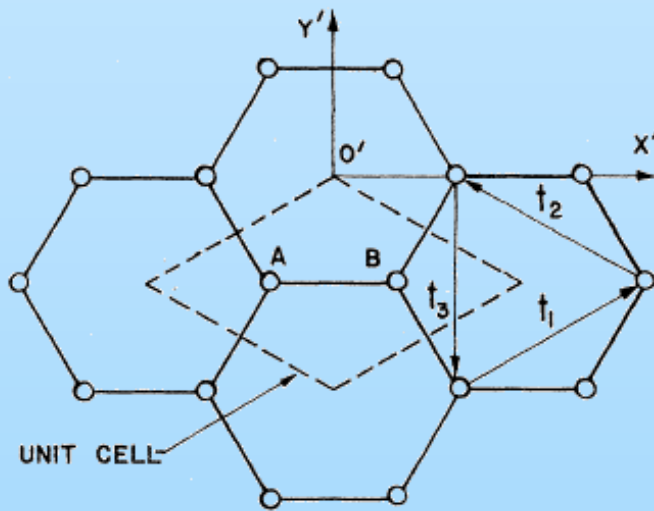


Figura 21 Reticolo reciproco in due dimensioni: \mathbf{A} e \mathbf{B} sono perpendicolari a gruppi di piani (linee) nel reticolo cristallino, cioè alle linee parallele rispettivamente a \mathbf{b} e \mathbf{a} . Qualsiasi vettore fra punti del reticolo reciproco è perpendicolare a qualche piano nel reticolo cristallino.



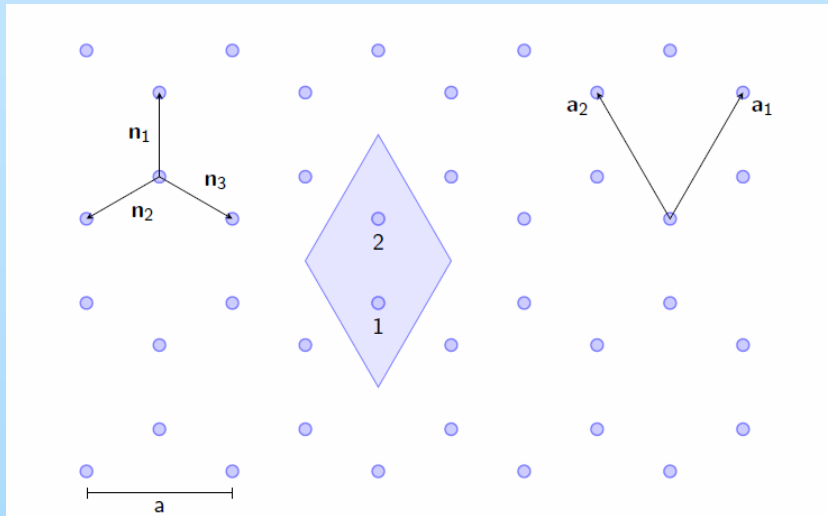
Grafene: cella elementare e I zona di Brillouin



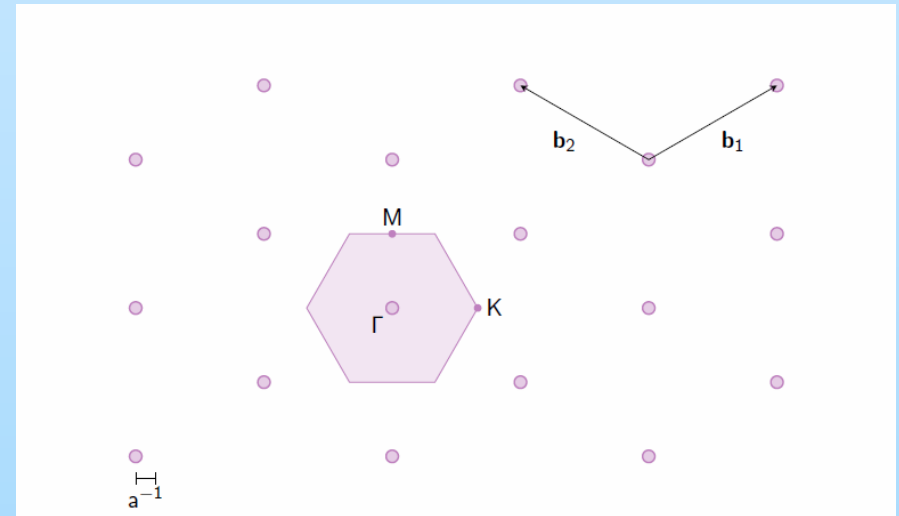
Reticolo reciproco (I zona di B.)



Grafene: cella elementare e I zona di Brillouin



Reticolo diretto: a_1 e a_2 vettori primitivi, n_1 , n_2 e n_3 vettori primi vicini



Reticolo reciproco: b_1 e b_2 vettori primitivi, in rosa I zona di B.



Tight Binding (LCAO)

$$\psi(\mathbf{r}) = \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} \phi(\mathbf{r} - \mathbf{R}),$$

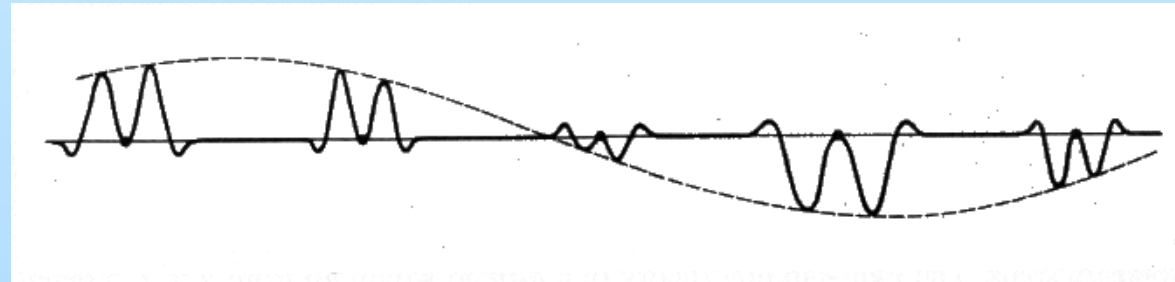
ϕ funzioni di Wannier

$$\phi(\mathbf{r}) = \sum_n b_n \psi_n(\mathbf{r}).$$

ψ_n orbitali atomici (indicati con $X(\mathbf{r})$ di seguito)

$$\psi(\mathbf{r} + \mathbf{R}) = e^{i\mathbf{k} \cdot \mathbf{R}} \psi(\mathbf{r}).$$

Condizione di Bloch



Se c 'è una base nella cella.....

$$\psi_{\mathbf{k}}(\mathbf{r}) = \sum_{j\alpha} c_{j\alpha} e^{i\mathbf{k} \cdot \mathbf{d}_j} \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot \mathbf{R}} \phi_{j\alpha}(\mathbf{r} - \mathbf{R} - \mathbf{d}_j),$$

dove i $\phi_{j\alpha}(\mathbf{r})$ sono gli orbitali di un singolo atomo isolato di numero atomico Z_j centrato nell'origine, individuati dall'indice $\alpha \in \{1s, 2s, 2p_x \dots\}$. \mathbf{R} indica un generico vettore del reticolo di Bravais, j è un indice che individua i siti della base del cristallo, \mathbf{d}_j è la posizione del sito j all'interno della cella unitaria ed infine i $c_{j\alpha}$ sono i coefficienti incogniti della combinazione lineare.



Grafene: Proprietà elettroniche

$$\psi_{2\pi} = \frac{1}{\sqrt{3}} [\psi(2S) + \sqrt{2}\psi(2P_x)]$$

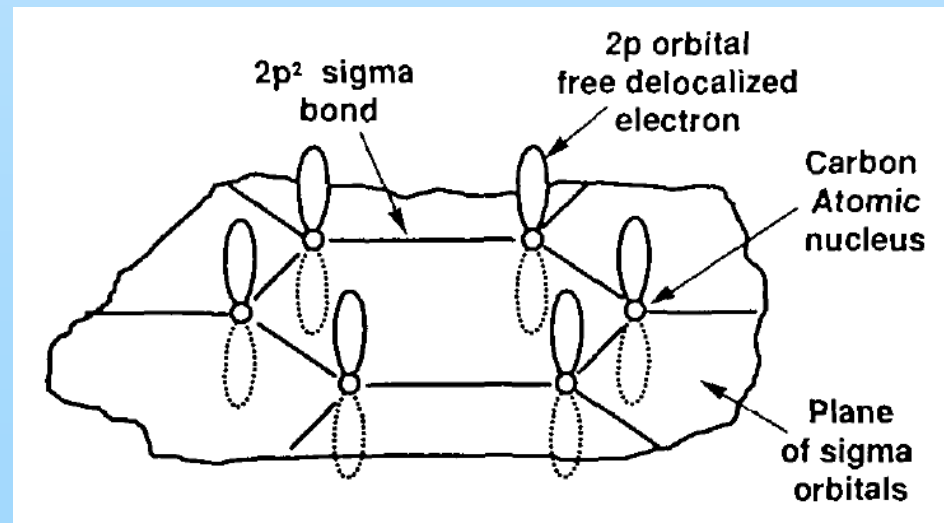
$$\psi_{2\pi/3} = \frac{1}{\sqrt{3}} \left[\psi(2S) - \frac{1}{\sqrt{2}}\psi(2P_x) + \sqrt{\frac{3}{2}}\psi(2P_y) \right]$$

Nel piano

$$\psi_{4\pi/3} = \frac{1}{\sqrt{3}} \left[\psi(2S) - \frac{1}{\sqrt{2}}\psi(2P_x) - \sqrt{\frac{3}{2}}\psi(2P_y) \right]$$

P_z fuori dal piano

$$P_z = \frac{1}{2\sqrt{6}a^5} r e^{-\frac{r}{2a}} \sqrt{\frac{3}{8\pi}} \cos\theta$$



X-ray absorption measurements of high resolving power for potassium, which is expected to show wider departure from free electrons, have been carried out by Platt.¹⁶ The *K* edge investigated shows quite close agreement with his theoretically predicted absorption which was based on the assumption that the electrons are free. No evidence existed to show an energy gap. This, of course, is at best supporting evidence of the non-existence of a gap in potassium since gaps

¹⁶ J. B. Platt, Phys. Rev. **69**, 337 (1946).

may exist which could be completely masked by the eigenvalue dependence upon wave vector direction.

ACKNOWLEDGMENTS

The authors are indebted to Dr. W. A. Bowers for permission to publish his results on the five additional states shown in Table IV and also wish to thank Dr. Bowers for continuing the application of the method when the war interrupted the work.

PHYSICAL REVIEW

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MAY 1, 1947

The Band Theory of Graphite

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National Research Council of Canada, Chalk River Laboratory, Chalk River, Ontario

(Received December 19, 1946)

The structure of the electronic energy bands and Brillouin zones for graphite is developed using the "tight binding" approximation. Graphite is found to be a semi-conductor with zero activation energy, i.e., there are no free electrons at zero temperature, but they are created at higher temperatures by excitation to a band contiguous to the highest one which is normally filled. The electrical conductivity is treated with assumptions about the mean free path. It is found to be about 100 times as great parallel to as across crystal planes. A large and anisotropic diamagnetic susceptibility is predicted for the conduction electrons; this is greatest for fields across the layers. The volume optical absorption is accounted for.

1. INTRODUCTION

THE purpose of this paper is to develop a basis for the explanation of some of the physical properties of graphite through the band theory of solids. We shall be concerned primarily with a discussion of its electrical conductivity, but the treatment given makes possible the explanation not only of the electrical conductivity and its anisotropy but also the thermal conductivity, diamagnetic susceptibility, and optical absorption.

The electrical resistivity of single crystals of graphite is about 4 to 6×10^{-5} ohm-cm.¹ This corresponds to a conductivity of the order of that of a poor metal. The temperature coefficient of the conductivity is negative, as in the case of

a metal. Polycrystalline graphite, on the other hand, has a much higher resistivity which varies very strongly according to the type of graphite used, and has a *positive* temperature coefficient of conductivity² to about 1400°C, and negative thereafter. Since the crystals of commercial graphites tend to be of the order of 10^{-6} cm, and it is quite porous (density ~ 1.6 as against 2.25 for single crystals), it seems reasonable to attribute the high resistivity of polycrystalline graphite to the crystal boundaries, on which may be lodged impurity atoms. The latter would tend to be driven off on heating, thus accounting for the observed temperature dependence. We shall show, however, that the band theory would seem to make possible the explanation of the conductivity properties of single crystals.

* Now at McGill University.

¹ Given by E. Ryschewitsch, Zeits. f. Elektrochem. ang. physik. Chemie **29**, 474 (1923), as $3.9-6 \times 10^{-5}$ ohm-cm.

² C. A. Hansen, Trans. Am. Electrochem. Soc. **16**, 329 (1909) gives 137.5×10^{-5} at 0°C 82.5×10^{-5} at 1400°C.



Tight Binding nel grafene

(Wallace 1946)

Phys. Rev. **71** (1947) 622

$$\psi = \varphi_1 + \lambda \varphi_2$$

$$\left. \begin{aligned} \varphi_1 &= \sum_A \exp[2\pi i \mathbf{k} \cdot \mathbf{r}_A] X(\mathbf{r} - \mathbf{r}_A) \\ \varphi_2 &= \sum_B \exp[2\pi i \mathbf{k} \cdot \mathbf{r}_B] X(\mathbf{r} - \mathbf{r}_B) \end{aligned} \right\}$$

$$\int X(\mathbf{r} - \mathbf{r}_A) X(\mathbf{r} - \mathbf{r}_B) d\tau = 0.$$

Nessuna sovrapposizione tra gli orbitali p^z

$$H\psi = E\psi$$

$$\begin{vmatrix} H_{11} - ES & H_{12} \\ H_{21} & H_{22} - ES \end{vmatrix} = 0$$

$$H_{11} + \lambda H_{12} = ES,$$

$$H_{21} + \lambda H_{22} = \lambda ES,$$

$$H_{11} = \int \phi_1^* H \phi_1 d\tau, \quad H_{12} = H_{21}^* = \int \phi_1^* H \phi_2 d\tau,$$

$$H_{22} = \int \phi_2^* H \phi_2 d\tau$$

$$E = \frac{1}{2S} \{ H_{11} + H_{22} \pm ((H_{11} - H_{22})^2 + 4|H_{12}|^2)^{\frac{1}{2}} \}$$

$$S = \int \phi_1^* \phi_1 d\tau = \int \phi_2^* \phi_2 d\tau = N \text{ (celle nel cr.)}$$




Grafene: Proprietà elettroniche

$H_{11} = H_{22}$ per simmetria

$$H_{11}' = H_{22}' = \frac{1}{N} H_{11} = \frac{1}{N} H_{22},$$

$$H_{12}' = \frac{1}{N} H_{12}$$

$$E = H_{11}' \pm |H_{12}'|.$$


+ fuori, - dentro la zona
di B. esagonale

$$\Delta E = 2 |H_{12}'|$$

$$H_{11}' = \frac{1}{N} \sum_{A, A'} \exp[-2\pi i \mathbf{k} \cdot (\mathbf{r}_A - \mathbf{r}_{A'})] \\ \times \int X^*(\mathbf{r} - \mathbf{r}_A) H X(\mathbf{r} - \mathbf{r}_{A'}) d\tau.$$

ponendo

$$E_0 = \int X^*(\mathbf{r}) H X(\mathbf{r}) d\tau,$$

$$\gamma_0' = - \int X^*(\mathbf{r} - \mathbf{e}') H X(\mathbf{r}) d\tau,$$

$\mathbf{e}' = \mathbf{a}_1$ Vettore che congiunge primi vicini A

$$H_{11}' = E_0 - 2\gamma_0' (\cos 2\pi k_y a + 2 \cos \pi k_x a \sqrt{3} \cos \pi k_y a)$$



Grafene: Proprietà elettroniche

$$H = H_0 + (H - H_0)$$

H_0 Hamiltoniana di un atomo di C isolato

$$H - H_0 = V - U < 0$$

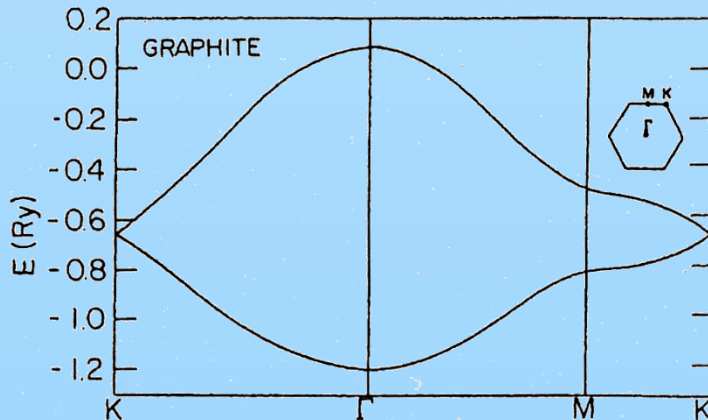
V Potenziale periodico del reticolo

U Potenziale di un atomo di C

$$H_0 X = E_0 X$$

$$E_0 = \bar{E} - \int X^*(\mathbf{r})(U - V)X(\mathbf{r})d\tau$$

$$\gamma_0' = \int X^*(\mathbf{r} - \boldsymbol{\rho}') (U - V)X(\mathbf{r})d\tau > 0$$

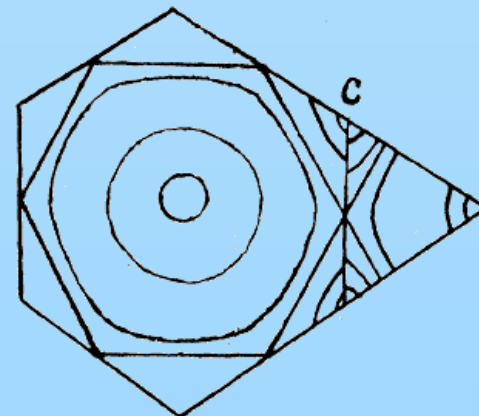


$$\gamma_0 = \int X^*(\mathbf{r} - \boldsymbol{\rho})(U - V)X(\mathbf{r})d\tau > 0$$

$\boldsymbol{\rho} = \mathbf{AB}$ Reticoli contigui

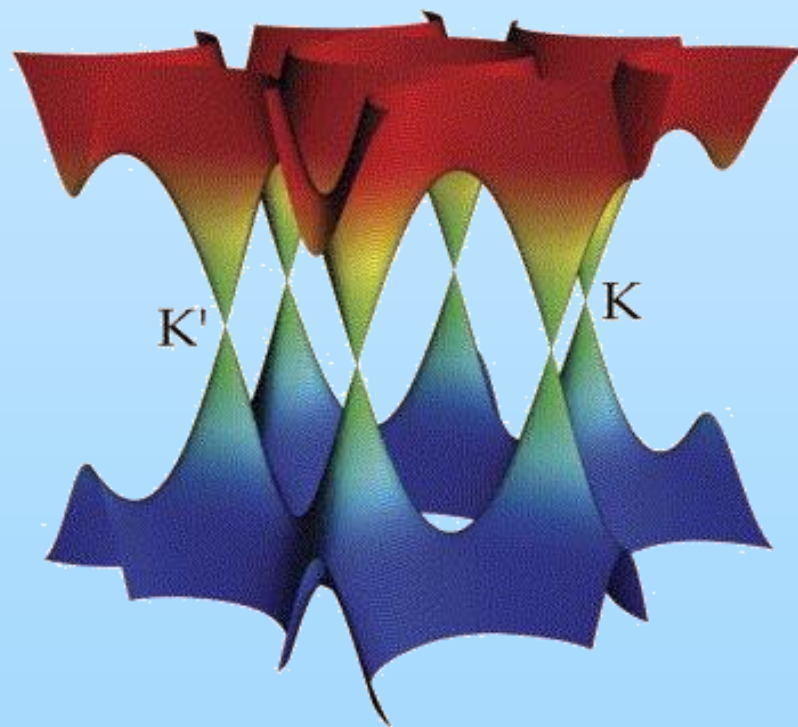
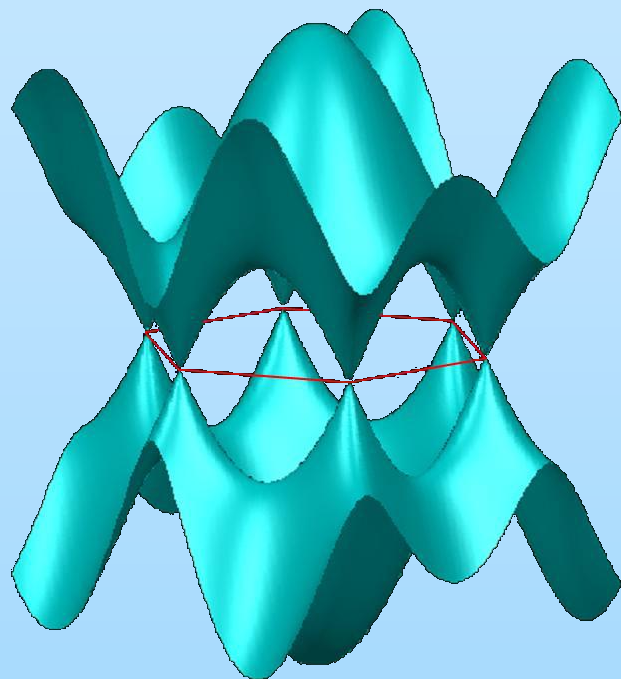
$$H_{12}' = -\gamma_0(\exp[-2\pi i k_x(a/\sqrt{3})] + 2 \cos \pi k_y a \cdot \exp[2\pi i k_x(a/2\sqrt{3})]),$$

$$|H_{12}'|^2 = \gamma_0^2(1 + 4 \cos^2 \pi k_y a + 4 \cos \pi k_y a \cos \pi k_x \sqrt{3} a)$$



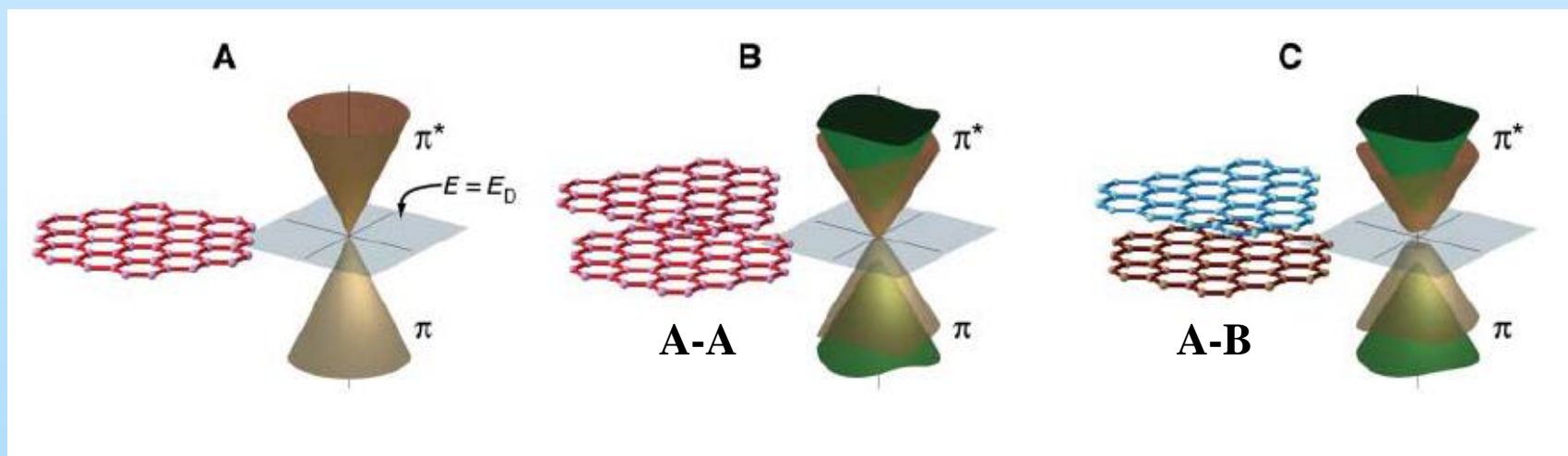


Grafene: Proprietà elettroniche





Multigrafene (2 strati)





Robust superconductivity in magic-angle multilayer graphene family

Jeong Min Park ^{1,3}✉, Yuan Cao^{1,3}, Li-Qiao Xia ¹, Shuwen Sun¹, Kenji Watanabe ², Takashi Taniguchi ² and Pablo Jarillo-Herrero ¹✉

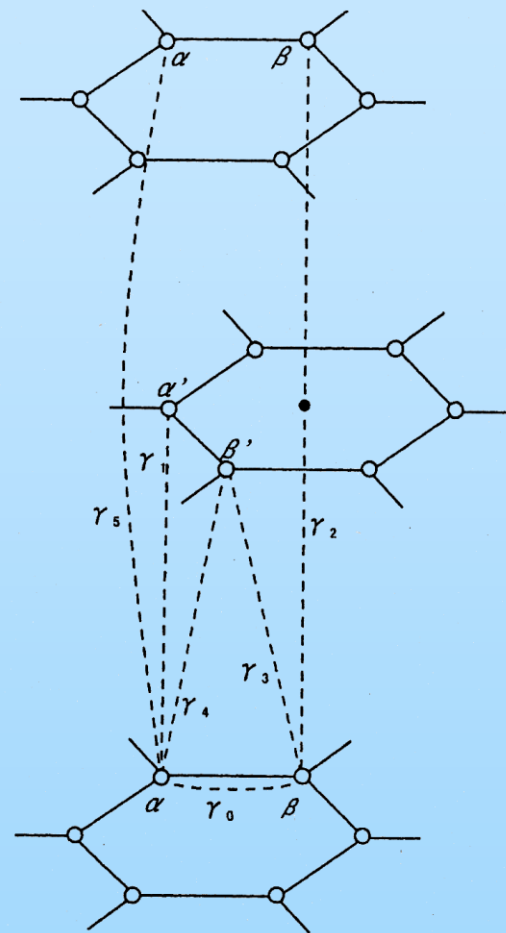
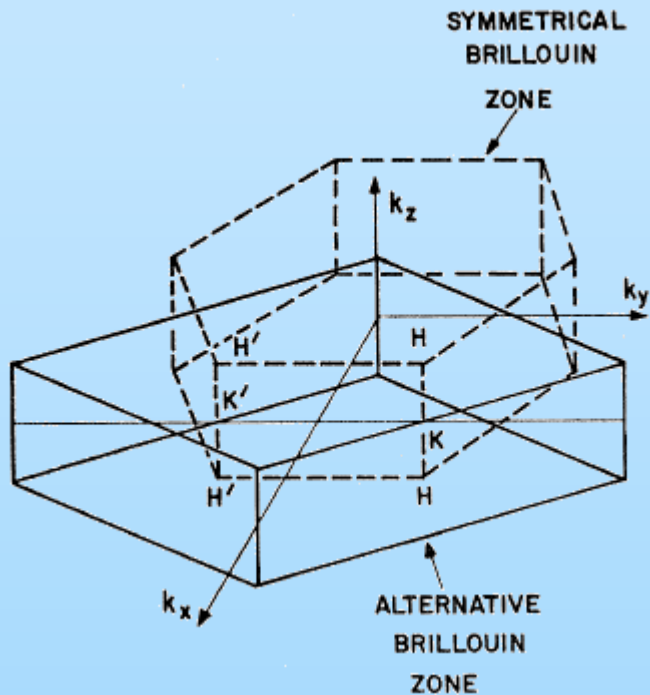
The discovery of correlated states and superconductivity in magic-angle twisted bilayer graphene (MATBG) established a new platform to explore interaction-driven and topological phenomena. However, despite multitudes of correlated phases observed in moiré systems, robust superconductivity appears the least common, found only in MATBG and more recently in magic-angle twisted trilayer graphene. Here we report the experimental realization of superconducting magic-angle twisted four-layer and five-layer graphene, hence establishing alternating twist magic-angle multilayer graphene as a robust family of moiré superconductors. This finding suggests that the flat bands shared by the members play a central role in the superconductivity. Our measurements in parallel magnetic fields, in particular the investigation of Pauli limit violation and spontaneous rotational symmetry breaking, reveal a clear distinction between the $N=2$ and $N>2$ -layer structures, consistent with the difference between their orbital responses to magnetic fields. Our results expand the emergent family of moiré superconductors, providing new insight with potential implications for design of new superconducting materials platforms.

Moiré quantum matter results from stacking two or more atomically thin materials with a lattice mismatch or at a relative twist angle¹. Motivated by the discovery of magic-angle twisted bilayer graphene (MATBG)^{2,3}, in the past few years moiré systems with different types of constituent layers and structures have been created, hosting a number of correlated and topological states. Phenomena including but not limited to correlated insulators, quantum anomalous Hall effect, ferromagnetism, and generalized Wigner crystals have been discovered and reproduced in various new moiré systems^{4–19}. However, for the first few years robust and reproducible moiré superconductivity was seen only in MATBG^{3,20,21}, despite reports of signatures of superconductivity in a few other systems^{5,6,8,9,11,15,22,23}.

studied, providing insights into the nature of the correlated states, non-trivial topology and superconductivity^{2,3,20,21,30–36}. It has been theoretically shown³⁷ that for three or more twisted layers of graphene, there are similar series of ‘magic’ angles if the layers are alternatively twisted by $(\theta, -\theta, \dots)$ (Fig. 1a). The values of such angles can be analytically computed from the bilayer value in the chiral limit, where the interlayer hopping at AA sites is turned off³⁷. As illustrated in Fig. 1b, they are in fact elegantly related by simple trigonometric transformations, that is the largest magic angle can be expressed as $\theta_N = \theta_\infty \cos \frac{\pi}{N+1}$, where N is the number of layers and $\theta_\infty = 2\theta_{N=2}$ is the asymptotic limit of the largest magic angle as $N \rightarrow \infty$. As N increases, the magic angle increases and the moiré length scale decreases. The real magic-angle values deviate slightly



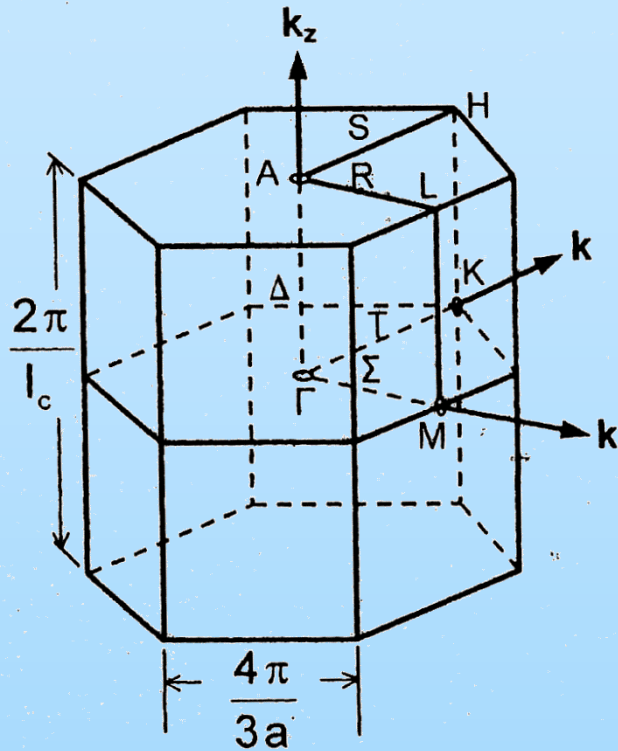
Grafite: Proprietà elettroniche



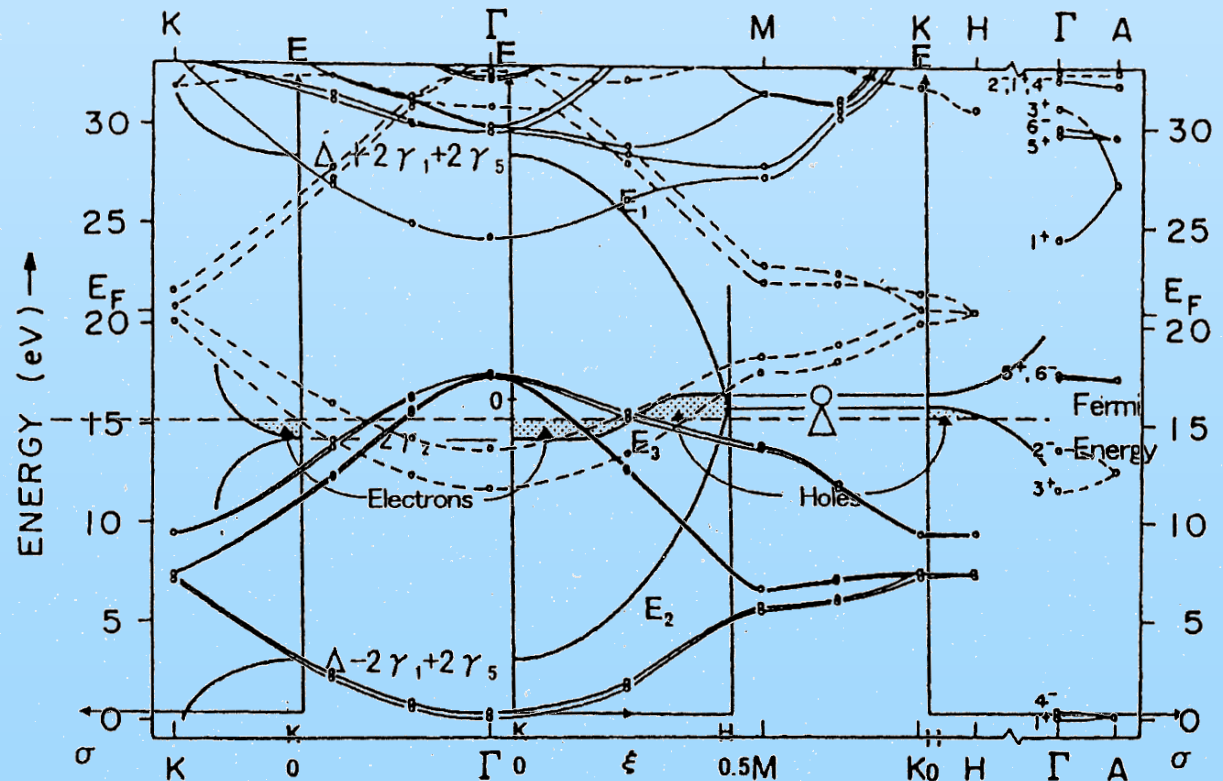
$$\gamma_0 \gg \gamma_n$$

$$\begin{aligned} \gamma_0 &= 3.16, \gamma_1 = 0.39, \\ \gamma_2 &= -0.020, \gamma_3 = 0.315, \gamma_4 \simeq 0.044, \\ \gamma_5 &= 0.038; \Delta = -0.008 \text{ eV} \end{aligned}$$

Grafite: Proprietà elettroniche



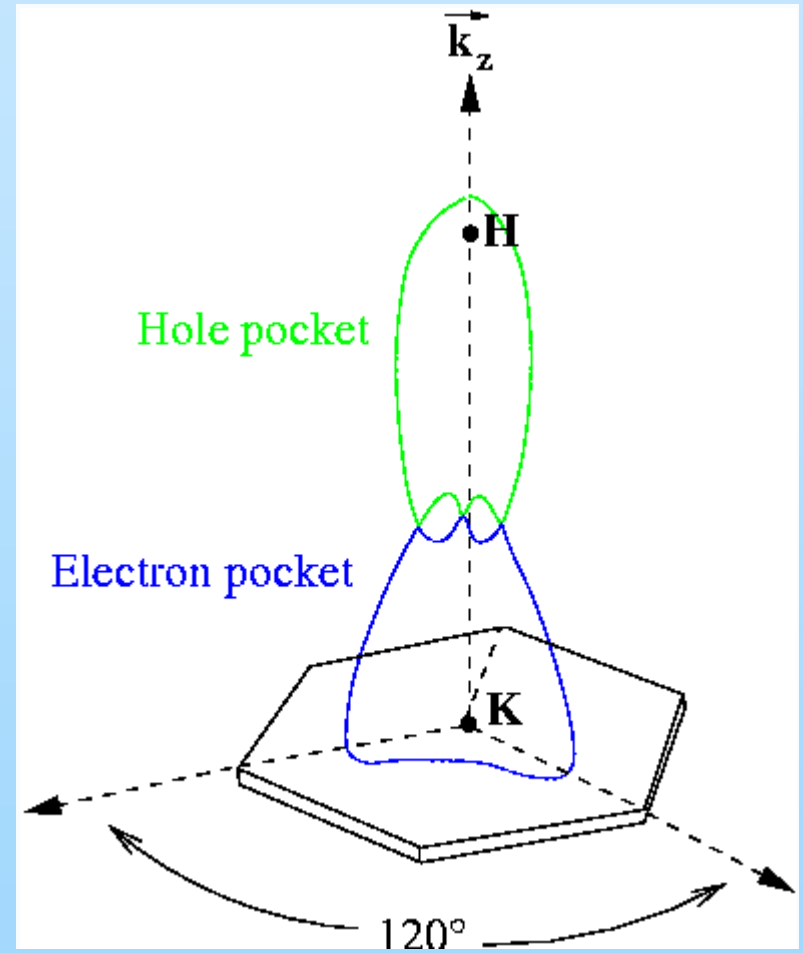
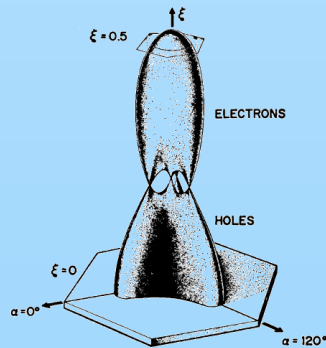
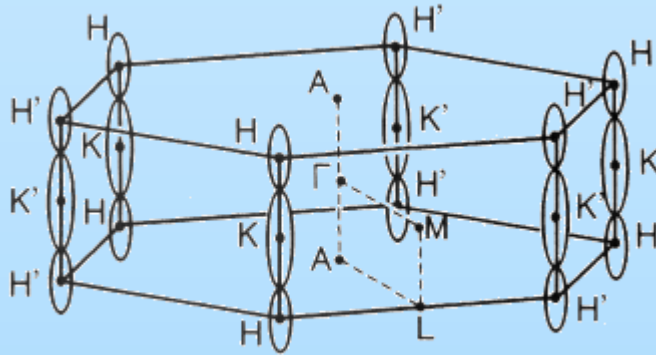
4 bande (tratteggiate)



$$\begin{aligned} \gamma_0 &= 3.16, \gamma_1 = 0.39, \\ \gamma_2 &= -0.020, \gamma_3 = 0.315, \gamma_4 \approx 0.044, \\ \gamma_5 &= 0.038; \Delta = -0.008 \text{ eV} \end{aligned}$$



Grafite: Superficie di Fermi



Dresselhaus 1964



Grafite: Superficie di Fermi

