



Carbon, its allotropic states and Graphite

M. Riccò



PERIODIC TABLE

Atomic Properties of the Elements

Period

Atomic Number
Ground-state Level
Symbol
Name
Atomic Weight
Ground-state Configuration
Ionization Energy (eV)

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 ¹³³ Cs	
speed of light in vacuum	c 299 792 458 m s ⁻¹ (exact)
Planck constant	h 6.626 070 15 × 10 ⁻³⁴ J s (exact)
elementary charge	e 1.602 176 634 × 10 ⁻¹⁹ C
electron mass	m_e 9.109 383 56 × 10 ⁻³¹ kg
proton mass	m_p 1.672 6 × 10 ⁻²⁷ kg
fine-structure constant	α 1/137.036
Rydberg constant	R_∞ 10 973 732 m ⁻¹
	$R_\infty c$ 13.6057 eV
Boltzmann constant	k 1.380 658 × 10 ⁻²³ J K ⁻¹

■ Solids
■ Liquids
■ Gases
■ Artificially Prepared

Group	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
IA	IIA	IIIB	IVB	VB	VIB	VII	VIII	VIII	VIII	VIII	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18		
1	H Hydrogen 1.00794 1s 13.5984																	He Helium 4.002602 1s ² 24.5874	
2	Li Lithium 6.941 1s ² 2s 5.3917	Be Beryllium 9.012182 1s ² 2s ² 9.3227															F Fluorine 18.9984032 1s ² 2s ² 2p ⁵ 4.2226	Ne Neon 20.1797 1s ² 2s ² 2p ⁶ 21.5645	
3	Na Sodium 22.989770 [Ne] 3s 5.1391	Mg Magnesium 24.3050 [Ne] 3s ² 7.6462															Cl Chlorine 35.453 [Ne] 3s ² 3p ⁵ 9.676	Ar Argon 39.948 [Ne] 3s ² 3p ⁶ 15.7596	
4	K Potassium 39.0983 [Ar] 4s 4.3407	Ca Calcium 40.078 [Ar] 4s ² 6.1132	Sc Scandium 44.955910 [Ar] 3d ¹ 4s 6.5615	Ti Titanium 47.88 [Ar] 3d ² 4s 6.6281	V Vanadium 50.9415 [Ar] 3d ³ 4s 6.7665	Cr Chromium 51.9961 [Ar] 3d ⁵ 4s 7.4340	Mn Manganese 54.938049 [Ar] 3d ⁵ 4s 7.4340	Fe Iron 55.845 [Ar] 3d ⁶ 4s 7.9024	Co Cobalt 58.933200 [Ar] 3d ⁷ 4s 7.8810	Ni Nickel 58.6934 [Ar] 3d ⁸ 4s 7.6398	Cu Copper 63.546 [Ar] 3d ¹⁰ 4s 7.7264						Br Bromine 79.904 [Ar] 3d ¹⁰ 4s ² 4p ⁵ 8.138	Kr Krypton 83.798 [Ar] 3d ¹⁰ 4s ² 4p ⁶ 13.9996	
5	Rb Rubidium 85.4678 [Kr] 5s 4.1771	Sr Strontium 87.62 [Kr] 5s ² 5.6949	Y Yttrium 88.90585 [Kr] 4d ¹ 5s 6.2173	Zr Zirconium 91.224 [Kr] 4d ² 5s 6.6339	Nb Niobium 92.90638 [Kr] 4d ⁴ 5s 6.7589	Mo Molybdenum 95.94 [Kr] 4d ⁵ 5s 7.0924	Tc Technetium (98) [Kr] 4d ⁵ 5s 7.28	Ru Ruthenium 101.07 [Kr] 4d ⁷ 5s 7.3605	Rh Rhodium 102.90550 [Kr] 4d ⁸ 5s 7.4589	Pd Palladium 106.42 [Kr] 4d ¹⁰ 8.3369	Ag Silver 107.8682 [Kr] 4d ¹⁰ 5s 7.5762	Cd Cadmium 112.411 [Kr] 4d ¹⁰ 5s ² 8.9938	In Indium 114.818 [Kr] 4d ¹⁰ 5s ² 5p 5.7864	Tl Thallium 204.3833 [Hg] 6s ² 6.1062	Pb Lead 207.2 [Hg] 6p ² 7.4167	Bi Bismuth 208.98038 [Hg] 6p ³ 7.2655	Po Polonium (209) [Hg] 6p ⁴ 8.414	At Astatine (210) [Hg] 6p ⁵ 8.414	Rn Radon (222) [Hg] 6p ⁶ 10.7485
6	Cs Cesium 132.90545 [Xe] 6s 3.8939	Ba Barium 137.327 [Xe] 6s ² 5.2117		Hf Hafnium 178.49 [Xe] 4f ¹⁴ 5d ² 6s ² 6.8251	Ta Tantalum 180.9479 [Xe] 4f ¹⁴ 5d ³ 6s ² 7.5496	W Tungsten 183.84 [Xe] 4f ¹⁴ 5d ⁴ 6s ² 7.6840	Re Rhenium 186.207 [Xe] 4f ¹⁴ 5d ⁵ 6s ² 7.8335	Os Osmium 190.23 [Xe] 4f ¹⁴ 5d ⁶ 6s ² 8.4382	Ir Iridium 192.222 [Xe] 4f ¹⁴ 5d ⁷ 6s ² 8.9670	Pt Platinum 195.078 [Xe] 4f ¹⁴ 5d ⁹ 6s ¹ 8.9588	Au Gold 196.96657 [Xe] 4f ¹⁴ 5d ¹⁰ 6s ¹ 9.2255	Hg Mercury 200.59 [Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 10.4375							
7	Fr Francium (223) [Rn] 7s 4.0727	Ra Radium (226) [Rn] 7s ² 5.2784																	
										</									

Atomic Number	Ground-state Level
58	1s ²
Symbol	Ce
Name	Cerium
Atomic Weight	140.116
Ground-state Configuration	[Xe] 4f ¹ 5d ¹ 6s ²
Ionization Energy (eV)	5.5387

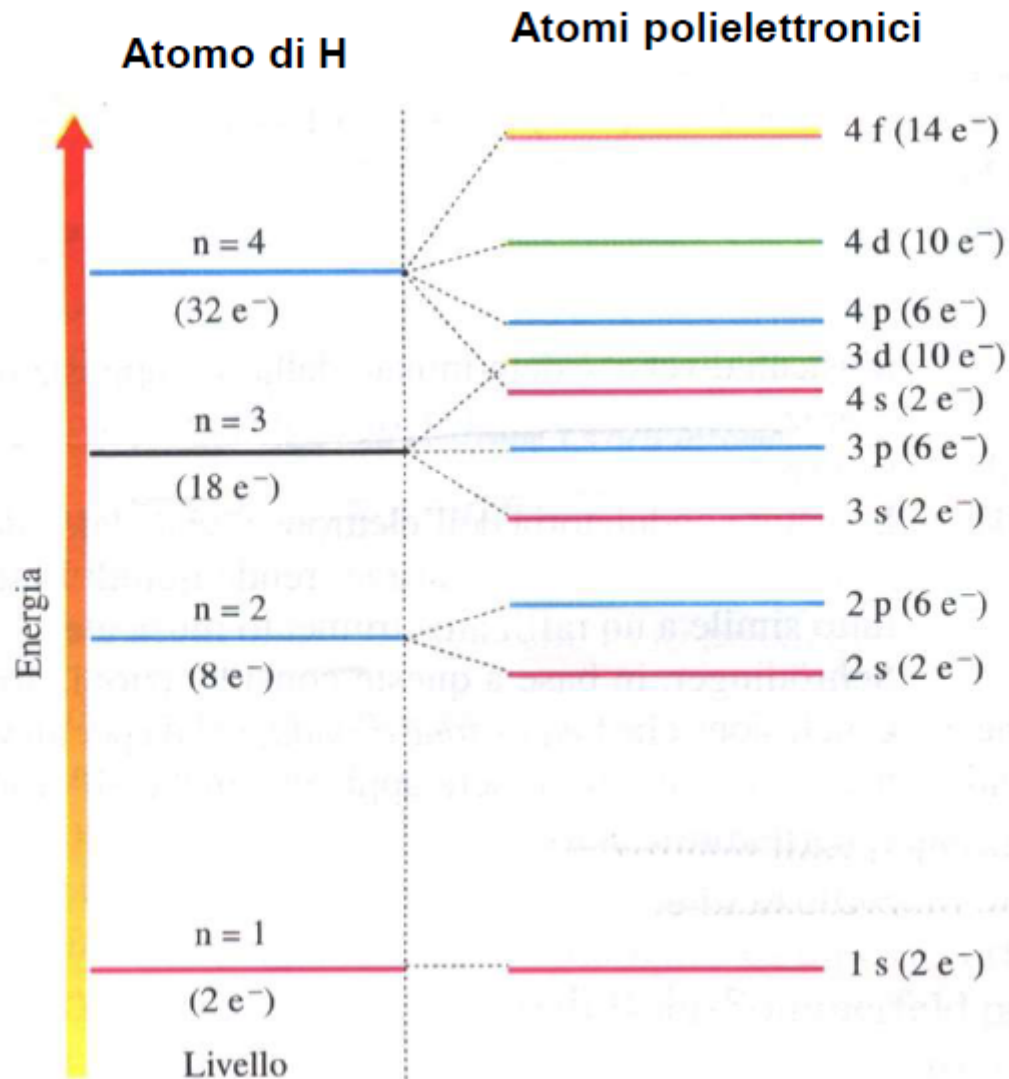
[†]Based upon ¹²C. () indicates the mass number of the most stable isotope.

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

NIST SP 966 (September 2003)



- ^{12}C Isotope $\rightarrow$ natural abundance (98.93%, $S=0$)
- ^{13}C Isotope $\rightarrow$ important for NMR (1.07%, $S=1/2$)
- ^{14}C Isotope $\rightarrow$ important for archaeological dating (average lifespan 5730 years)



The energy of each electron in multi-electron atoms depends not only on n , but also on l ; a fundamental consequence of inter-electronic interactions.

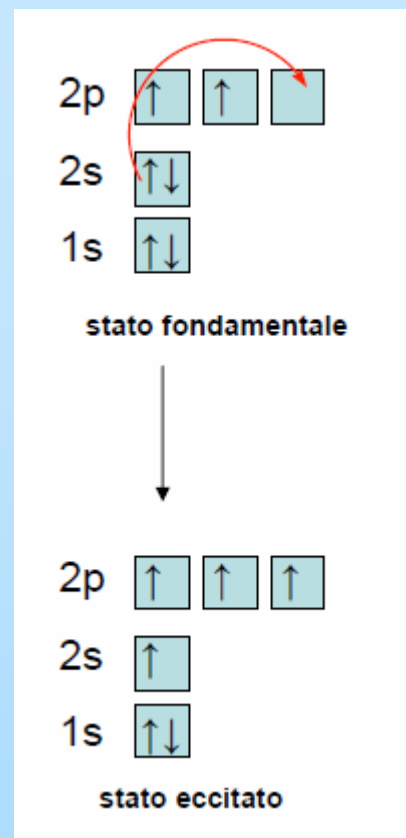
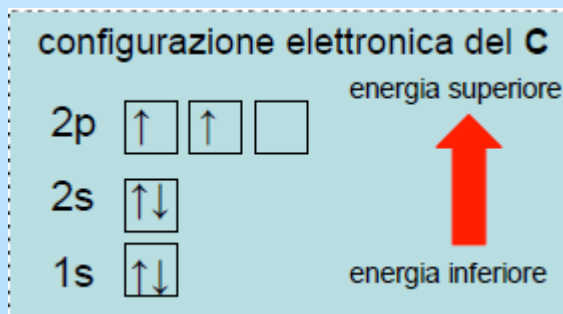
Splitting of energy levels into multiple sublevels with distinct and increasing energy, for a given n value, as l increases.

Between level 3 and level 4, there is an **overlap of energy levels**.



sp^3 hybridization

Configuration: [He] $2s^2 2p^2$



orbitale s



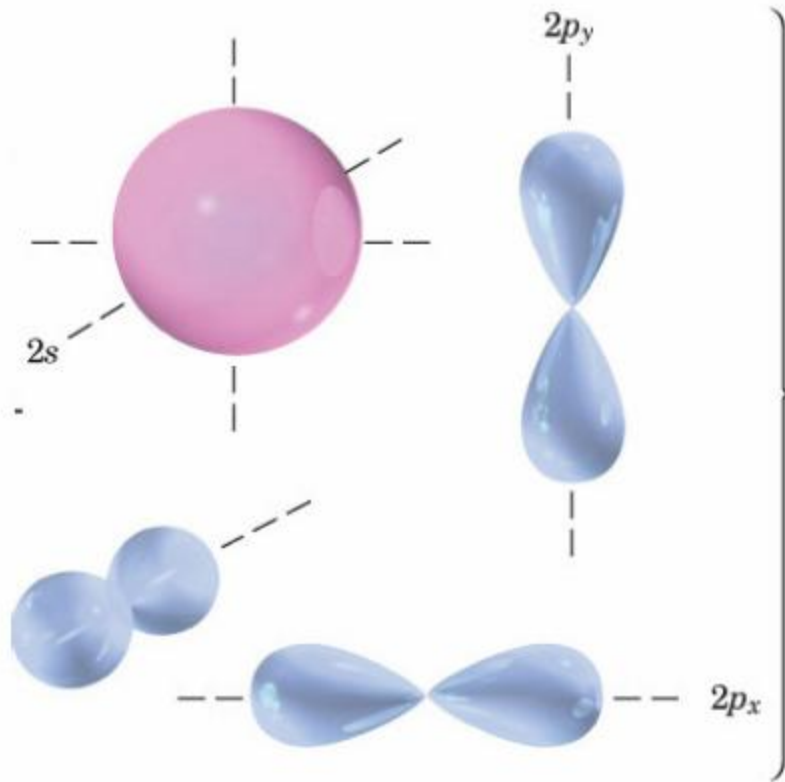
orbitale p



orbitale sp^3



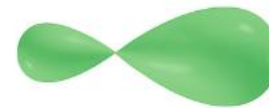
sp^3 hybridization



Hybridization
→



Four sp^3
tetrahedral orbitals

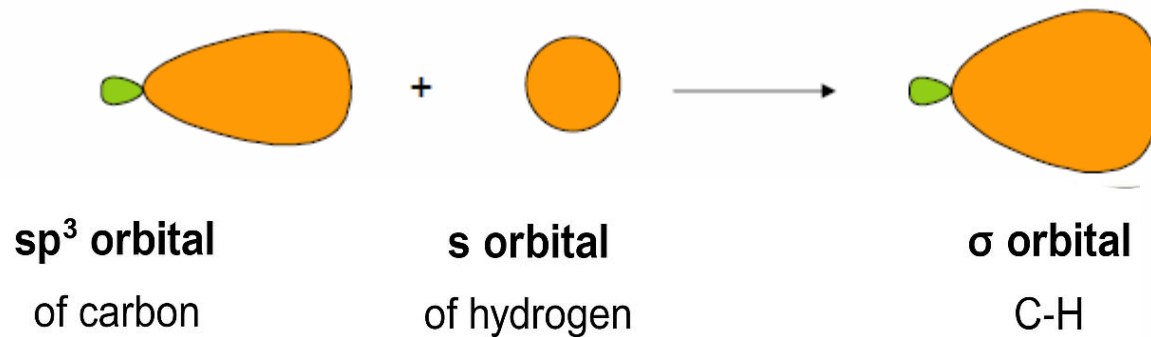


sp^3 orbital

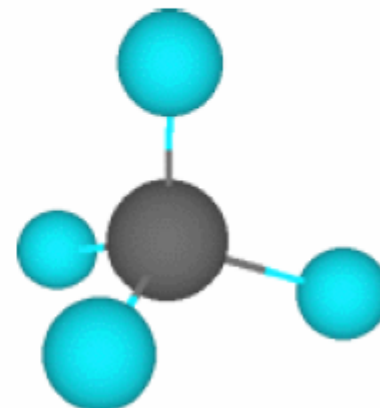


sp^3 hybridization

Methane

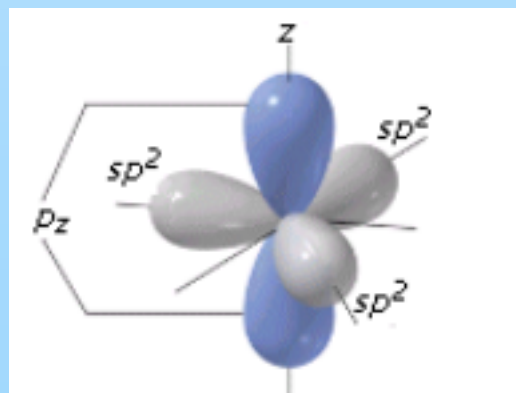
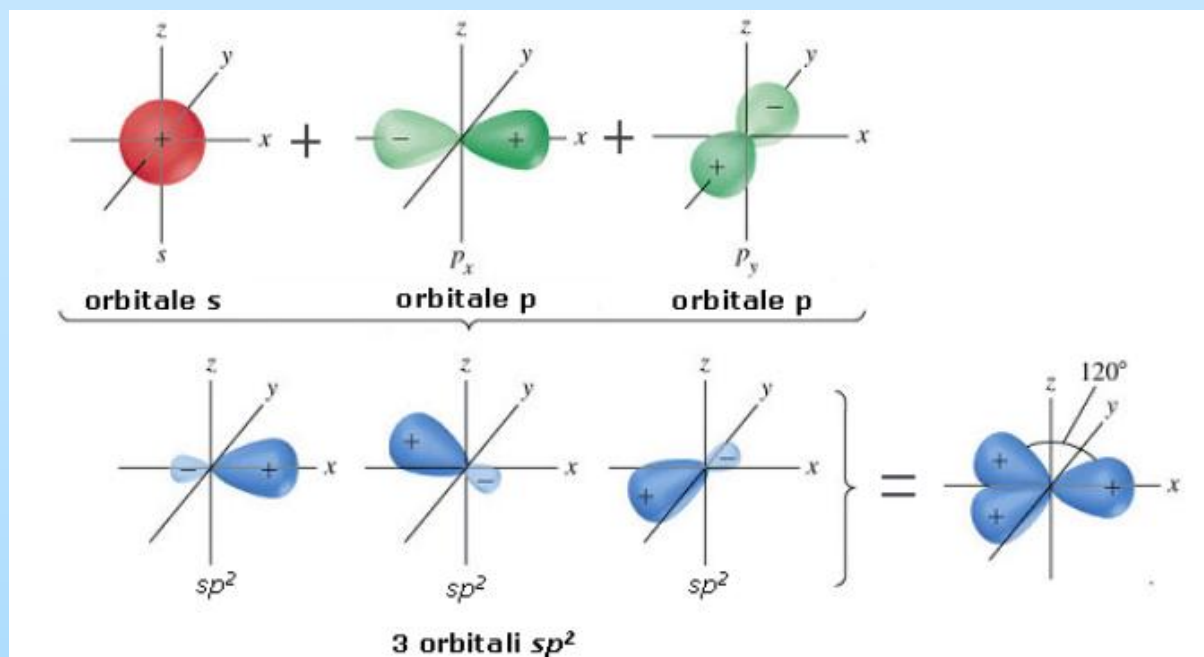


The bond angle formed by each H-C-H equals exactly 109.5° (tetrahedral angle)



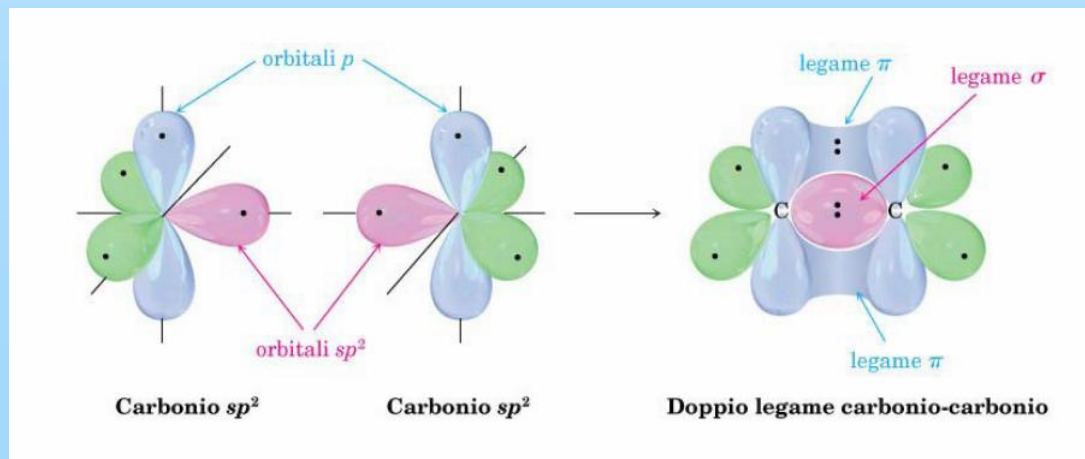
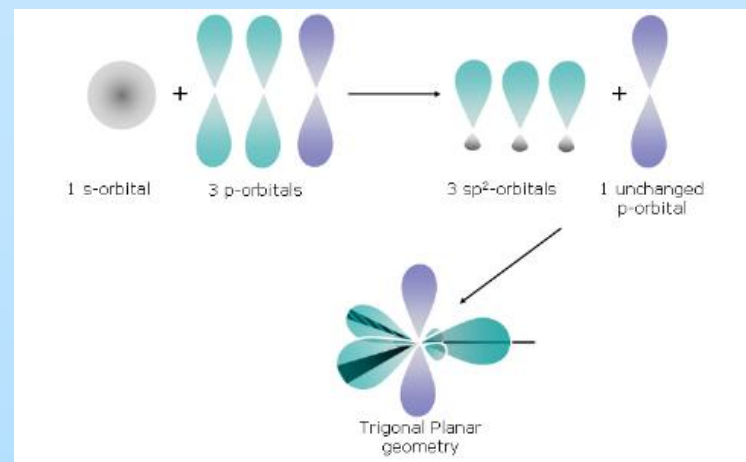
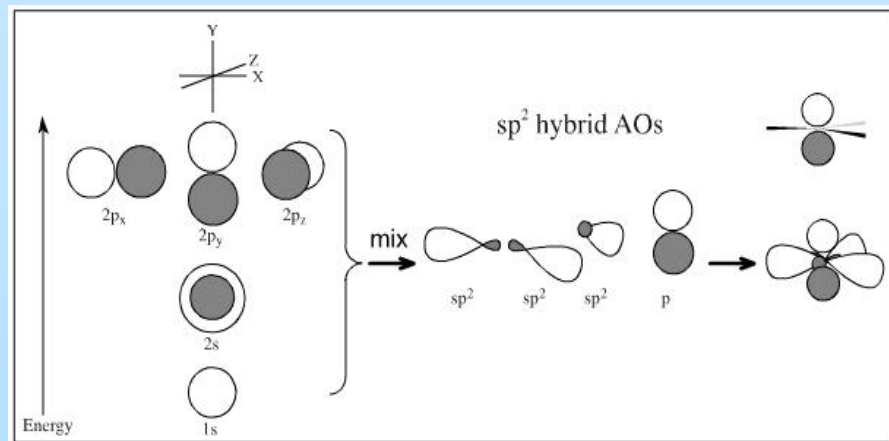


sp^2 hybridization





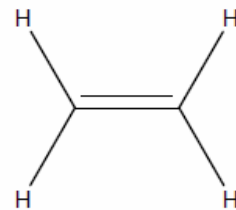
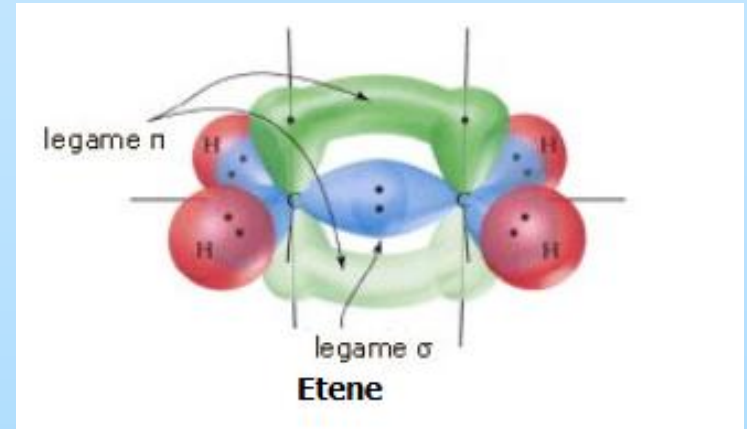
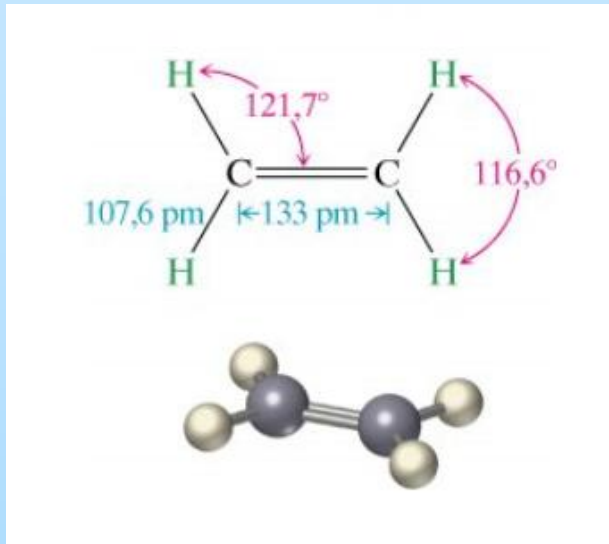
sp² hybridization



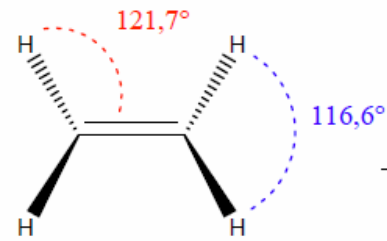


sp^2 hybridization

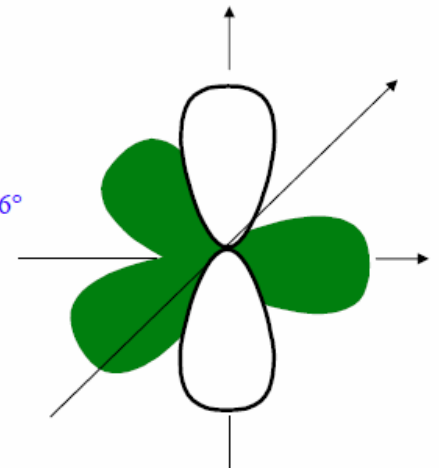
Ethylene



vista dall'alto

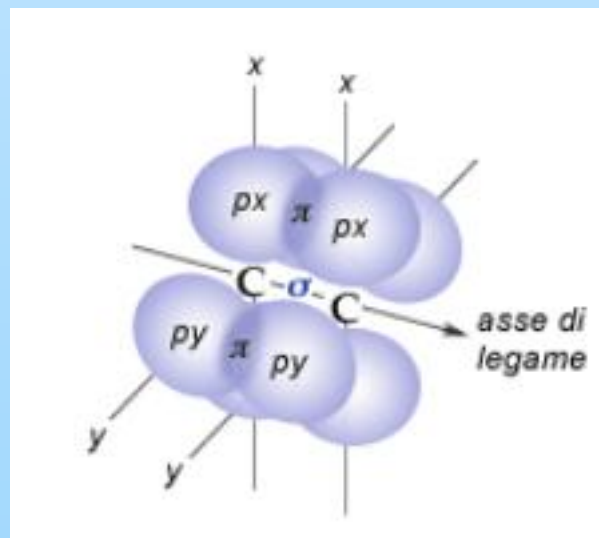
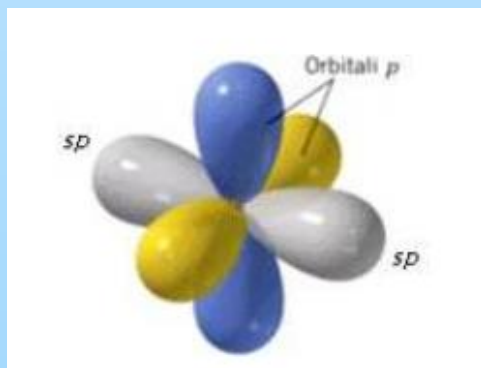
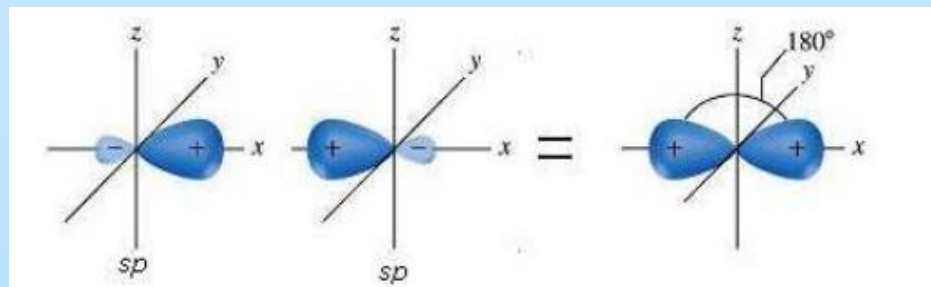
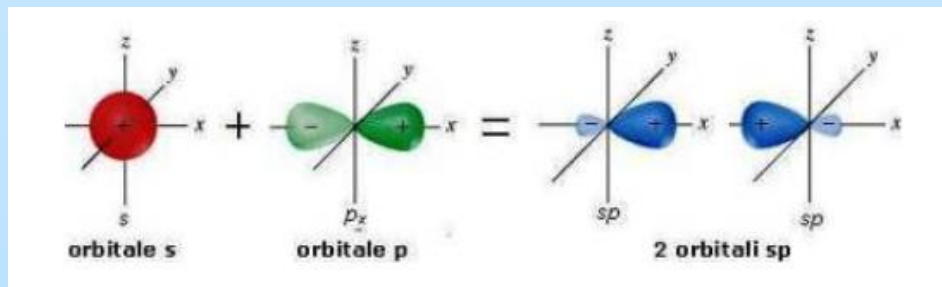


vista laterale





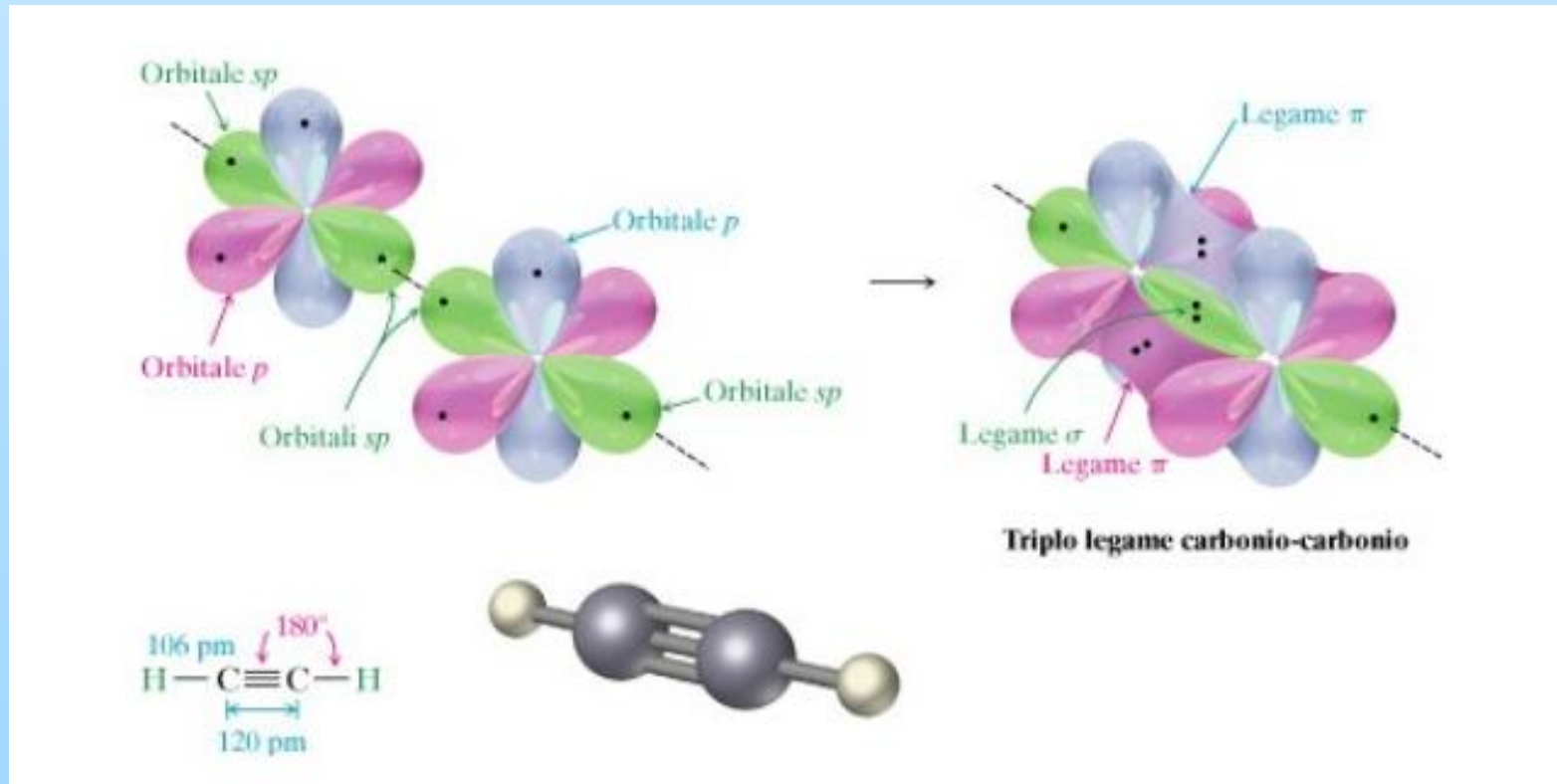
sp hybridization





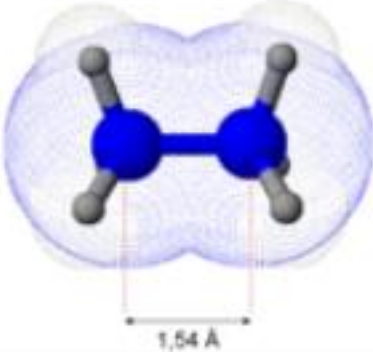
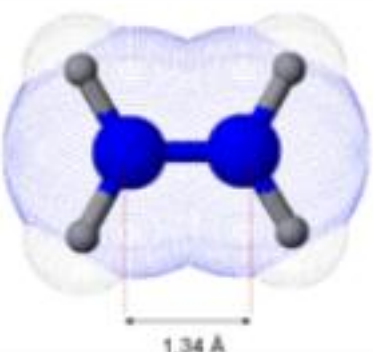
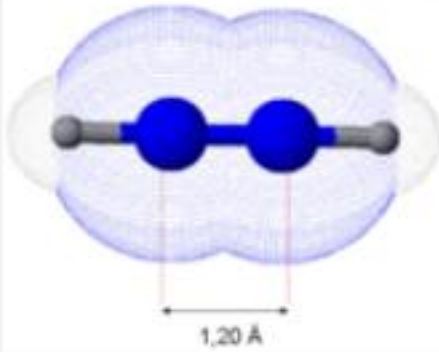
sp hybridization

Acetilene



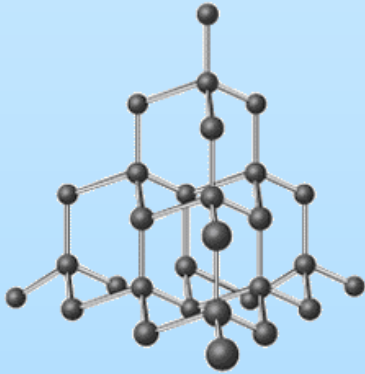


sp^n hybridization

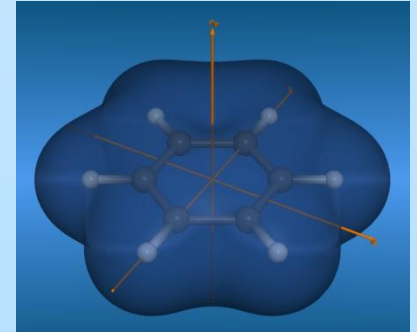
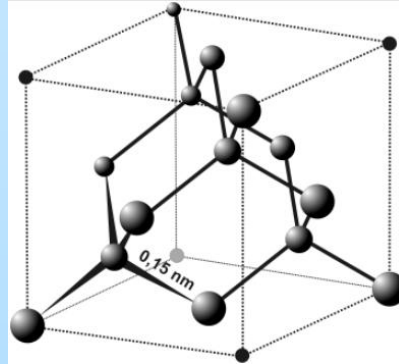
		
1,54 Å	1,34 Å	1,20 Å
Legame singolo Carbonio-Carbonio	Legame doppio Carbonio- Carbonio	Legame triplo Carbonio- Carbonio
Ibridizzazione sp^3	Ibridizzazione sp^2	Ibridizzazione sp



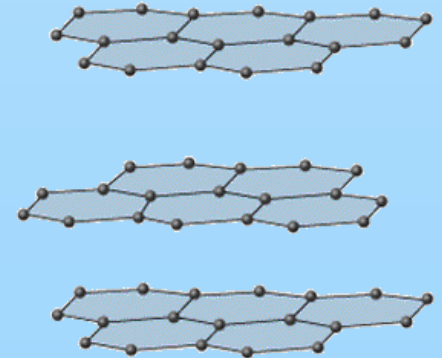
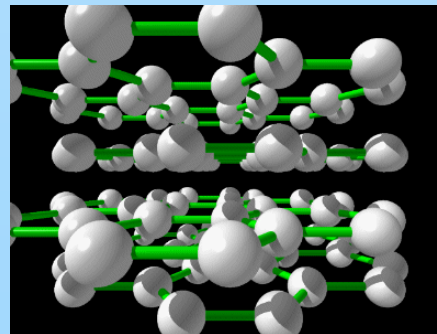
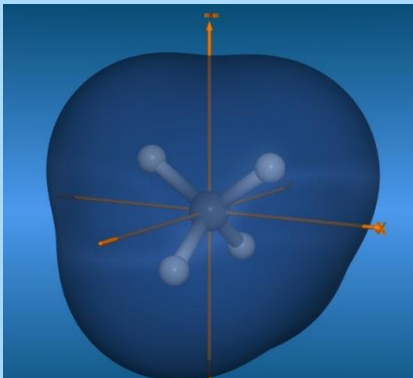
Allotropic states of carbon



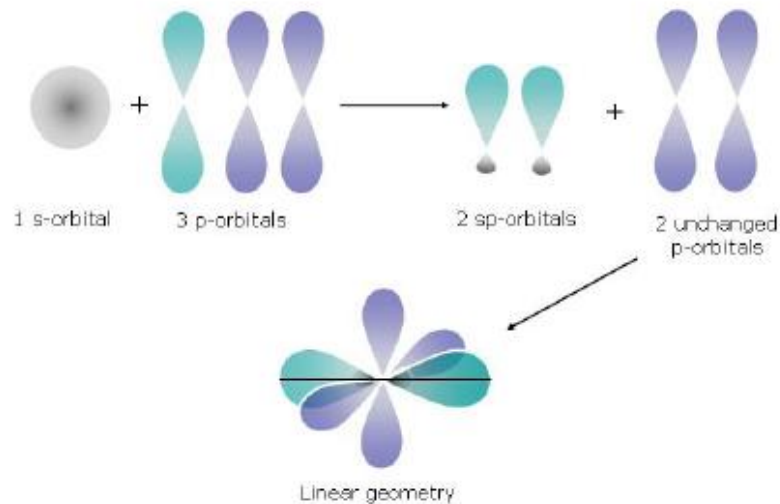
Diamond



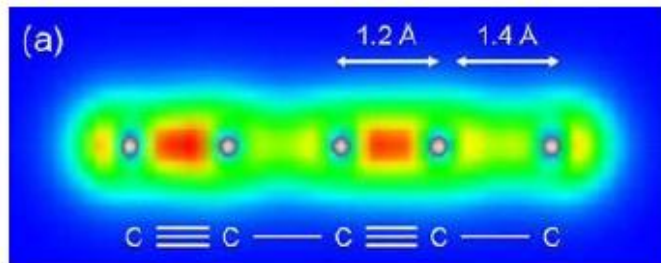
Graphite



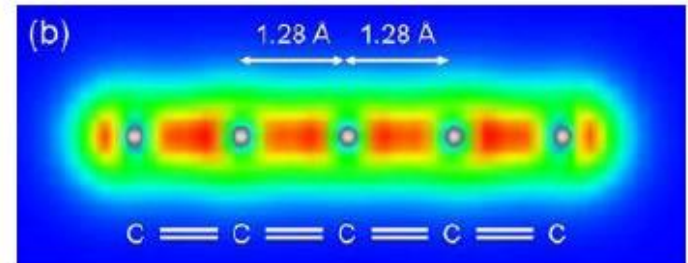
Ibridizzazione sp



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

A. El Goresy¹, G. Donnay¹

+ 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



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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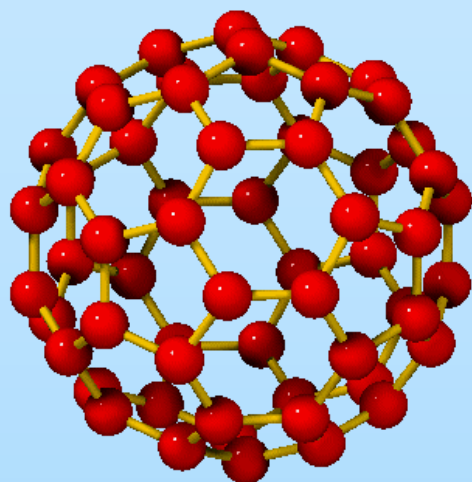
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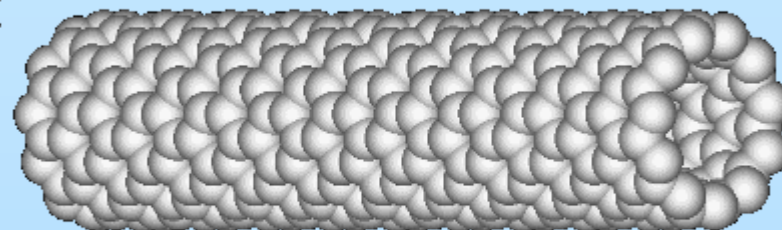


Allotropic states of carbon



Fullerene (C₆₀)

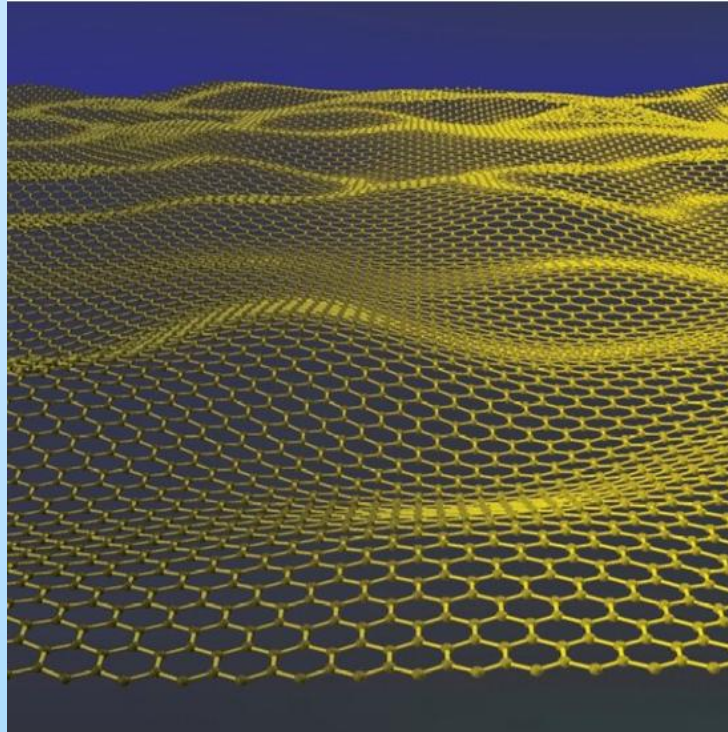
Curl, Kroto e Smalley, Nobel
Prize in Chemistry 1996



Nanotubi

(Iijima 1991)

Nanostructures.....



Graphene

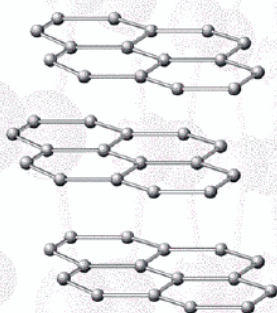
K. Novoselov, A. Geim

Nobel Prize in Physics 2010



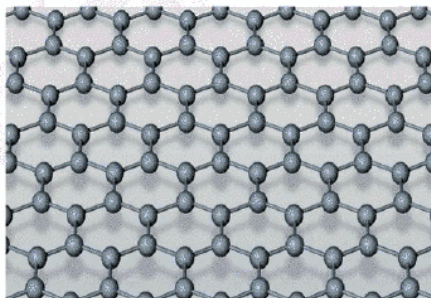
GRAPHENE ALLOTROPES

3D



Graphite

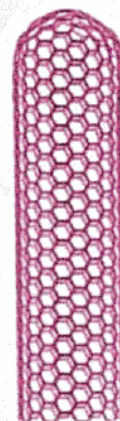
2D



graphene

PRESUMED
NOT TO EXIST
IN THE FREE STATE

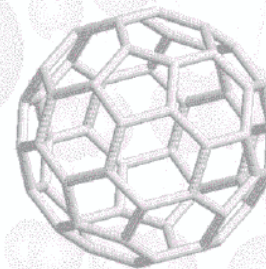
1D



**Carbon
Nanotube**

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

0D



Buckyballs

Kroto et al 1985



Diamond ↔ Graphite

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}	-29×10^{-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.



Phase Diagram

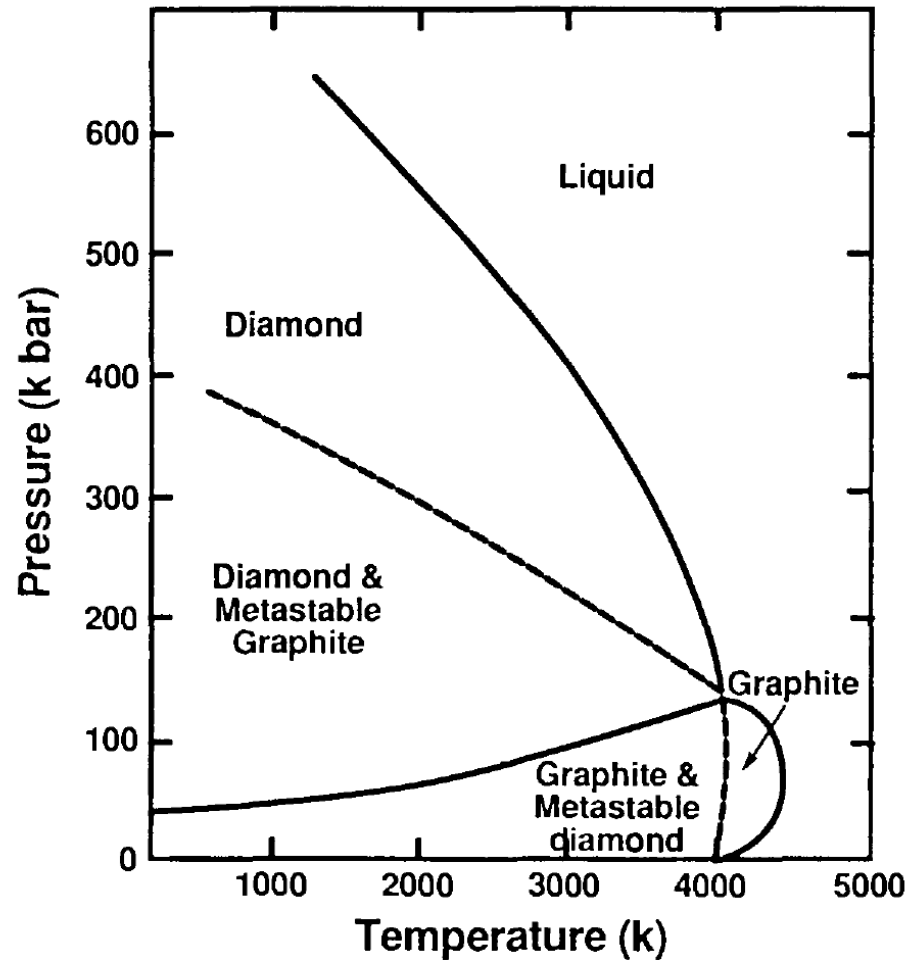
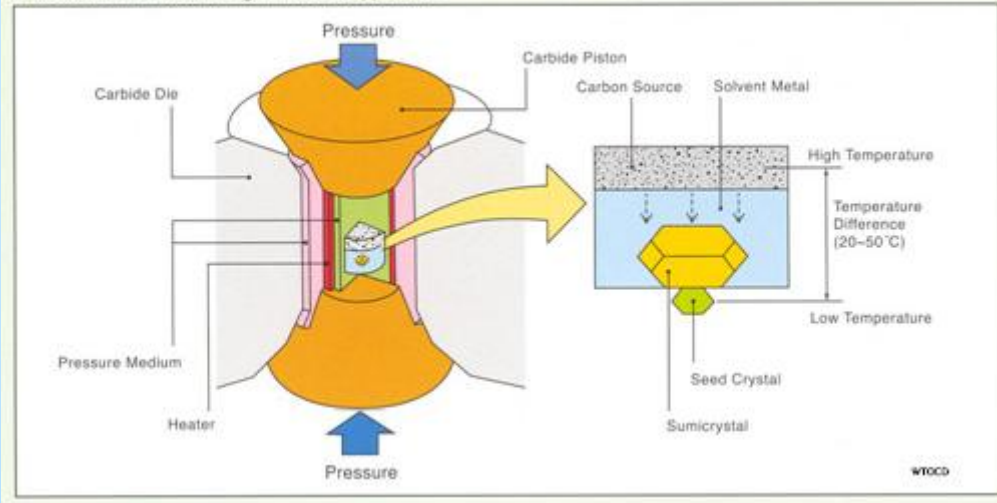


Figure 2.20. Carbon phase diagram.

Diamond synthesis

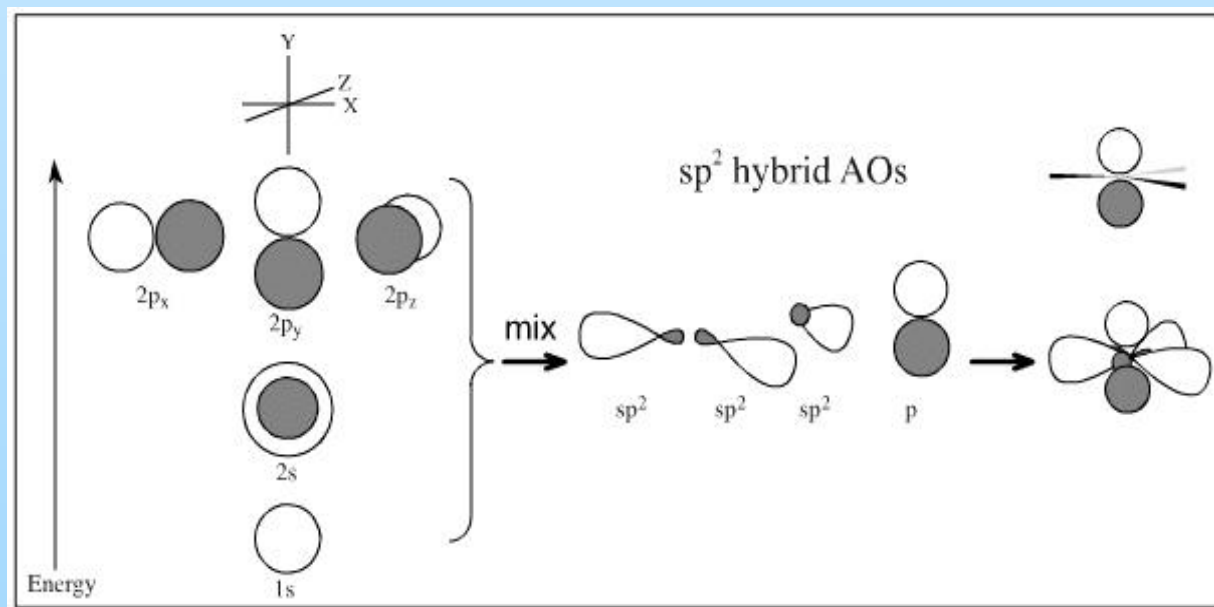
Cross Section of the Ultrahigh Pressure Apparatus





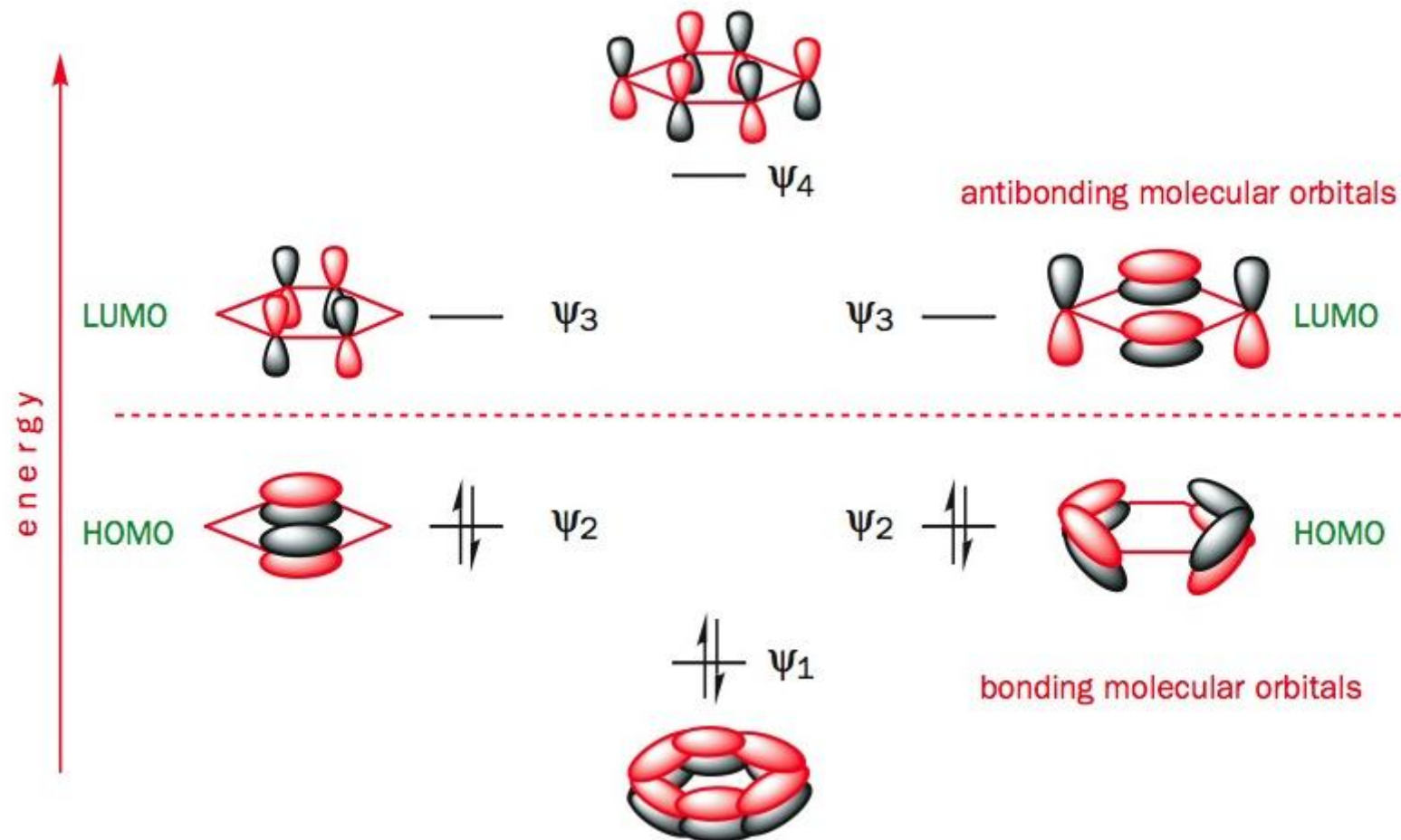
sp^2 hybridization

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



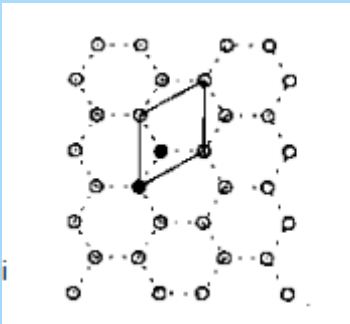
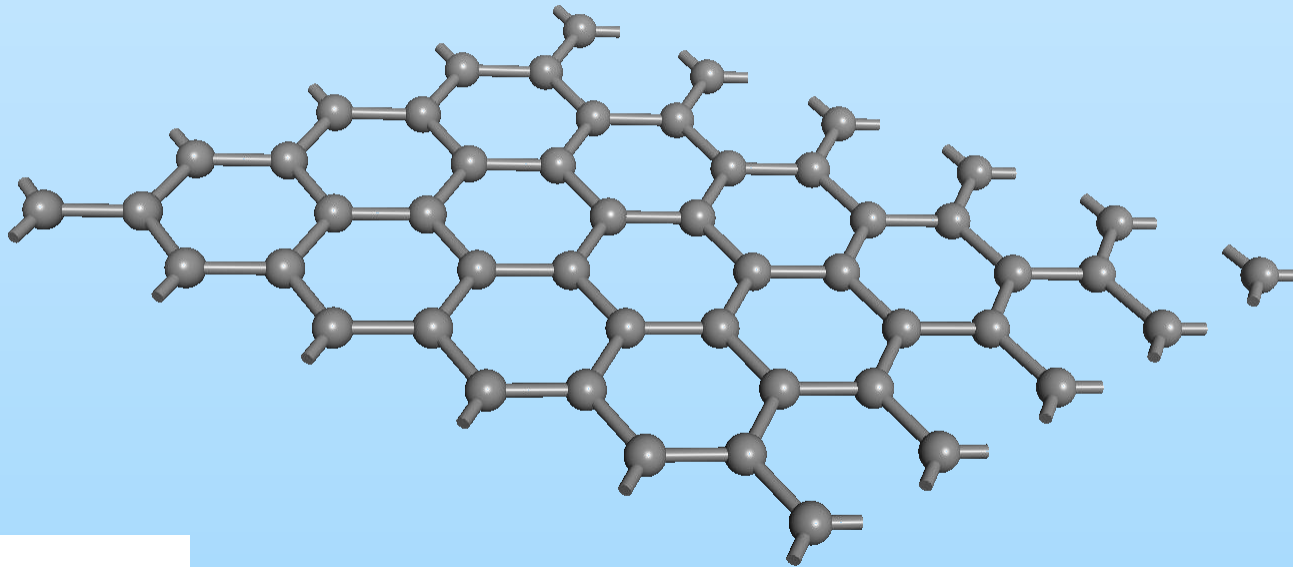


sp^2 hybridization: benzene





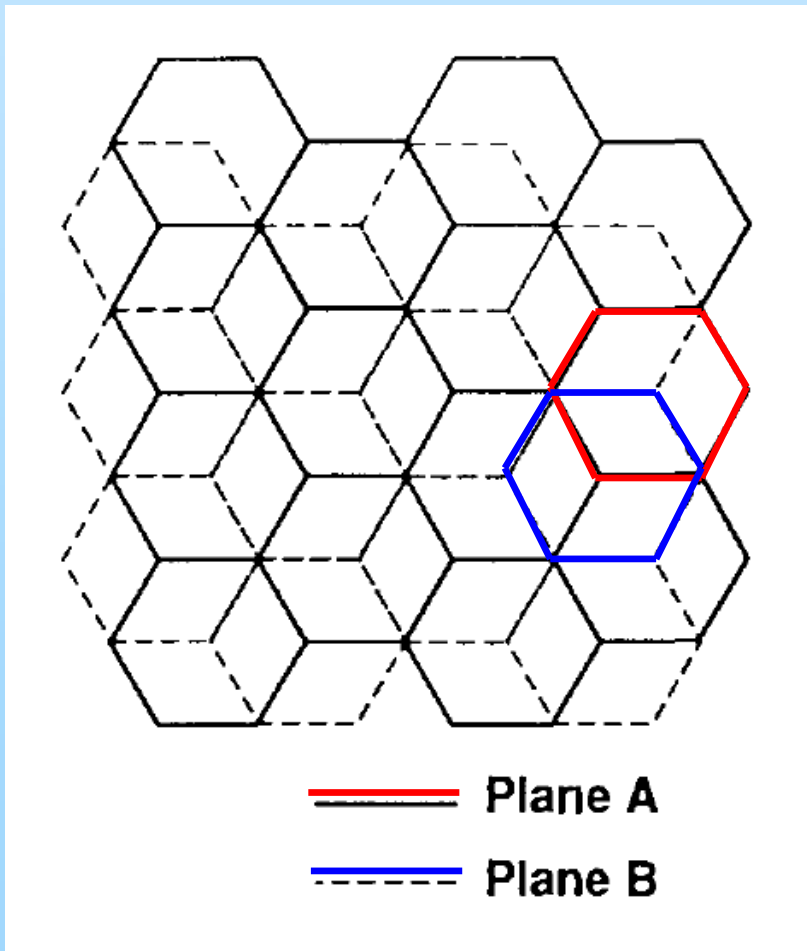
sp^2 hybridization: : graphene



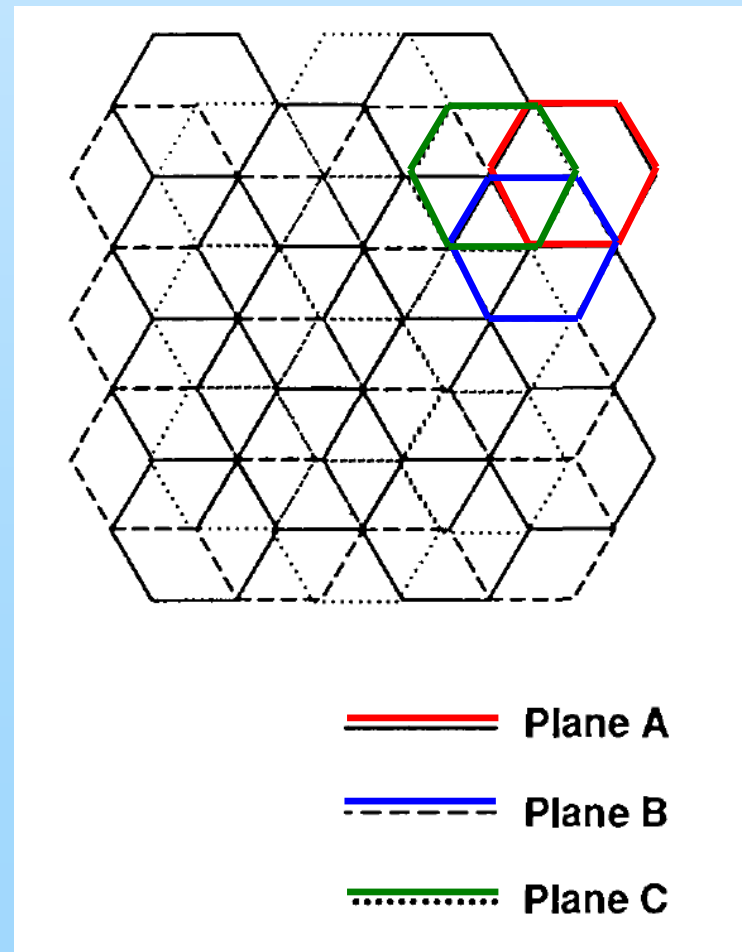


Graphite Structure

hexagonal graphite

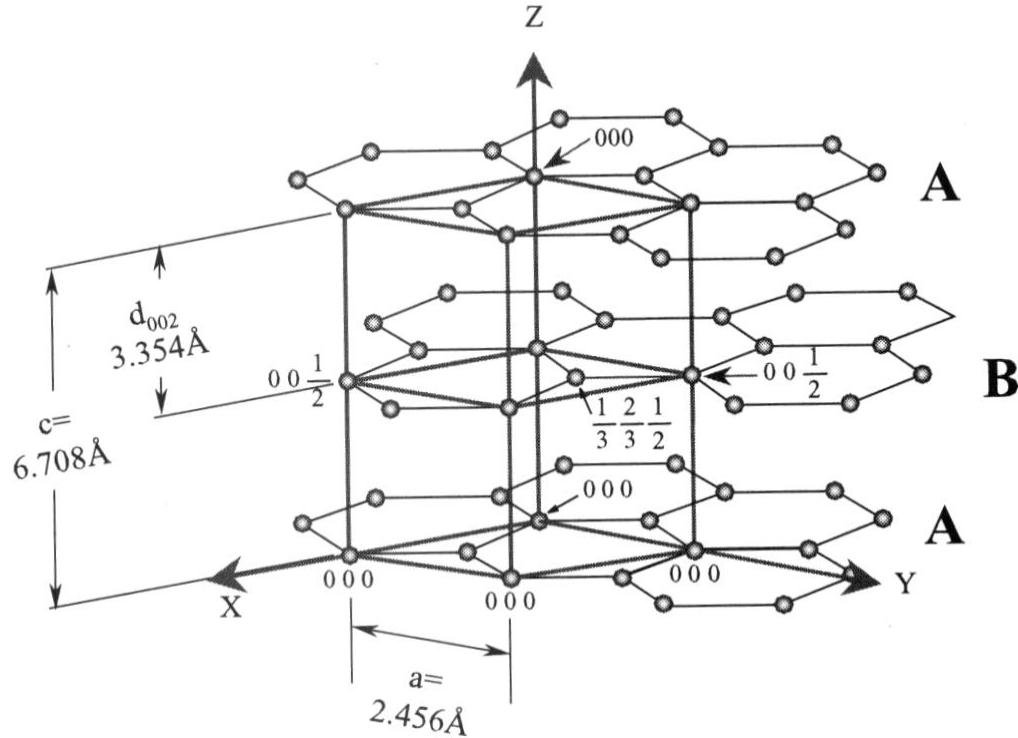


rhombohedral graphite





Hexagonal graphite: unit cell

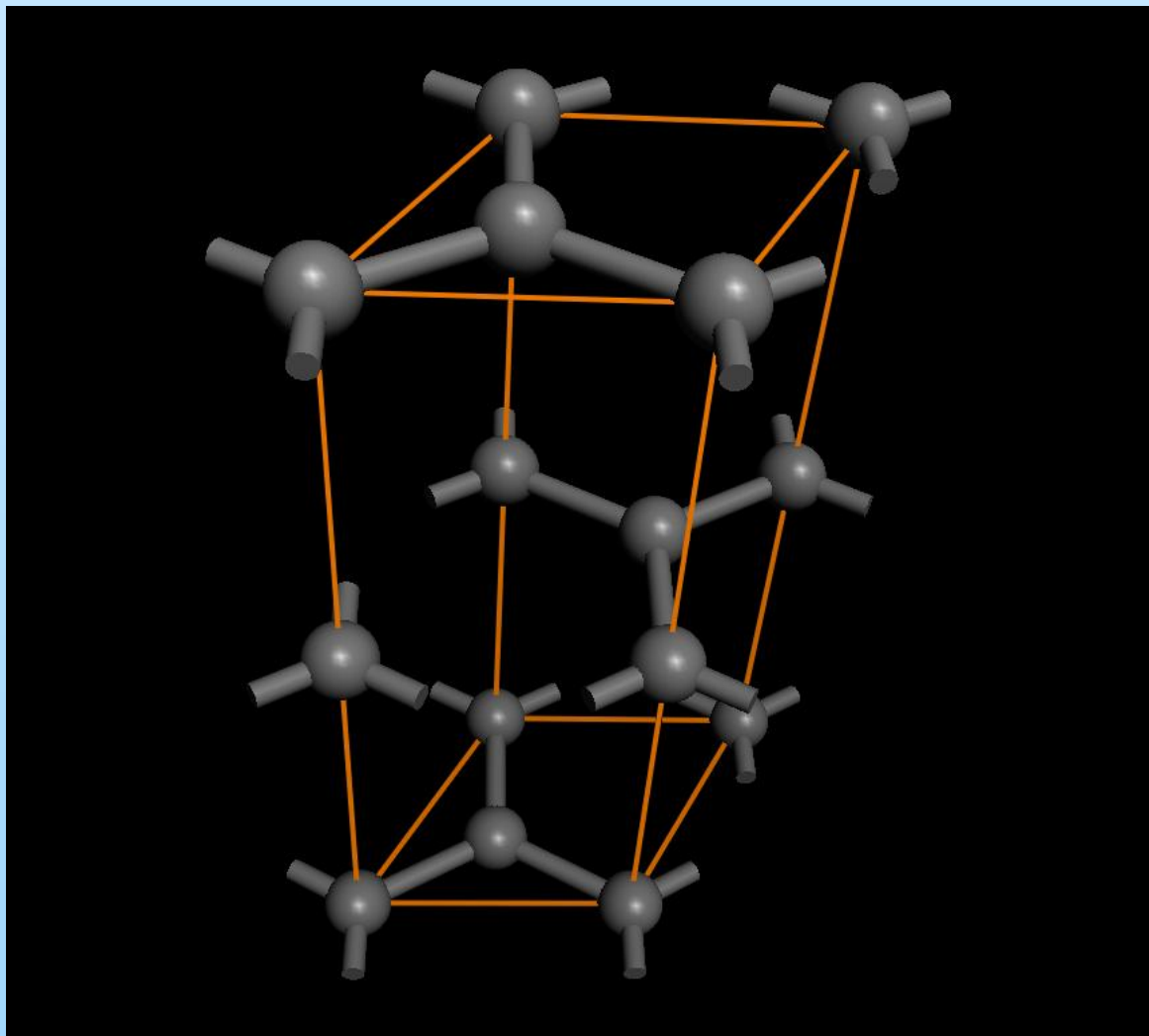


$$d(\text{C}=\text{C}) = 1.42 \text{ \AA}$$



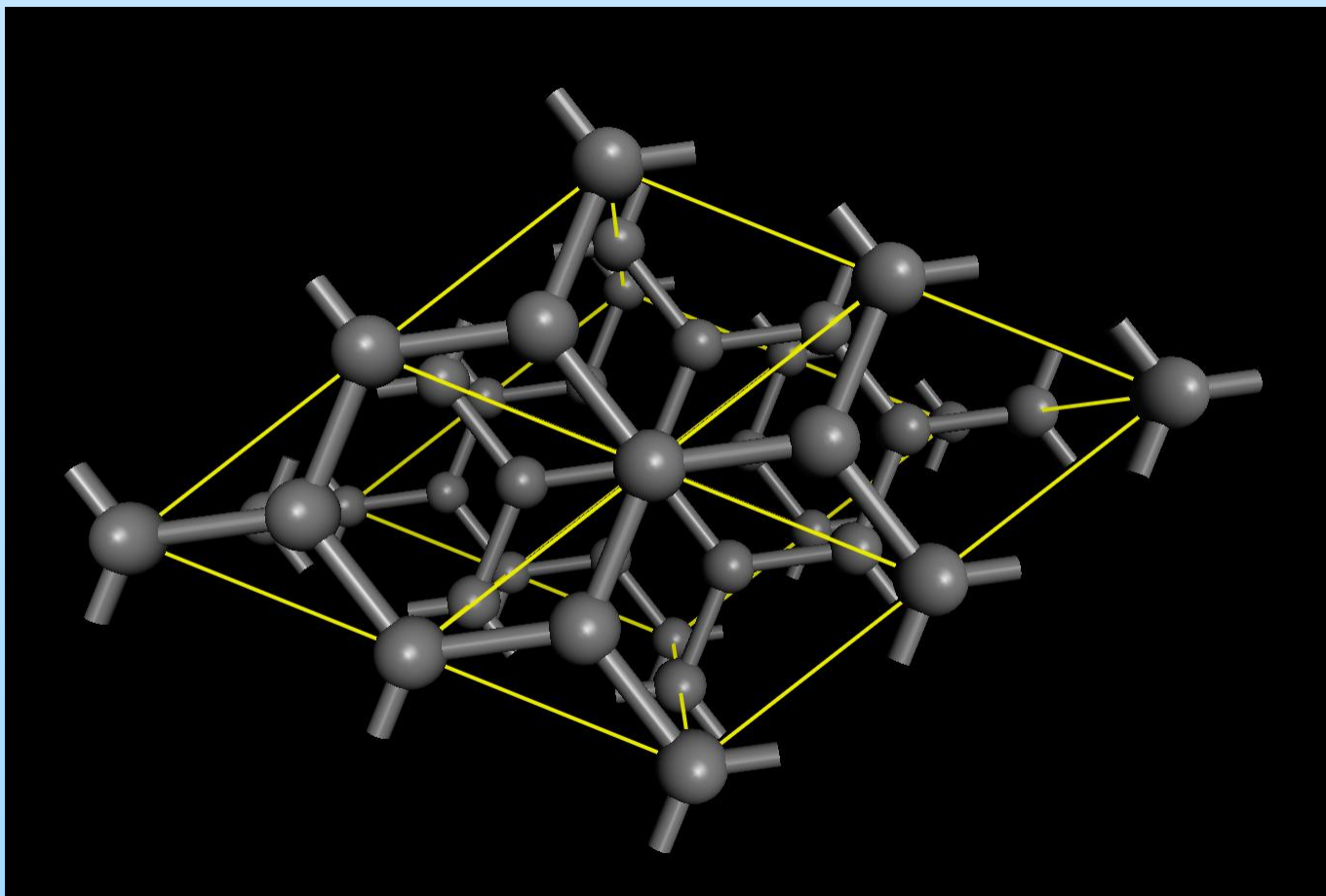
Graphite unit cell

Hexagonal group P 63 MMC #194





Graphite unit cell



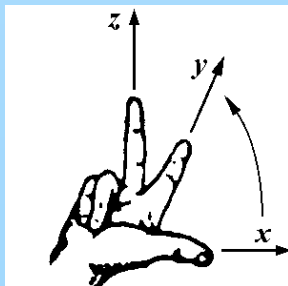


2D reciprocal lattice

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

EXAMPLE

Reciprocal lattice in two dimensions. A two-dimensional lattice (Fig. 21) has basis vectors $\mathbf{a} = 2\mathbf{x}$; $\mathbf{b} = \mathbf{x} + 2\mathbf{y}$. Find the basis vectors of the reciprocal lattice.



We can use our definitions for the three-dimensional case in this two-dimensional problem if we assume that $\mathbf{e}$ is parallel to the z -axis, so the plane of the reciprocal lattice vectors $\mathbf{A}$ and $\mathbf{B}$ will be in the plane of $\mathbf{a}$ and $\mathbf{b}$. Let $c=2$. Now

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

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

These results substituted in (33) give

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

as shown in figure 21.

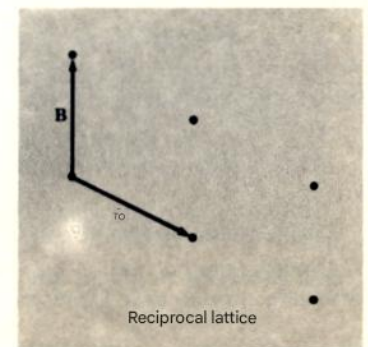
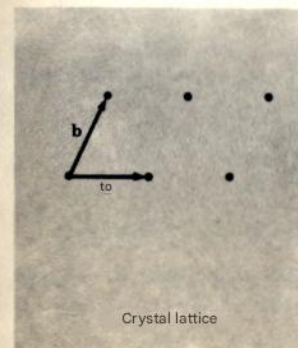
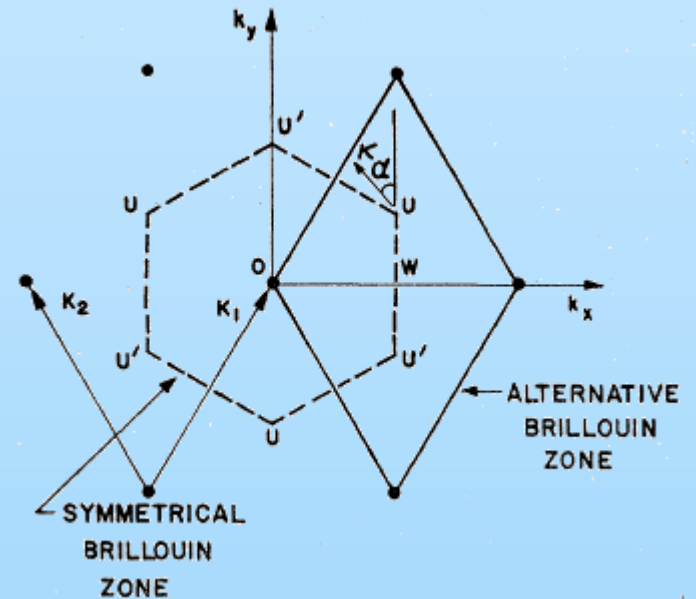
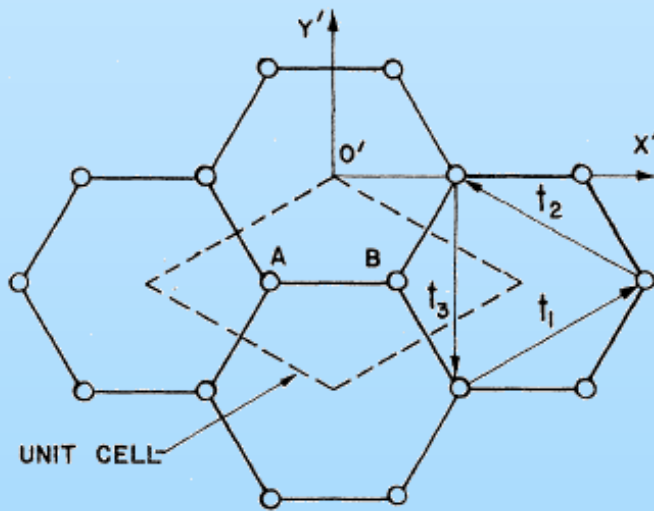


Figure 21 Reciprocal lattice in two dimensions: $\mathbf{A}$ and $\mathbf{B}$ are perpendicular to groups of planes (lines) in the crystal lattice, that is, to the lines parallel to $\mathbf{b}$ and $\mathbf{a}$, respectively. Any vector between points of the reciprocal lattice is perpendicular to some plane in the crystal lattice.



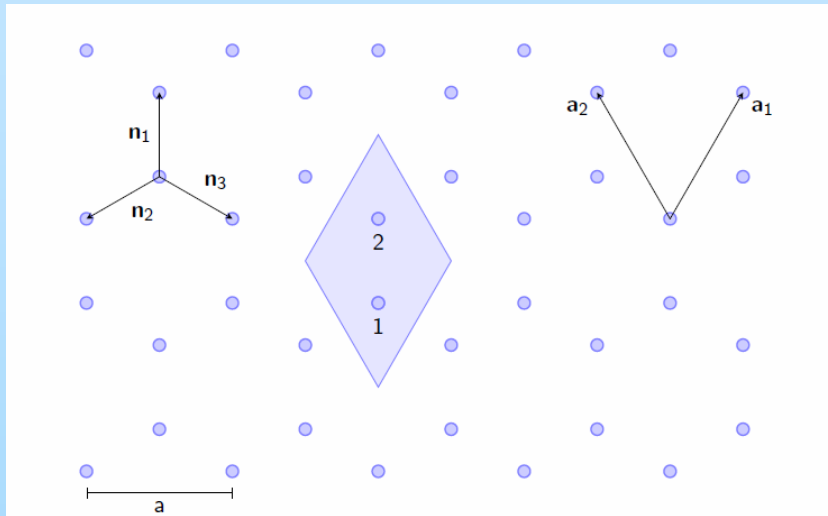
Graphene: unit cell and 1st Brillouin zone



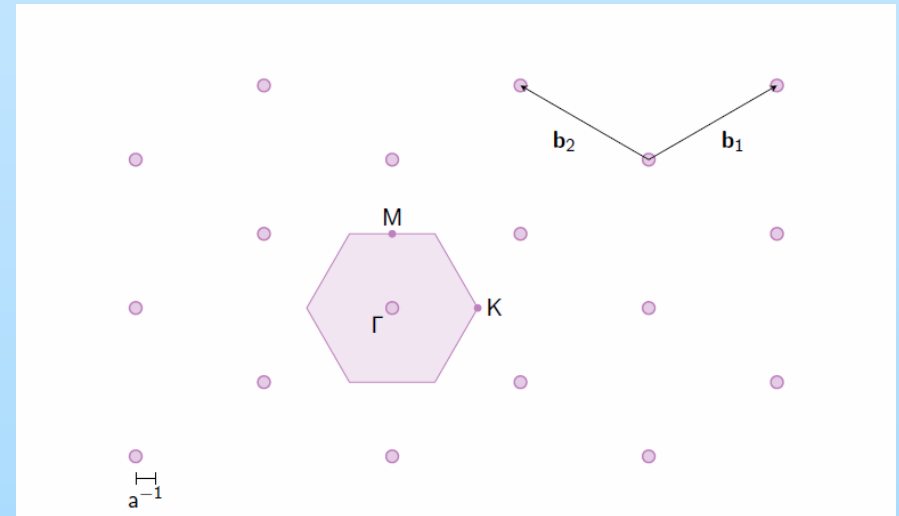
Reciprocal lattice (1 B. zone)



Graphene: unit cell and 1st Brillouin zone



Direct lattice: a_1 e a_2 primitive vectors, n_1 , n_2 e n_3 nearest neighbours vectors



Reciprocal lattice: b_1 e b_2 primitive vectors, pink: 1st B. zone



Tight Binding (LCAO)

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

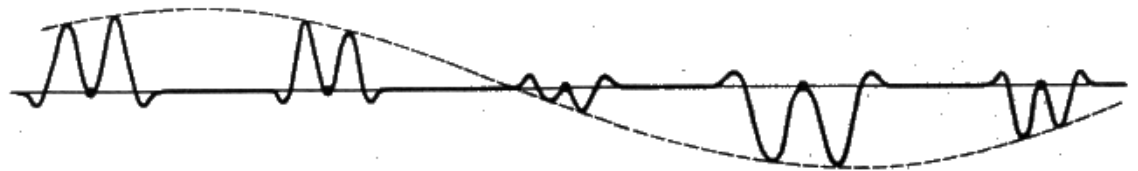
ϕ Wannier functions

ψ n atomic orbitals (denoted by $X(\mathbf{r})$ below)

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

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

Bloch condition



If the cell includes a basis.....

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

where $\phi_{j\alpha}(\mathbf{r})$ are the orbitals of a single isolated atom of atomic number Z_j centered at the origin, identified by the index $\alpha \in \{1s, 2s, 2p_x \dots\}$. $\mathbf{R}$ indicates a generic vector of the Bravais lattice, j is an index that identifies the base sites of the crystal, $\mathbf{d}_j$ is the position of the j site within the unitary cell and finally the $c_{j\alpha}$ are the unknown coefficients of the linear combination.



Graphene: Electronic Properties

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

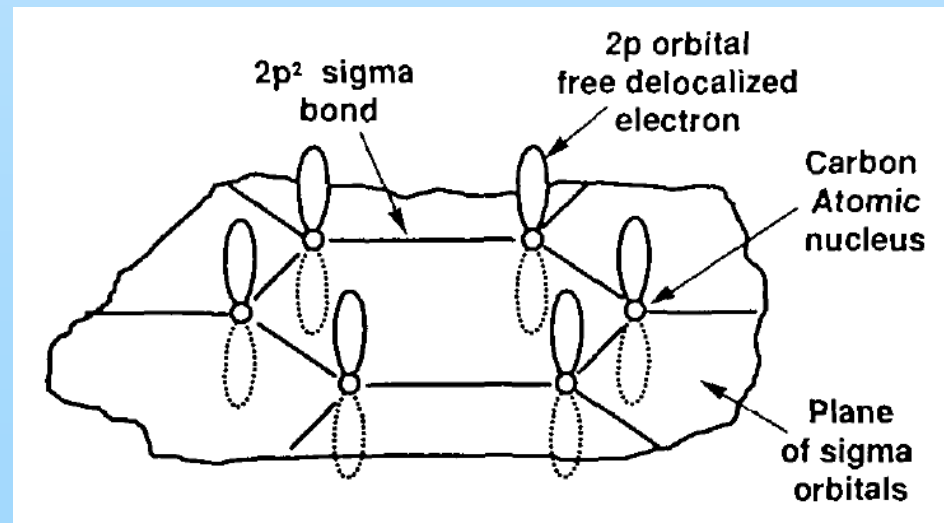
$$\psi_{2\pi/3} = \frac{1}{\sqrt{3}} \left[\psi(2S) - \frac{1}{\sqrt{2}}\psi(2P_x) + \sqrt{\frac{3}{2}}\psi(2P_y) \right]$$

In plane

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

P_z out of plane

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



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 – 6×10^{-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 in graphene

(Wallace 1946)

Phys. Rev. 71 (1947) 622

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

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

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

No overlap among p^z orbitals

$$H\psi = E\psi$$

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

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

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

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

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

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

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



Graphene: Electronic Properties

$$H_{11} = H_{22} \quad \text{By symmetry}$$

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

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

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

+ out, - in the
hexagonal B. zone

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

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

putting

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

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

$\mathbf{e}' = \mathbf{a}_1$ Vector connecting nearest neighbors A

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



Graphene: Electronic Properties

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

H_0 Hamiltonian of an isolated
C atom

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

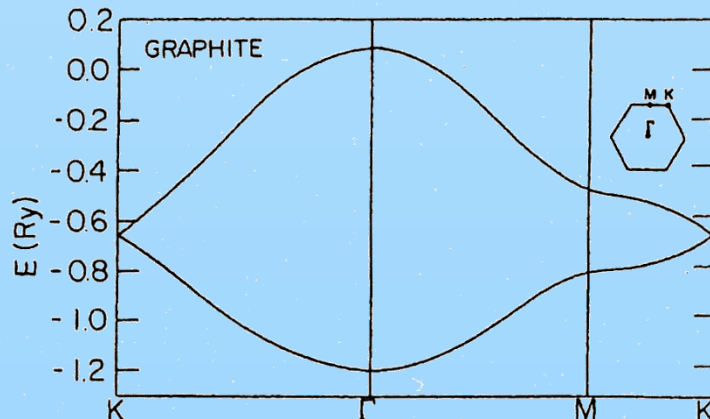
V Periodic lattice potential

U Potential of a C atom

$$H_0 X = E_0 X$$

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

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

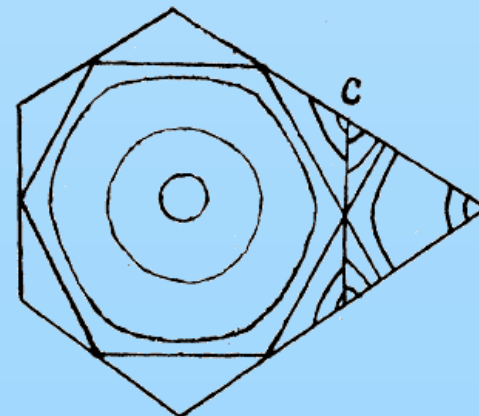


$$\gamma_0 = \int X^*(\mathbf{r} - \mathbf{\varrho})(U - V)X(\mathbf{r})d\tau > 0$$

$\mathbf{\varrho} = \mathbf{AB}$ Contiguous lattices

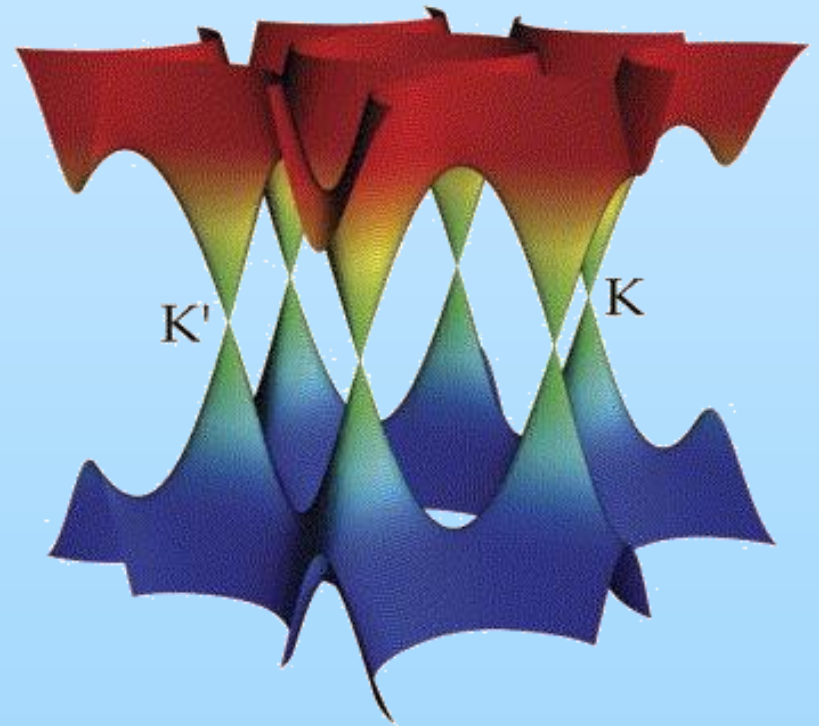
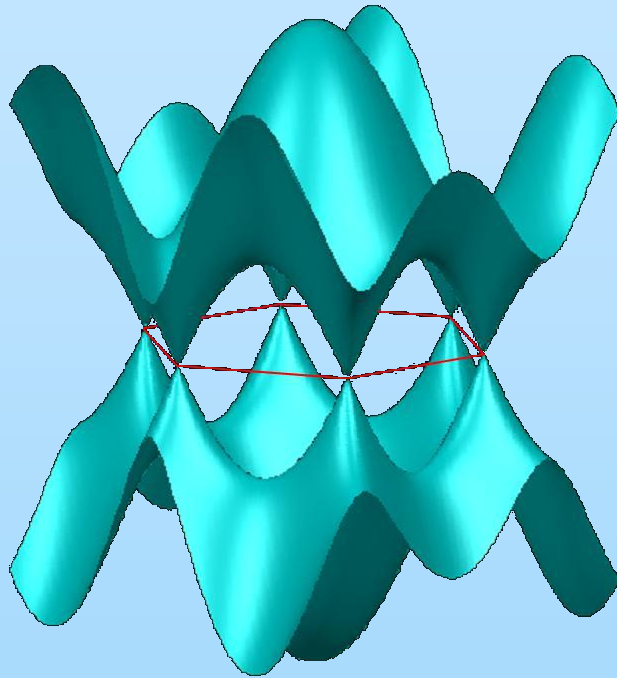
$$H_{12}' = -\gamma_0(\exp[-2\pi i k_x(a/\sqrt{3})] + 2 \cos \pi k_y a \cdot \exp[2\pi i k_x(a/2\sqrt{3})]),$$

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



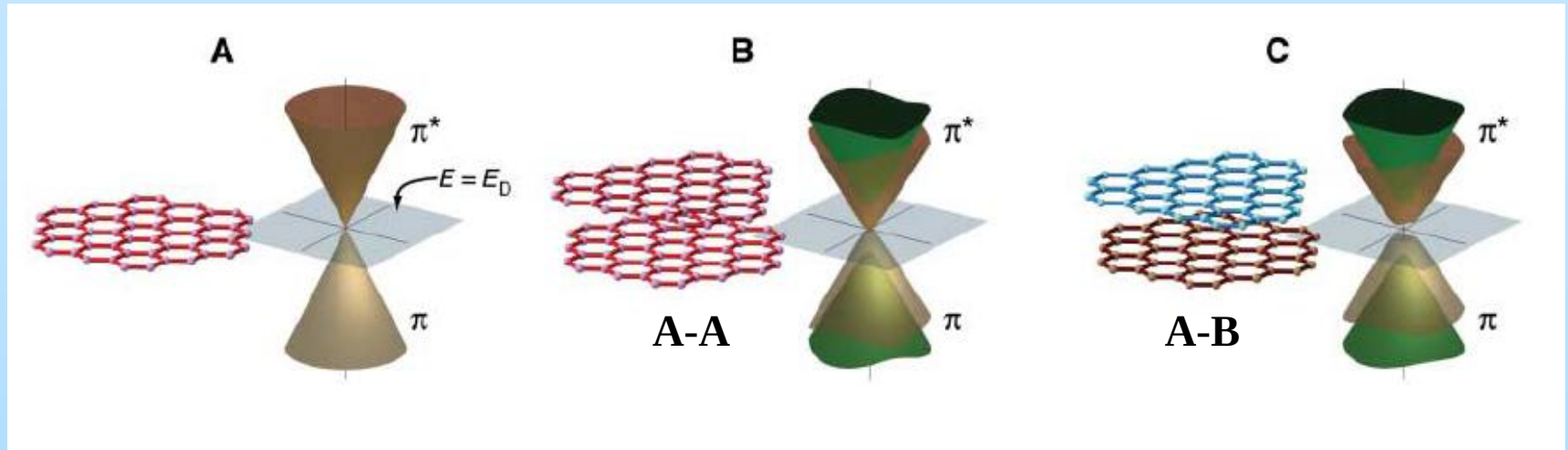


Graphene: Electronic Properties





Multigraphene (2 layers)





Robust superconductivity in magic-angle multilayer graphene family

Jeong Min Park^{1,3} , Yuan Cao^{1,3}, Li-Qiao Xia¹ , Shuwen Sun¹, Kenji Watanabe², Takashi Taniguchi²  and Pablo Jarillo-Herrero¹ 

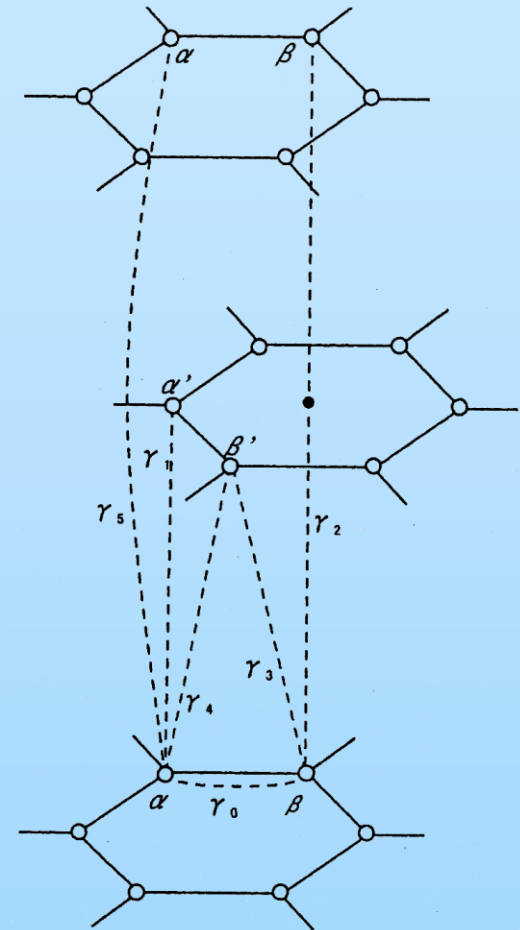
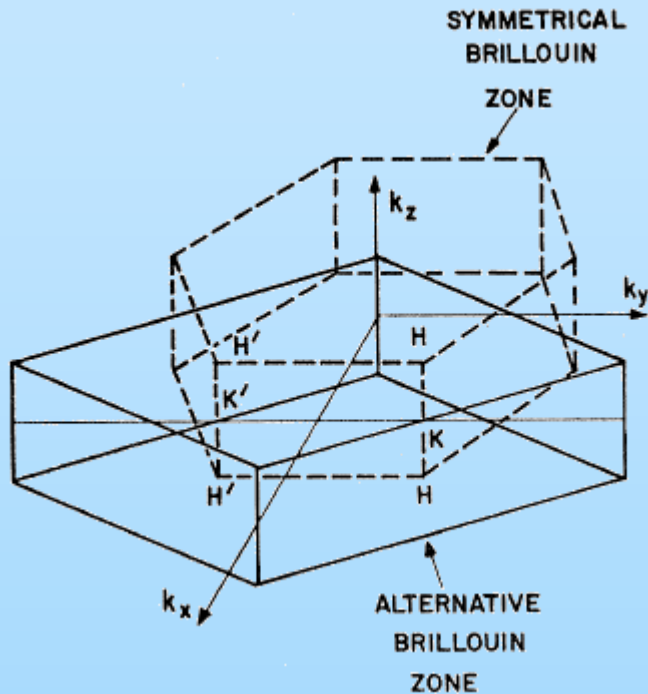
The discovery of correlated states and superconductivity in magic-angle twisted bilayer graphene (MATBG) established a new platform to explore interaction-driven and topological phenomena. However, despite multitudes of correlated phases observed in moiré systems, robust superconductivity appears the 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 $(\theta, -\theta, \theta, \dots)$ (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



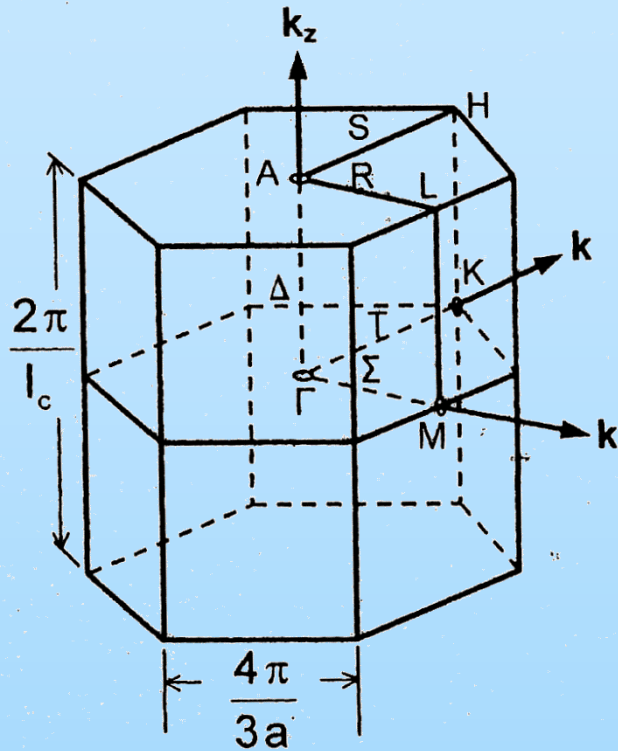
Graphite: electronic properties



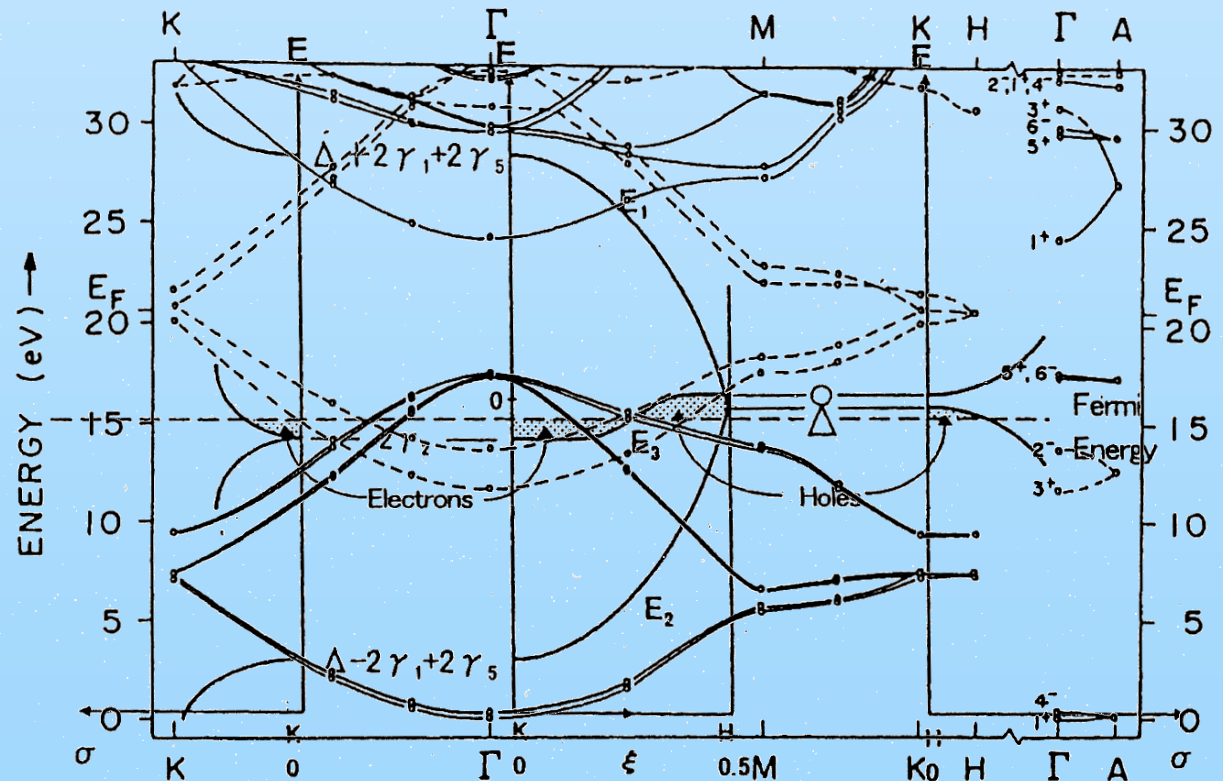
$$\gamma_0 \gg \gamma_n$$

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

Graphite: electronic properties



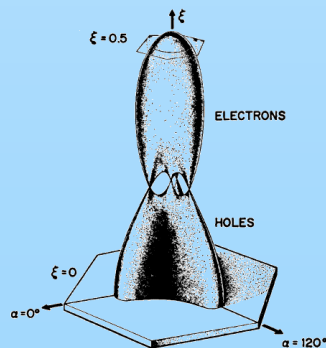
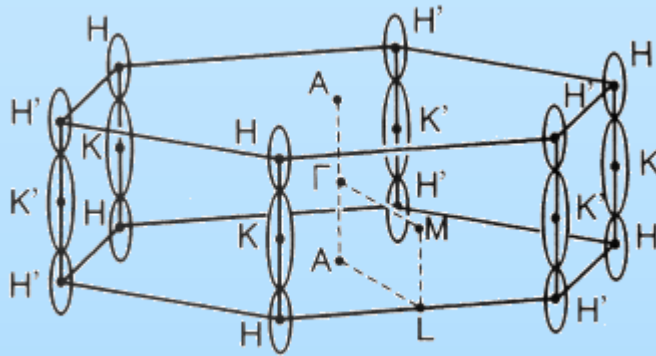
4 bande (tratteggiate)



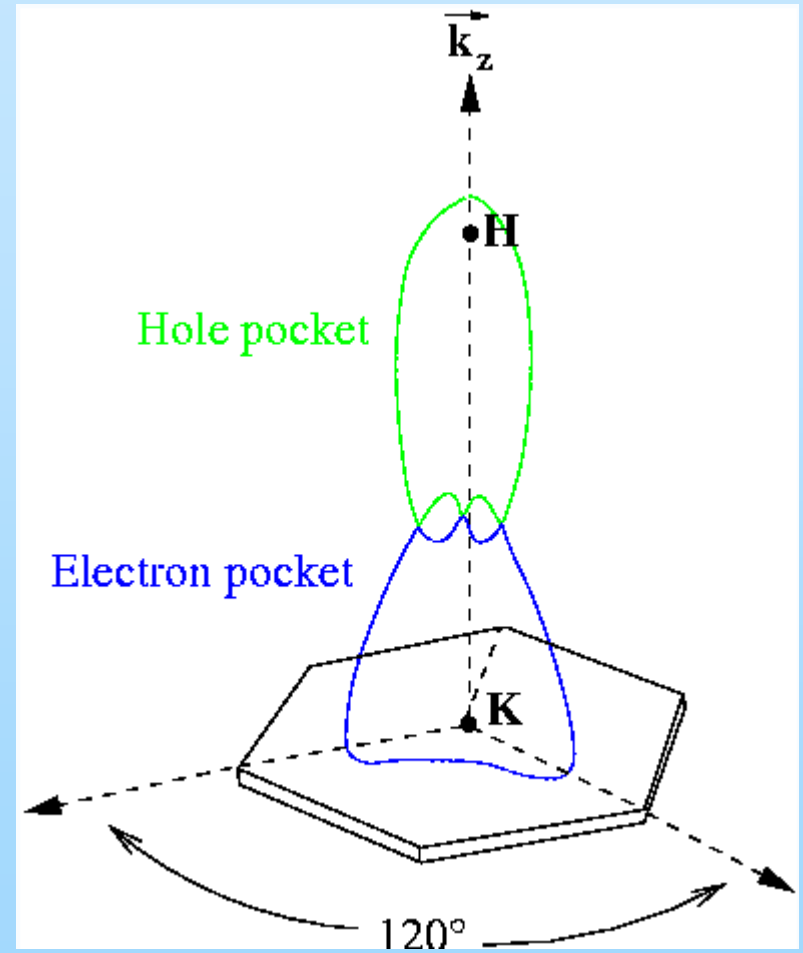
$$\begin{aligned} \gamma_0 &= 3.16, \gamma_1 = 0.39, \\ \gamma_2 &= -0.020, \gamma_3 = 0.315, \gamma_4 \simeq 0.044, \\ \gamma_5 &= 0.038; \Delta = -0.008 \text{ eV} \end{aligned}$$



Graphite: Fermi surface



Dresselhaus 1964





Graphite: Fermi surface

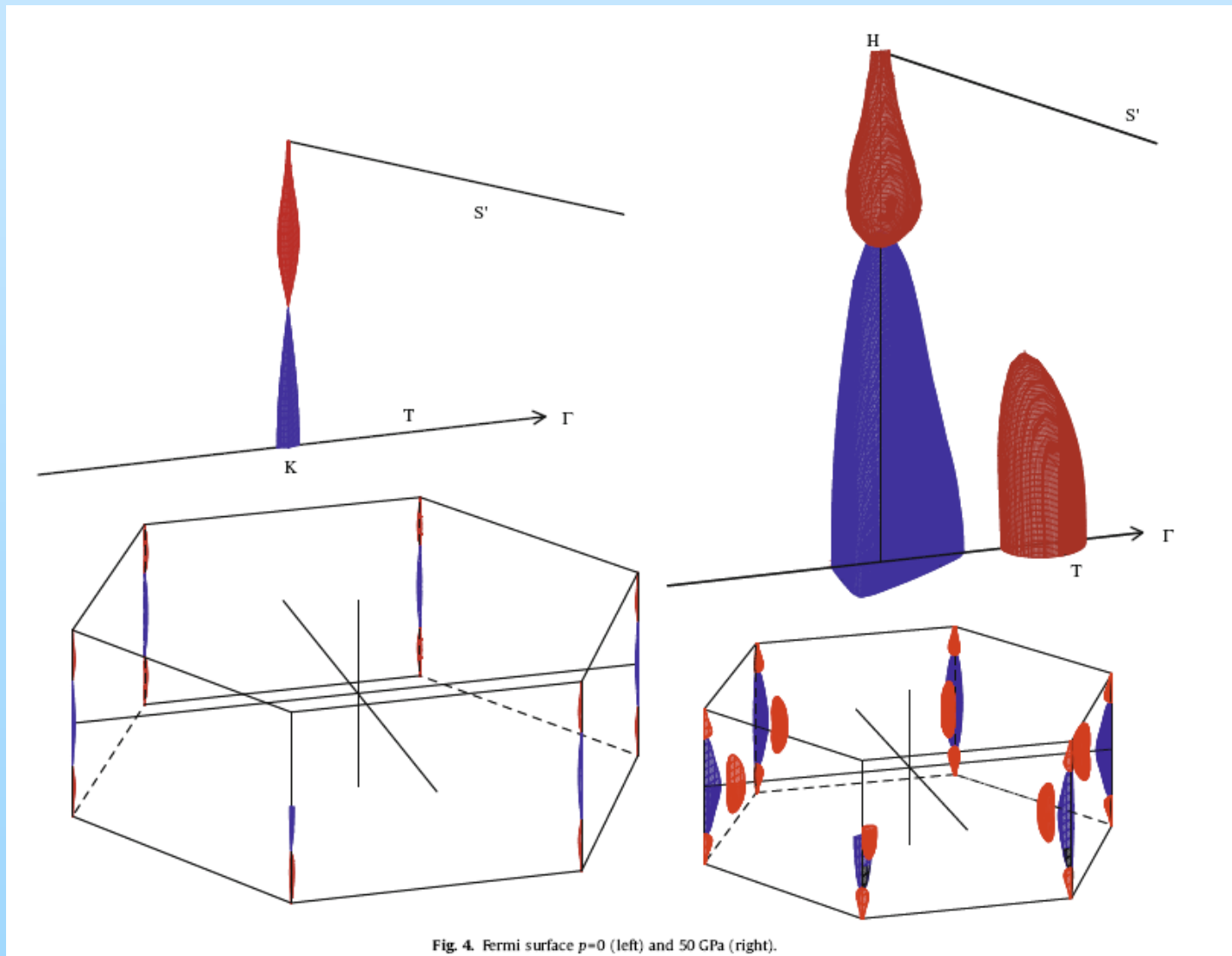


Fig. 4. Fermi surface $p=0$ (left) and 50 GPa (right).