Materials at CERN: Overview and novel graphite-matrix composites for collimators

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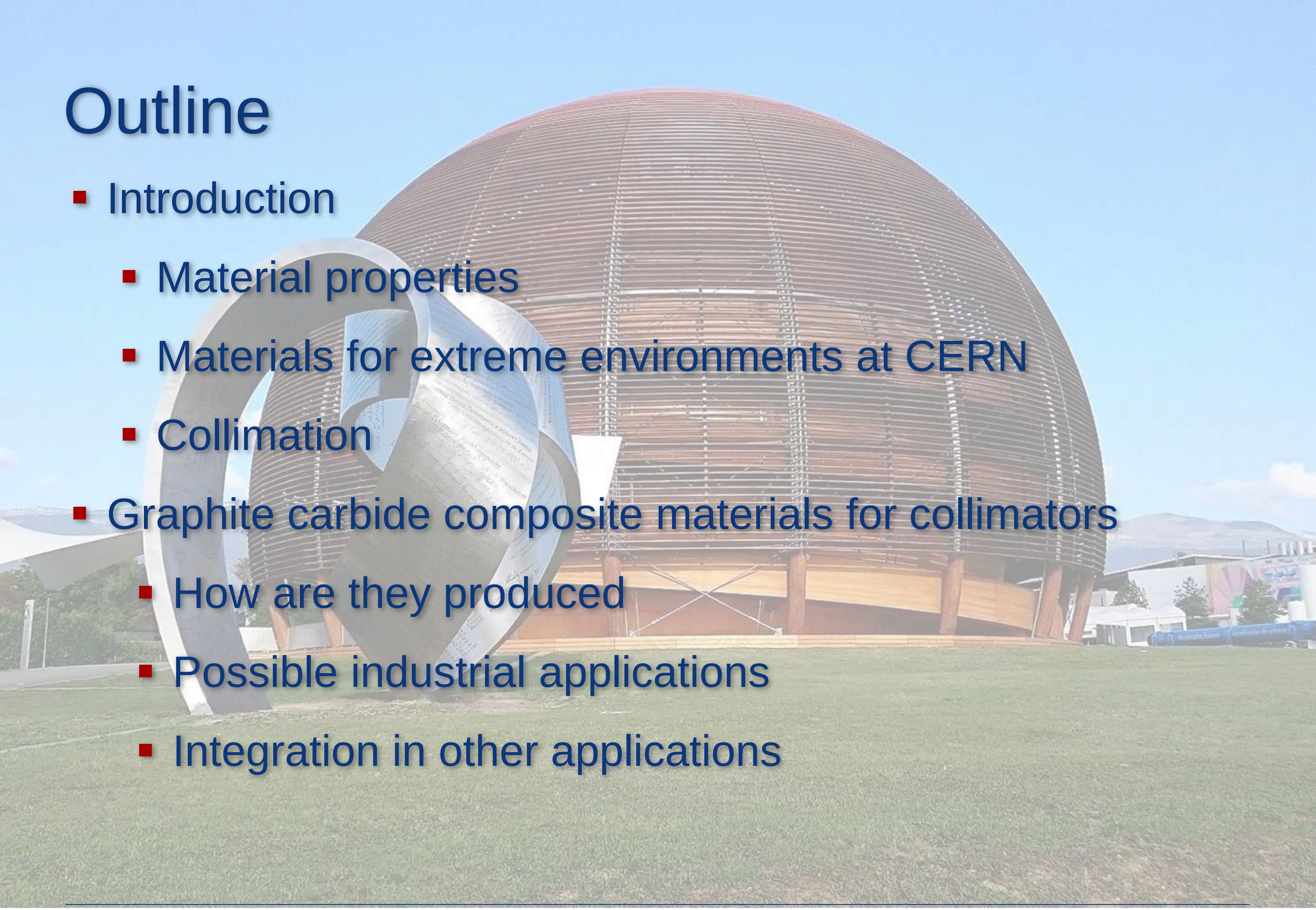
CERN Entrepreneurship Student Programme (CESP)
https://indico.cern.ch/event/797672/timetable/
CERN, Geneva (Switzerland) | 25-July-2019



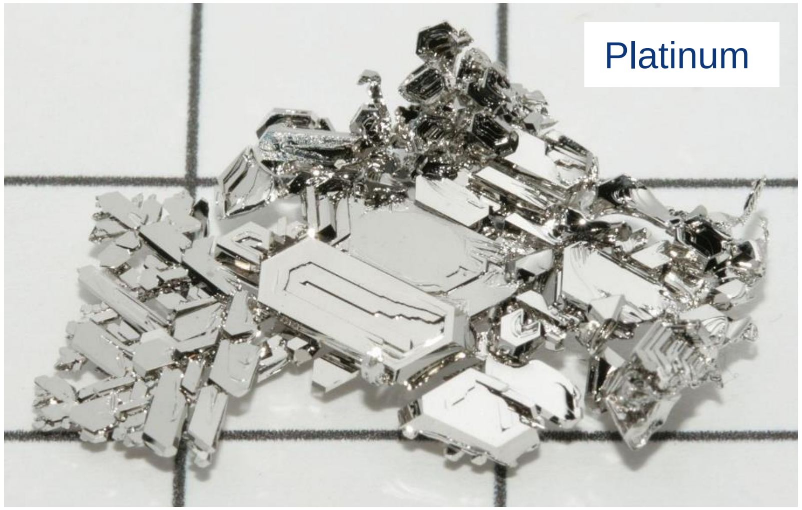
Outline

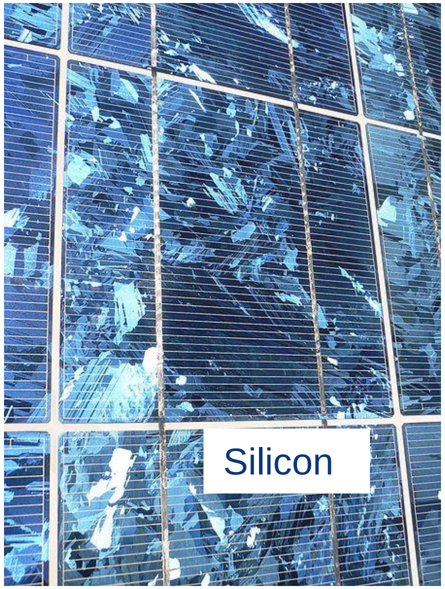
- Introduction
  - Material properties
  - Materials for extreme environments at CERN
  - Collimation
- Graphite carbide composite materials for collimators
  - How are they produced
  - Possible industrial applications
  - Integration in other applications

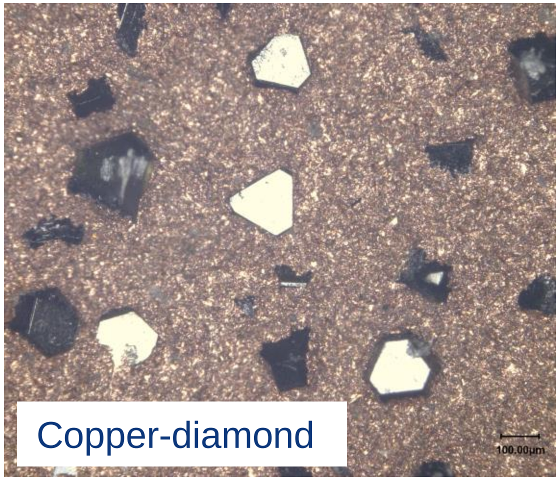
Introduction: Classification of materials

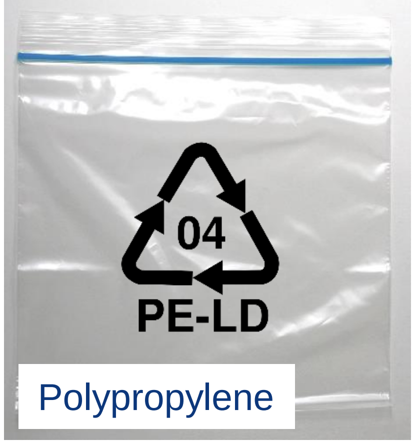
- Metals
- Ceramics
- Polymers
- Semiconductors

- Composites

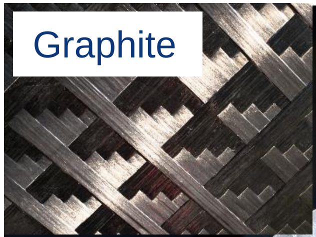

Platinum


Silicon


Copper-diamond



Polypropylene

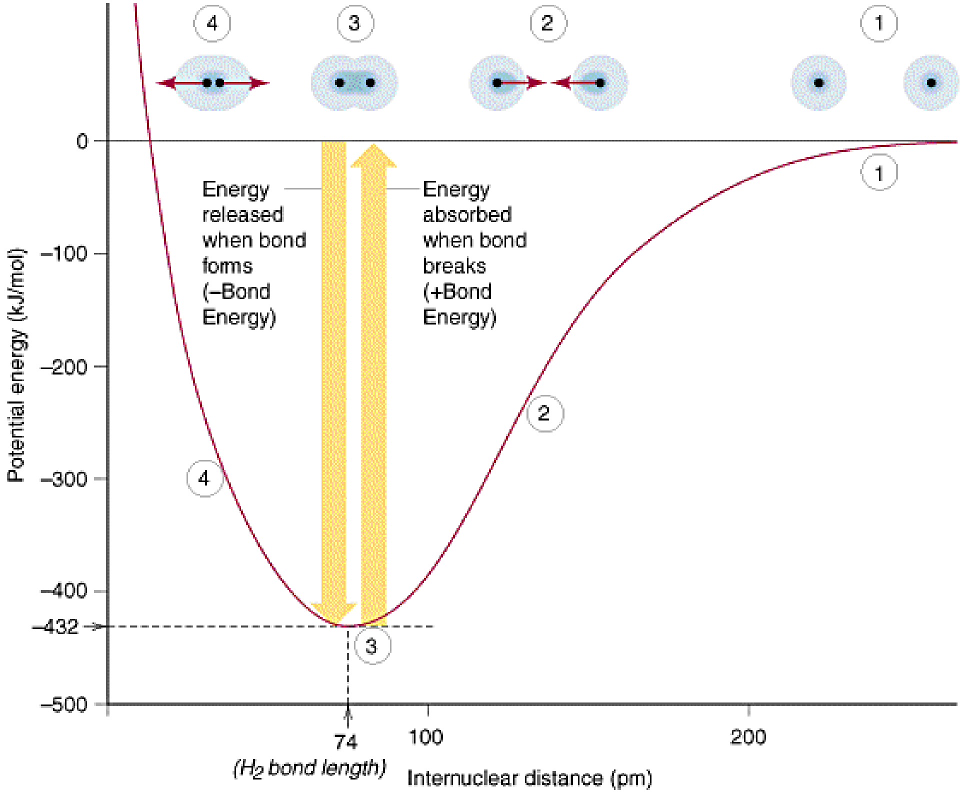

Graphite


Quartz (SiO_2)

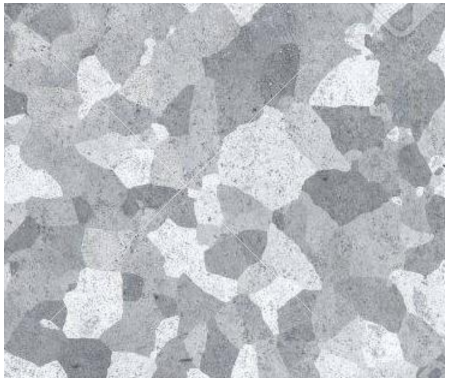
Engineering properties

- The electronic structure associated with chemical bonding affects all properties of materials except radioactivity [1]
- Therefore, an many of the physical properties of materials can be predicted with knowledge of the interatomic forces that bind the atoms together.
- Several types of atomic bonds:

  Ionic, Covalent, Metallic, Van der Waals, Hydrogen.



Most of the materials we use everyday are polycrystalline, and some are made of different phases. In these cases, not only the bond energy but also the microstructure defines the final properties.

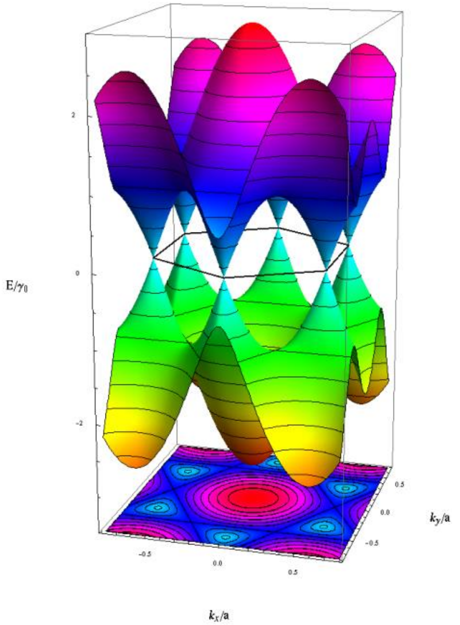


[1] 10.1126/science.1198543
[2] https://chem.libretexts.org

Electrical conductivity

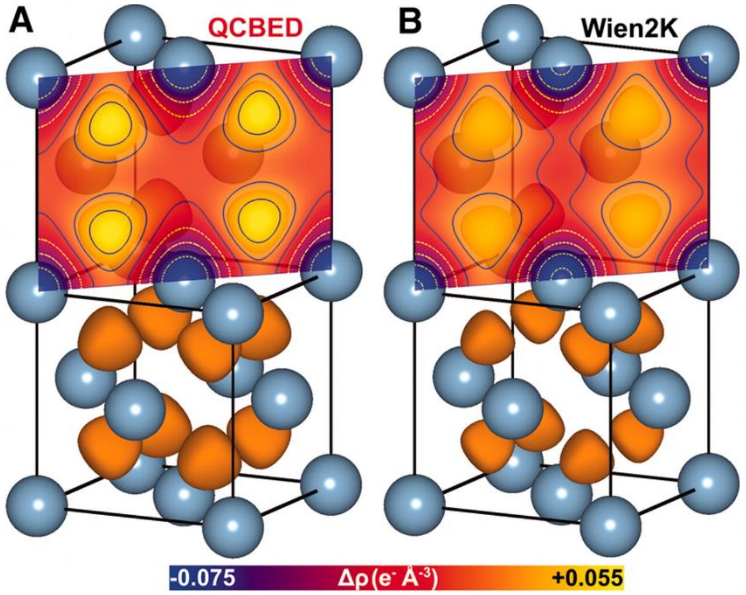
- The concept of an ideal metal is popularly expressed as a regular array of metal ions surrounded by a sea of delocalized valence electrons [1]
- Although a gross simplification, this model is often sufficient to give a qualitative account of many characteristic properties of metals such as their high electrical conductivity and lustrous or shiny appearance [1]
- Impurities, defects, etc. reduce mobility of electrons, reducing electrical conductivity. Alloys have lower electrical conductivity than pure metals

Graphene



Energy of electrons in graphene in the tight-binding model, https://dx.doi.org/10.1103/PhysRev.71.622

Aluminium, FCC (blue atoms)

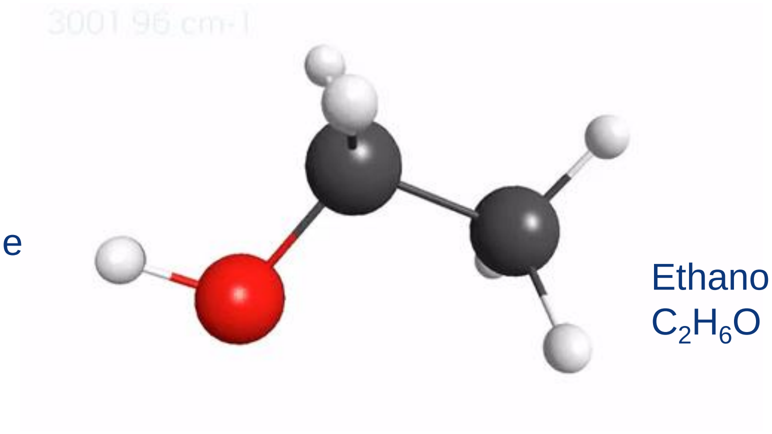


Colour scale: electron density

Material	γe [MSm^{-1}]
Ag	63
Cu	59
Au	41
Al	38
Steel	7.0
Graphite (PG) IP	2.5
Ti	2.4
Stainless steel	1.4
Graphite (PG) TP	0.0009

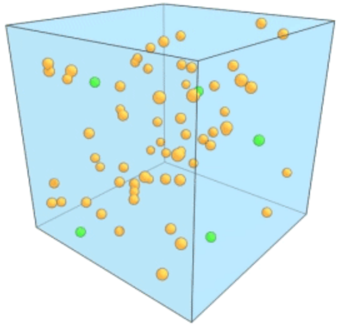
[1] DOI:10.1126/science.1198543

Heat capacity

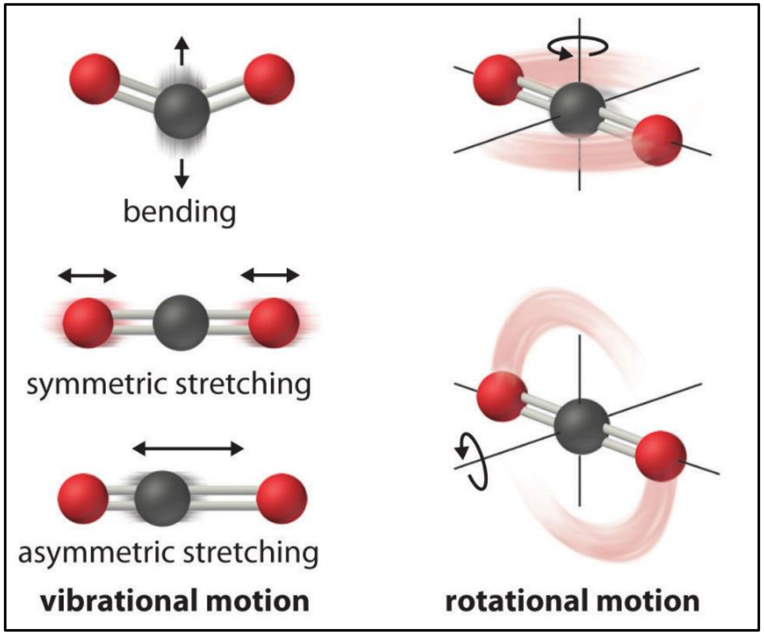


Ethanol
C_2H_6O

(Thermodynamic) **temperature** is an absolute measure of the average total internal energy of an object or objects (namely its kinetic energy) plus contributions from other factors.



Translation motion:
kinetic energy



Molecular Degrees of Freedom (+translation)

Specific heat or heat capacity is the amount of energy required to change the temperature of the material.

SI units: $\frac{J}{gK}$

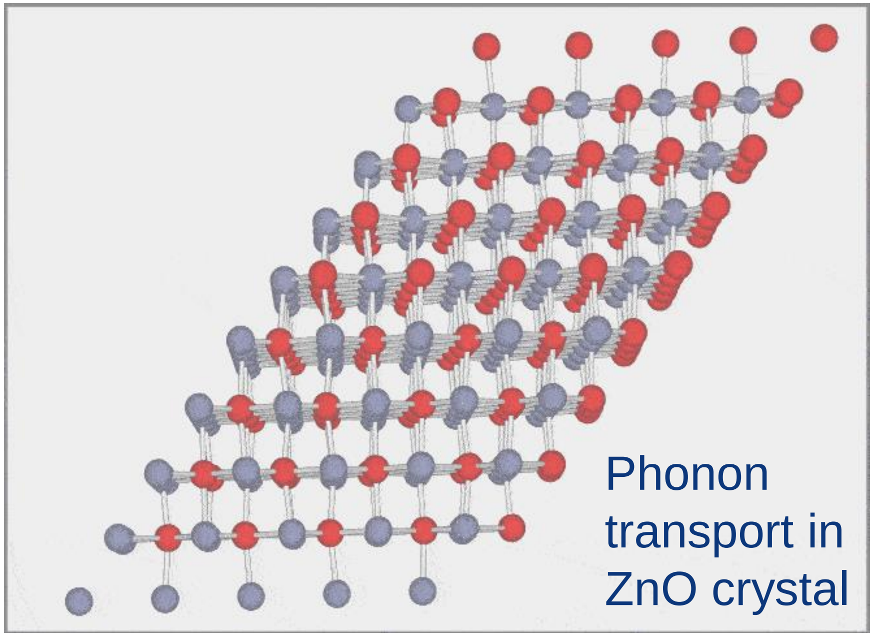
It varies with temperature

Material	C_P $[Jg^{-1}K^{-1}]$	$C_P \cdot \rho$ $[Jcm^{-3}K^{-1}]$
H_2O	4.1814	4.1814
Cu	0.385	3.423
Al	0.897	2.422
Fe	0.449	2.188
Au	0.129	2.492
C (Graphite)	0.709	1.602
C (Diamond)	0.427	1.499

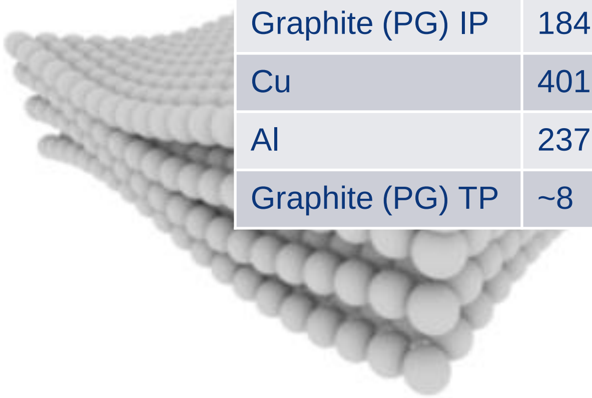
Thermal conductivity

- Thermal energy can be transferred by electrons or by phonons
- If thermal conduction is carried by electrons, the same mechanisms than for electrical conductivity apply.
- In graphite: main contribution is by phonons.
- Diamond: best solid thermal conductor (strong bonds, light and identical atoms). Only phonons.

Material	k at 20 °C [$Wm^{-1}K^{-1}$]
Diamond	1000-2200
Graphite (PG) IP	1840
Cu	401
Al	237
Graphite (PG) TP	~8



Phonon transport in ZnO crystal



Phonon transport in a 2D material

PG: Pyrolytic graphite

Thermal expansion coefficient

- The thermal expansion of a monodimensional body depends on its **thermal expansion coefficient (α)**:

$$\varepsilon = \alpha \cdot \Delta T$$

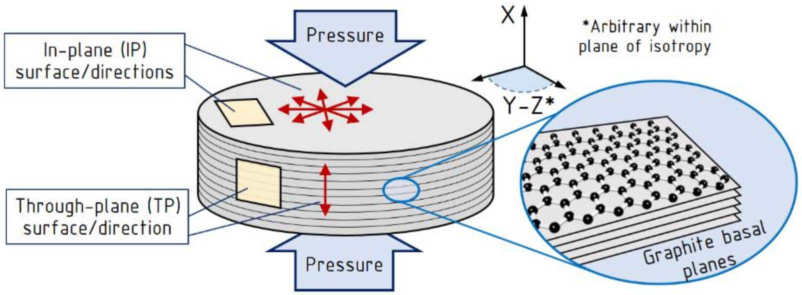
- α is measured in **K^{-1}**
- ΔT is the **temperature increase** (if the temperature goes down, ΔT is negative!)
- For α, the acronym **CTE** is largely used
- Metals normally have CTE higher than ceramic

Coefficient of linear thermal expansion α

Material	α at 20°C (1e-6/K)
Mercury	60
Graphite TP*	29
Lead	29
Aluminium	23
Brass	19
Stainless Steel	17.3
Copper	17
Gold	14
Iron or Steel	11.1
Carbon Steel	10.8
Glass	8.5
Tungsten	4.5
Pyrex	3.3
Diamond	1
Graphite IP*	-1

A.Bertarelli et al.

*

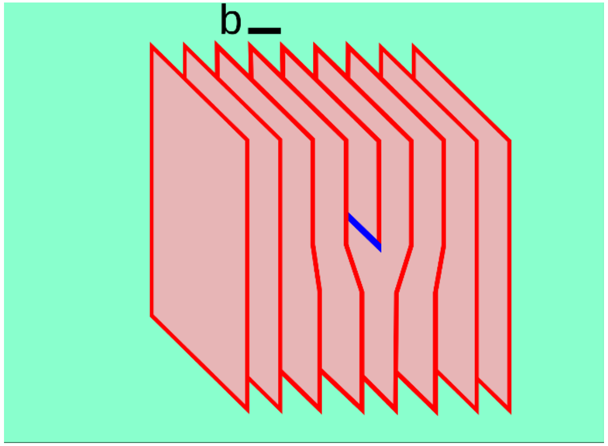


Mechanical properties

- Dislocation: crystallographic defect within a crystal structure.
- Grain: crystalline domain with a specific orientation
- Grain boundary: imaginary line separating grains

Video **Experiments with the Bubble Model of Metal Structure 1952 - Sir Lawrence Bragg, W.M Lomer, J.F. Nye**

Grain structure, elastic/plastic deformations: min 2:30-4:00

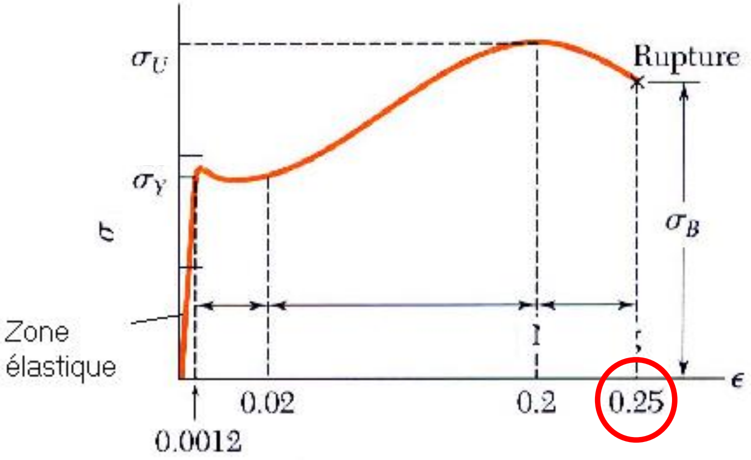


Schematic diagram (lattice planes) showing an edge dislocation. Burgers vector in black, dislocation line in blue.

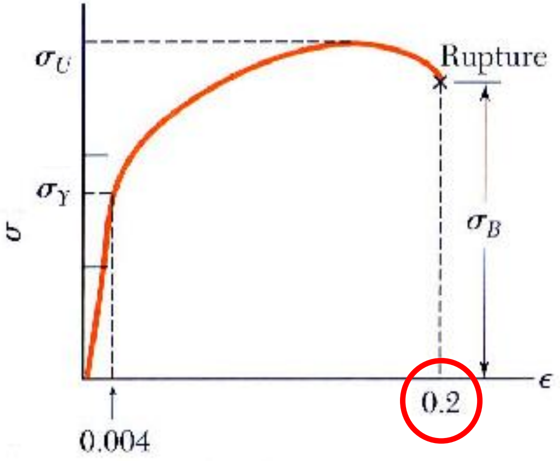
Example pure copper → As-received: 14% strain to rupture, UTS 350 MPa. Annealed: 30% strain to rupture, UTS 250 MPa.

Thermal treatment produces reduction in the number of dislocations, formation of a new set of equiaxed grains and grain growth

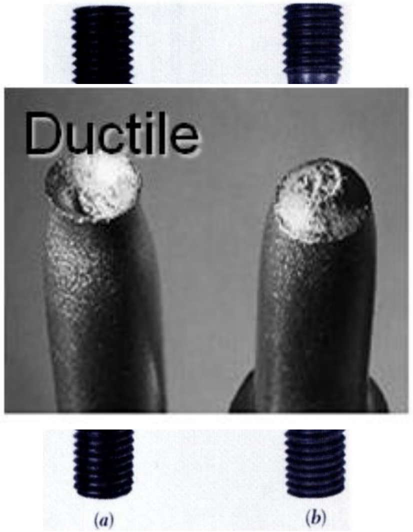
Stress strain curve for different materials



(a) Acier



(b) Aluminum



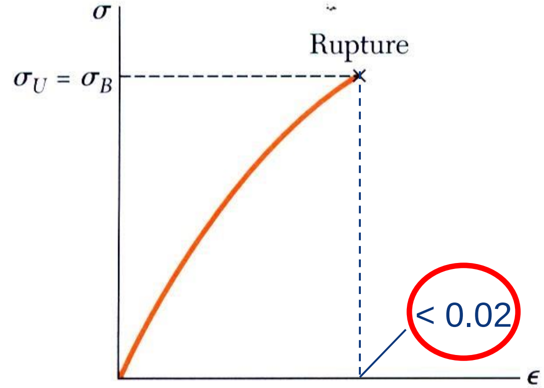
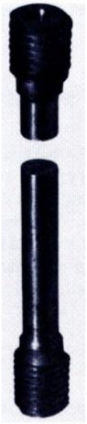
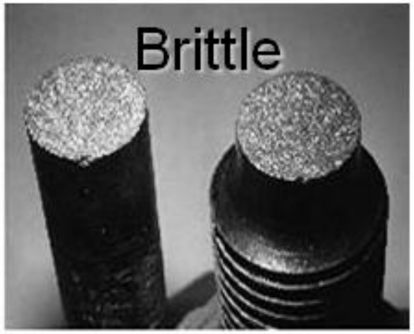


Fig. 2.11 Stress-strain diagram for a typical brittle material.

- Plastic deformation in brittle materials is (almost) inexistent!



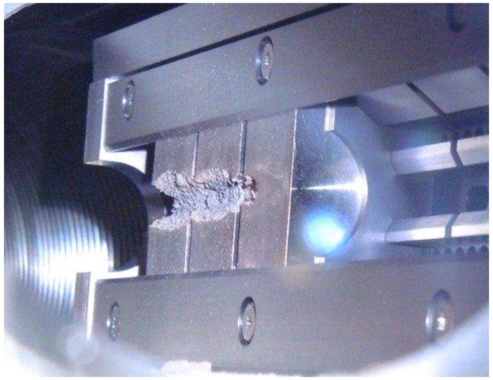


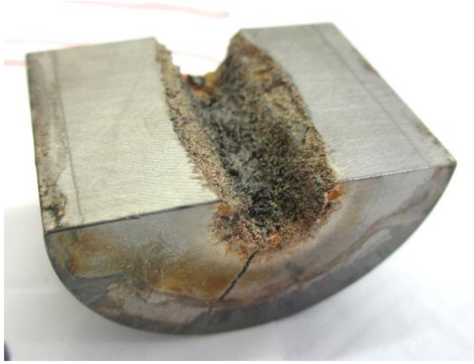
A.Bertarelli et al.

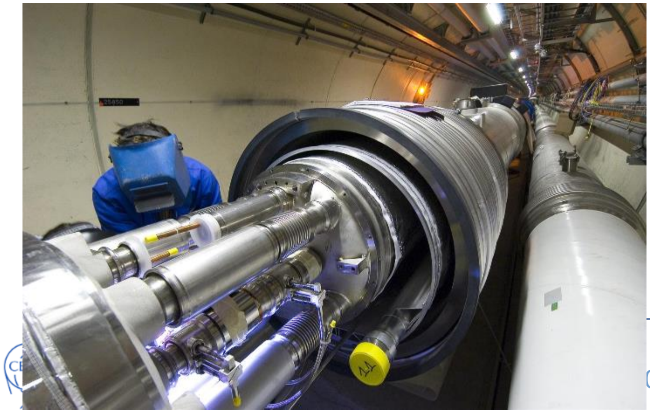
Extreme environments at CERN. Examples:

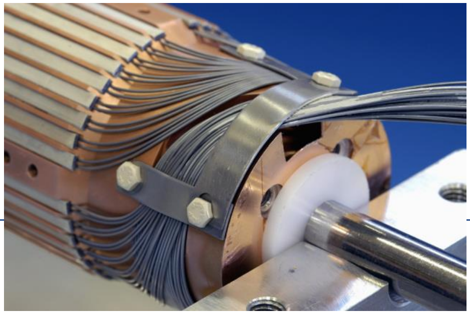
Ultra High Vacuum (UHV)

Interactions with the particle beam









Cryogenics & large magnetic fields

Materials for ultra-high vacuum

Stainless steel

Materials for high vacuum technology, an overview
Sgobba, Stefano
http://cds.cern.ch/record/983744

Stainless steels

- ✓Stainless steel: iron alloys containing a minimum of approx. 11 % Cr

- ✓Minimum amount n unpolluted atmospl

- ✓From this characte definition “st

- ✓Corrosion resistan film (“passive film” environments

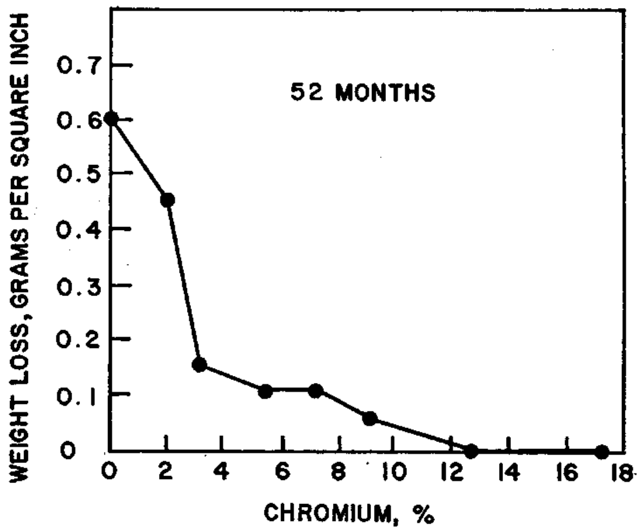


Figure 1.1 The influence of chromium on the atmospheric corrosion of low-carbon steel. (After Reference 1.)

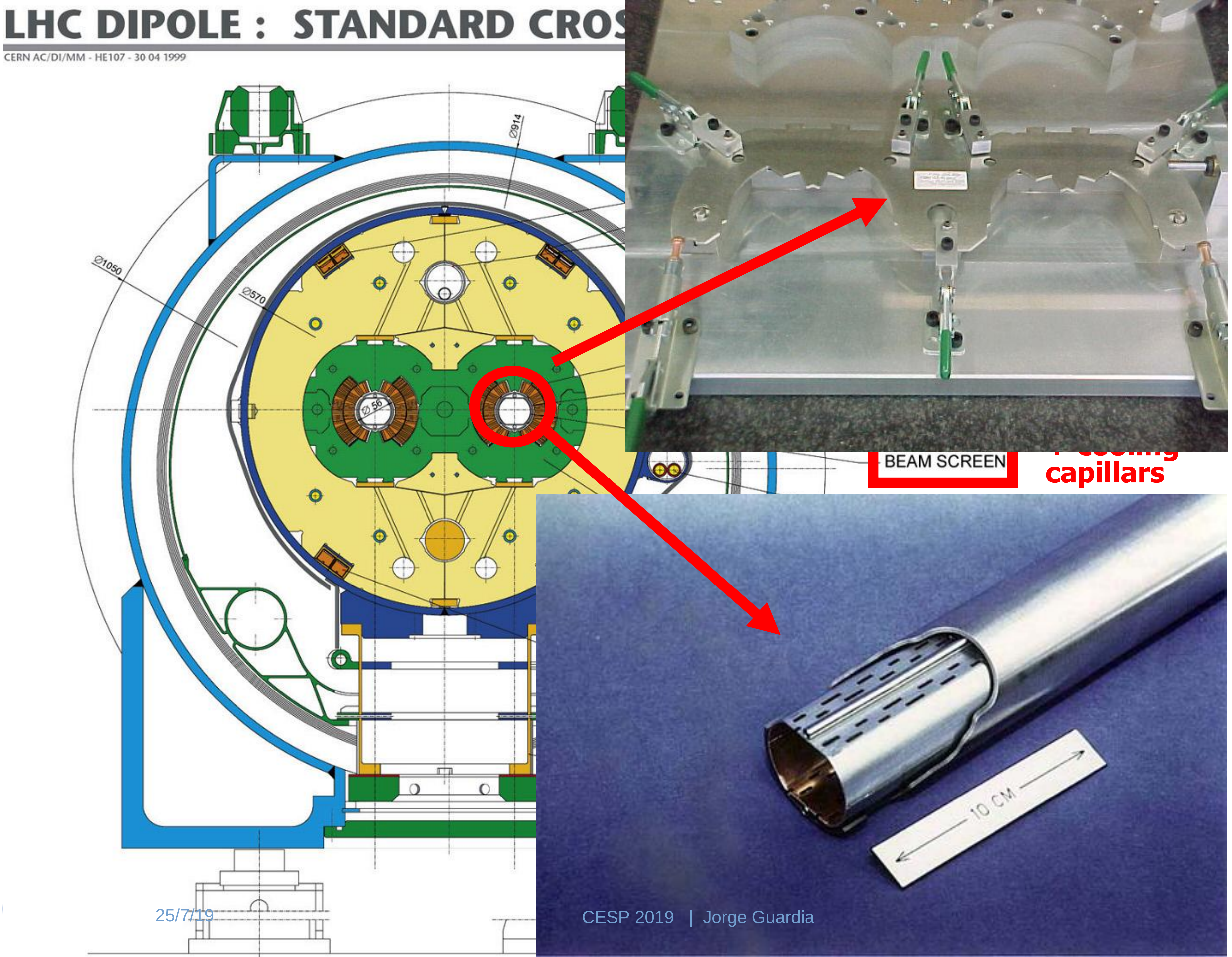
W.D. Binder and C.M. Brown, Proc. Am. Soc. Testing and Materials, **46**, 593 (1946)

- ✓Several hundred types, Cr up to 30 % or more

J. Sedricks, New York, Wiley, 1996[2]

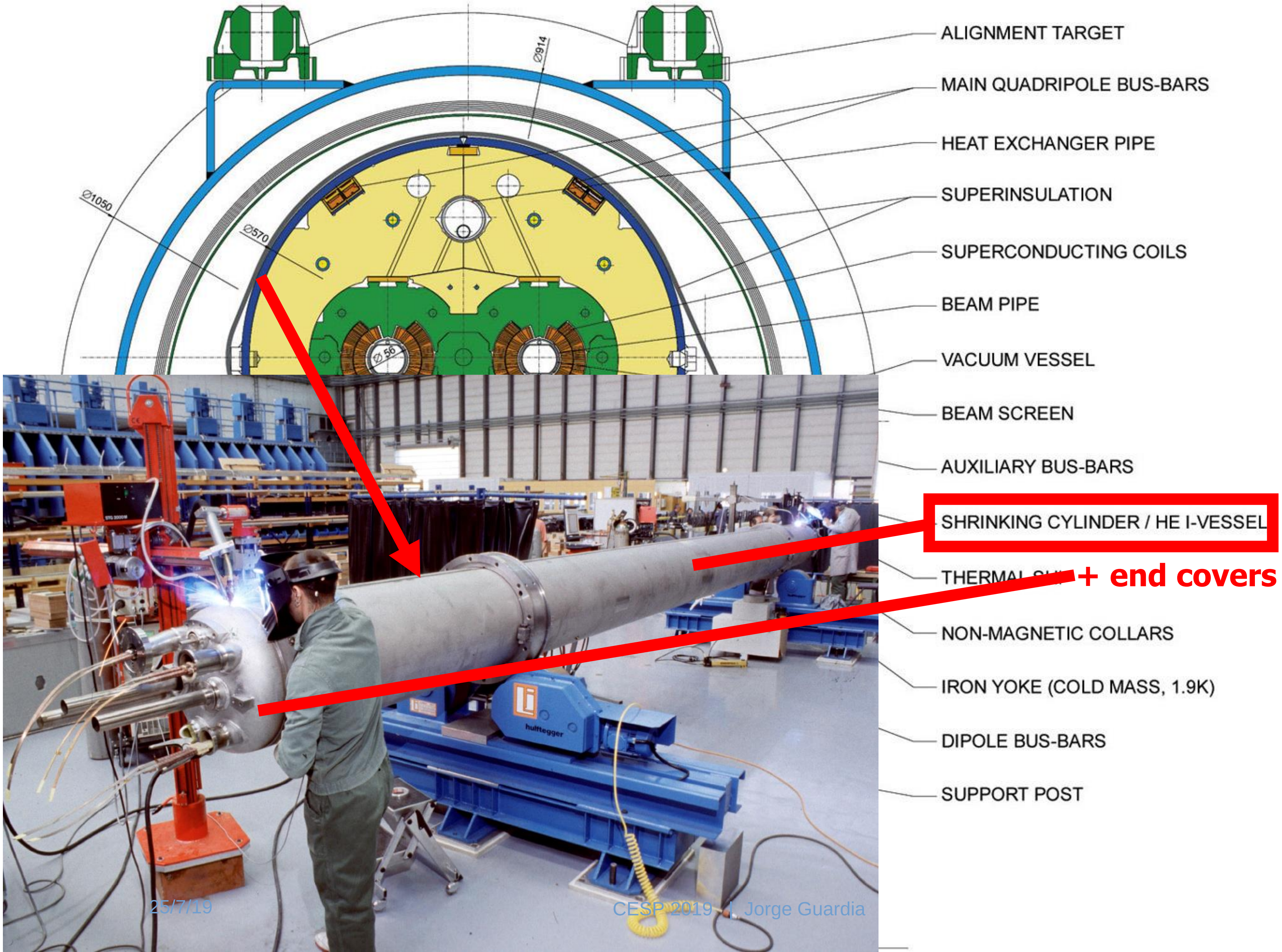
LHC DIPOLE : STANDARD CROS

CERN AC/DI/MM - HE107 - 30 04 1999



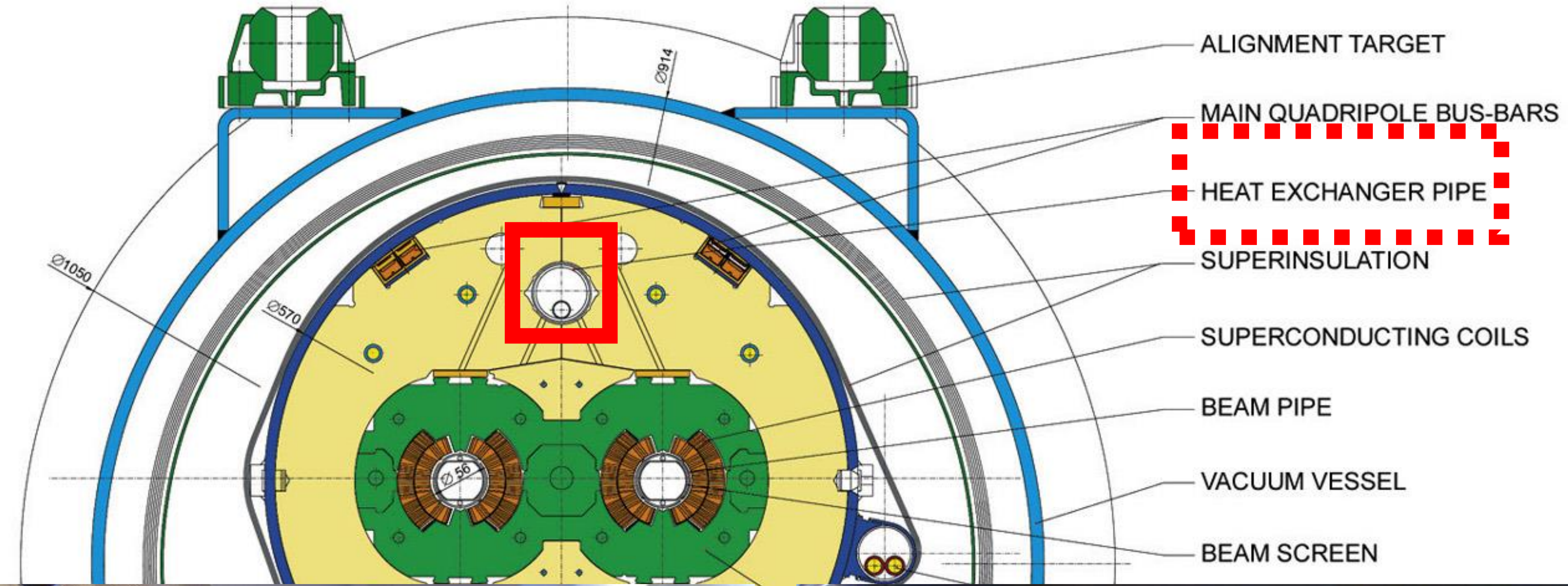
LHC DIPOLE : STANDARD CROSS-SECTION

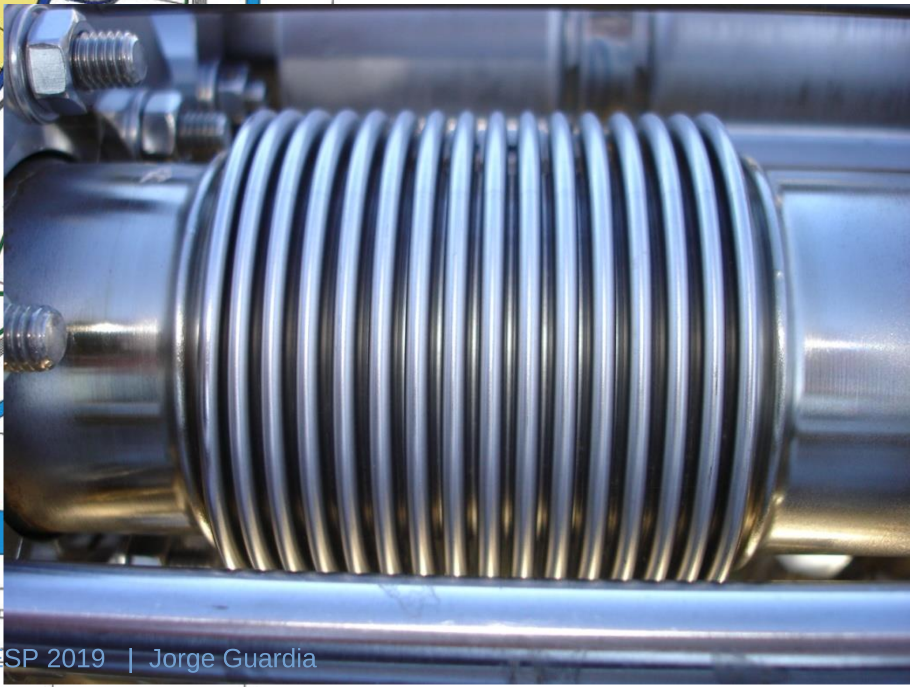
CERN AC/DI/MM - HE107 - 30 04 1999



LHC DIPOLE : STANDARD CROSS-SECTION

CERN AC/DI/MM - HE107 - 30 04 1999

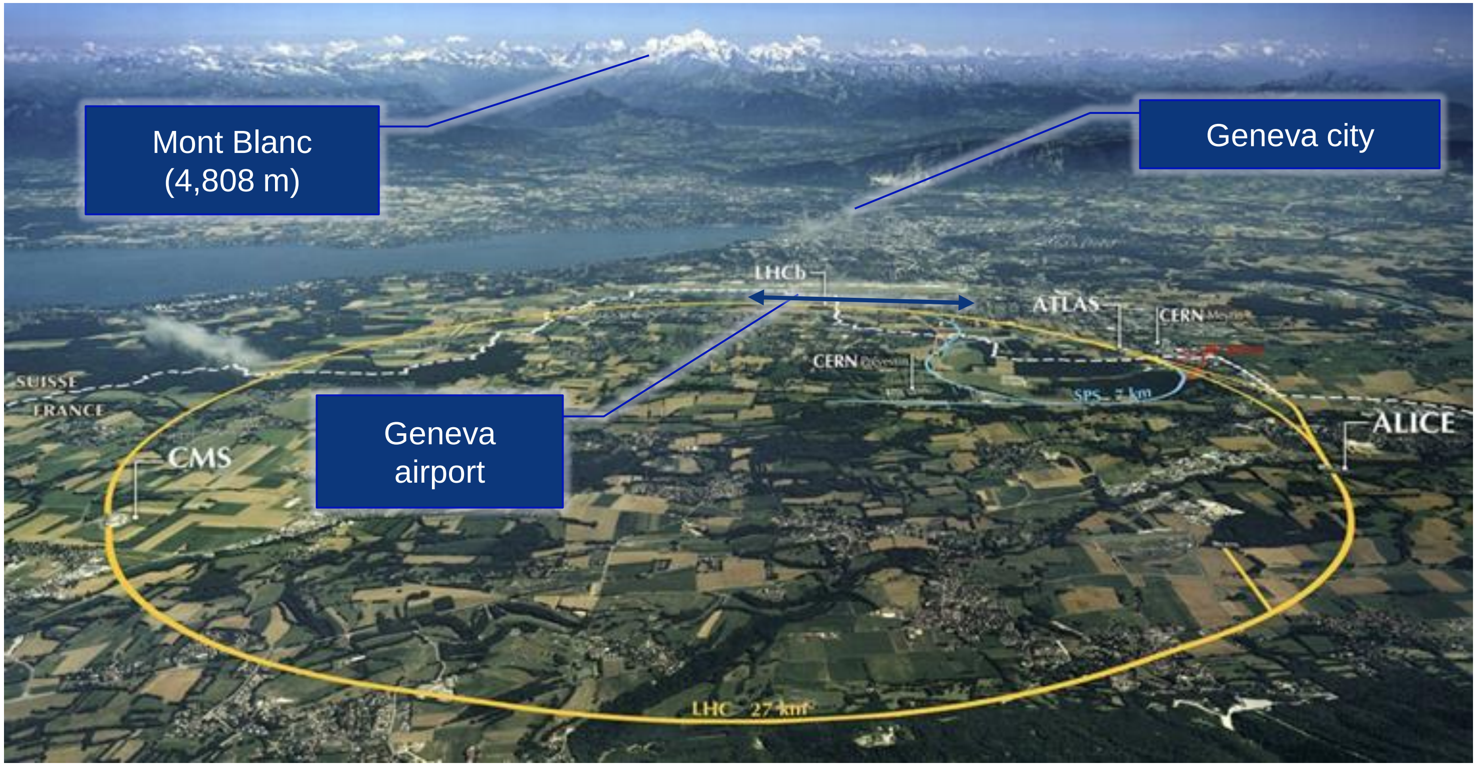




Collimation technology at CERN

CERN

- European Organization for Nuclear research. Largest high-energy physics laboratory
- The deepest structure and physics of matter are studied with the aid of **high-energy particle beams**
- **Large Hadron Collider (LHC)** is the biggest and most powerful particle accelerator in the world (27km)



Mont Blanc (4,808 m)

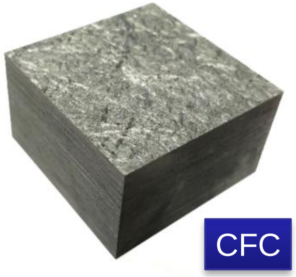
Geneva city

Geneva airport

- High luminosity LHC upgrade (HL-LHC) will further increase the total **energy** of the circulating beams

LHC Collimation Project at CERN

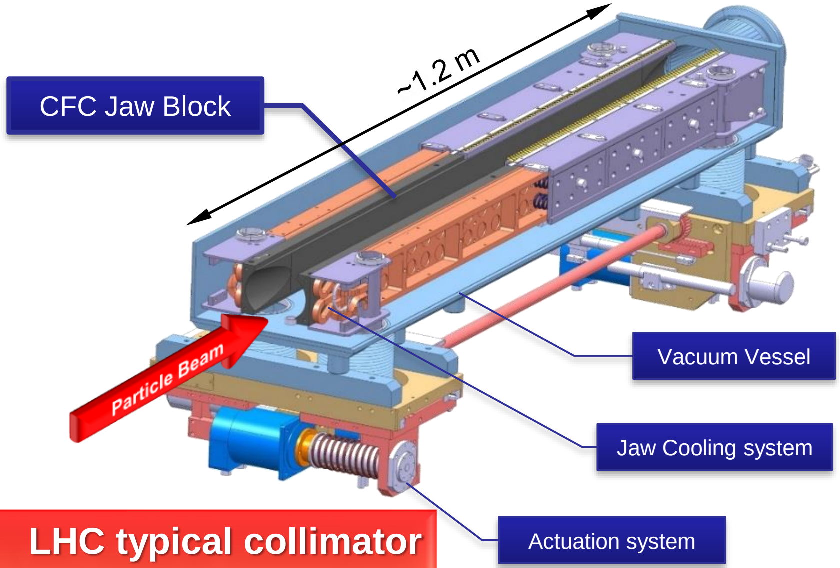
- The **energy** of the circulating particle beams is equivalent to that needed for melting one ton of copper in few µs **LHC: 362 MJ HL-LHC: 693 MJ**
- Need of a protection system → **Collimators**
- CFC successfully used for LHC baseline but not enough conductive for HL-LHC (resistive wall beam instabilities) → **New graphite-based composite**


CFC


HL-LHC beam energy: 693 MJ

v = 520 km/h

Fully loaded A320 plane


CFC Jaw Block

~1.2 m

Particle Beam

Vacuum Vessel

Jaw Cooling system

Actuation system

LHC typical collimator
Cutaway

Collimation

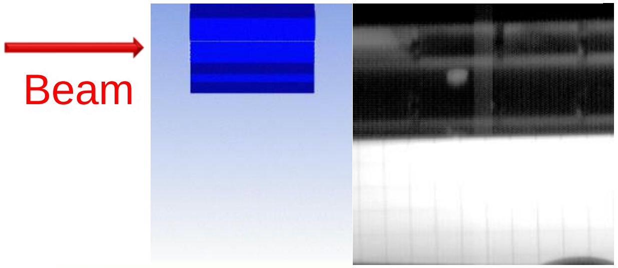
CERN document server: http://cds.cern.ch/record/1750704

Requirements of collimator materials

Extreme environment: thermal shocks (accidental beam impacts), UHV, ionizing radiation, high geometrical stability required…

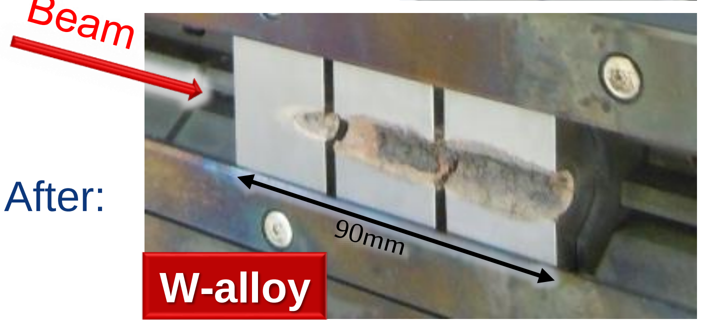
- ⬆ **Electrical Conductivity:** limit resistive-wall impedance (beam instabilities)
- ⬆ **Thermal Conductivity:** maintain geometrical stability under steady-state thermal loads
- ⬇ **CTE:** increase resistance to thermal shock induced by accidental beam impact
- ⬆ **Melting/Degradation Temperature:** withstand high temp
- ⬆ **Specific Heat:** improve thermal shock resistance (lowers
- ⬆ **Ultimate Strength:** improve thermal shock resistance
- ⬊ **Density:** balance to limit peak energy deposition while maintaining adequate cleaning efficiency
- ⬆ **Radiation-hardness:** improve component lifetime under long term particle irradiation
- ⬇ **Outgassing Rate:** ensure UHV compatibility

Carbon-based materials have the best compromise of properties: baseline.
Need of higher electrical conductivity → R&D

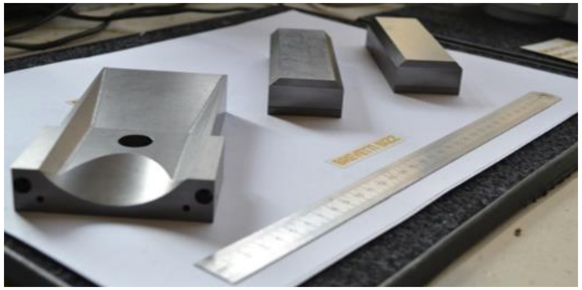


Before:

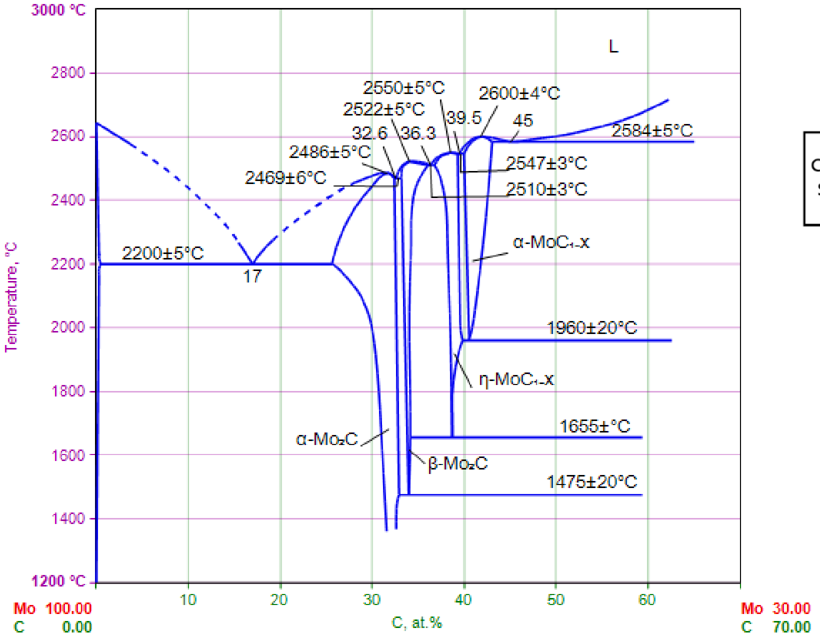
After:



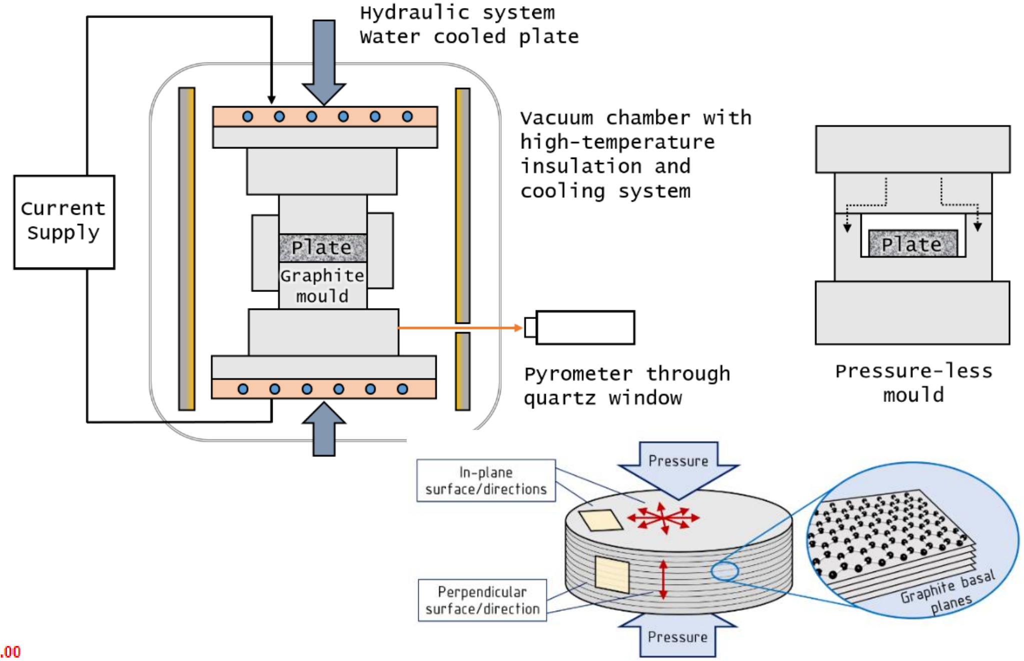
Molybdenum carbide - graphite



- Co-developed with SME Italian company
- Production: **spark plasma sintering** (SPS)
- Powders of graphite (~90-95vol.%), Mo (~4.5vol.%), CF (0-5vol.%) and Ti
- Melting point of the carbide (~ 2600 ºC) reached: **Liquid phase sintering**
- Post-sintering pressure-free thermal treatment: ~2100 °C (under M.P.) or ~2600 °C (above M.P.)



Phase diagram doi:10.1007/10040476_643



J.Guardia et al. Carbon (2018)
https://doi.org/10.1016/j.carbon.2018.04.010

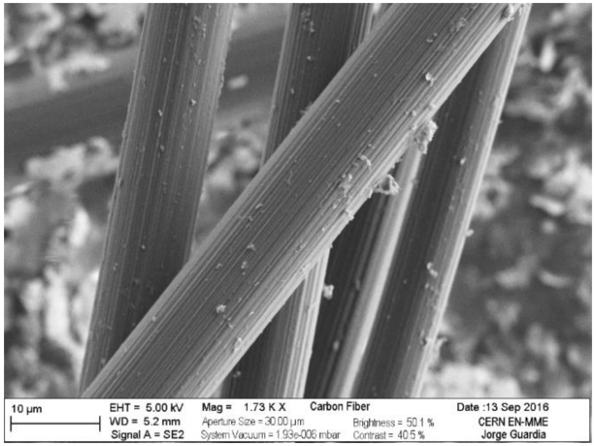
Molybdenum carbide - graphite production

Why Graphite?

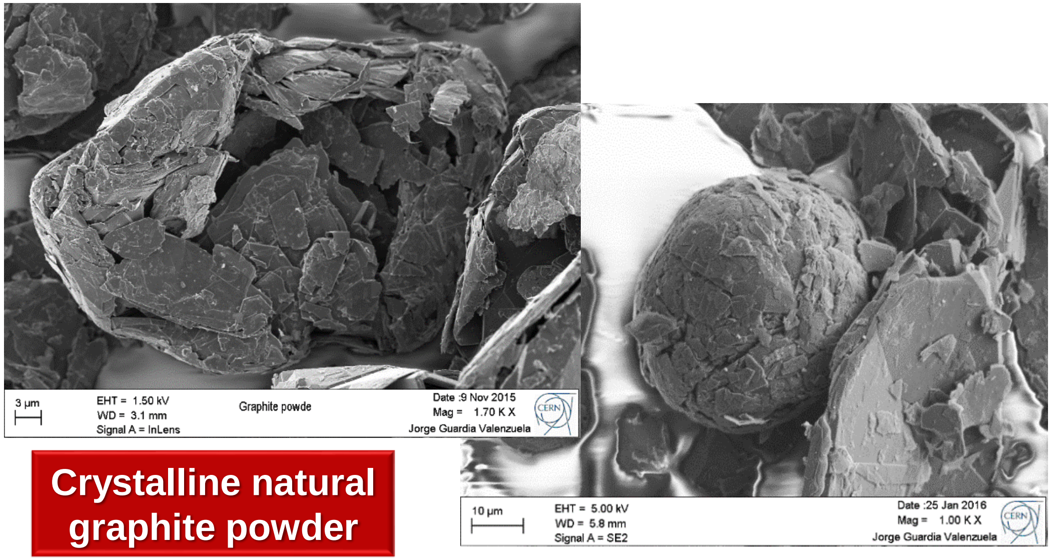
- Low CTE (along basal plane)
- High Thermal Conductivity (along basal plane)
- Low Density
- Very High Service Temperatures
- High Shockwave Damping
- Low cost
- Spheroidal-flake morphology

Why Carbon Fibres?

- Increase mechanical strength
- Contribute to Thermal Conductivity (highly ordered structure)
- Pitch-based



Carbon fibres



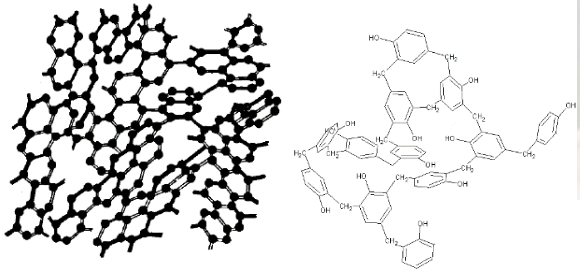
Crystalline natural graphite powder

Why Molybdenum (carbide)?

- Practical liquid-phase sintering temperature
- High mechanical strength, high melting temperature
- Density lower than Tungsten
- Catalyses graphitization

Catalytic graphitization

Precursors

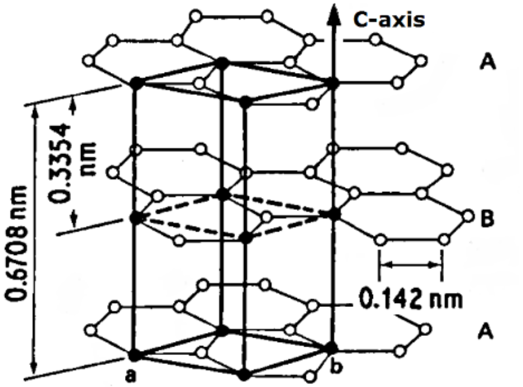


Graphitization

T>2300 K

In practise:
>3000 K for
days/weeks

Graphite

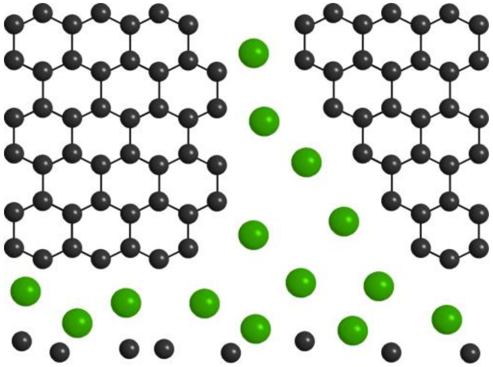


P. Ouzilleau et al, Carbon 109 (2016) 896 – 908.

Catalytic graphitization

- Use of “**catalytic additions**” to accelerate the process
- **Dissolution-precipitation mechanism**
  1. Carbon dissolution
  2. Carbon diffusion
  3. Precipitation of graphite on active sites
- Grain growth and grain connection
  - Well connected graphite-matrix
  - Orientation of graphite grains

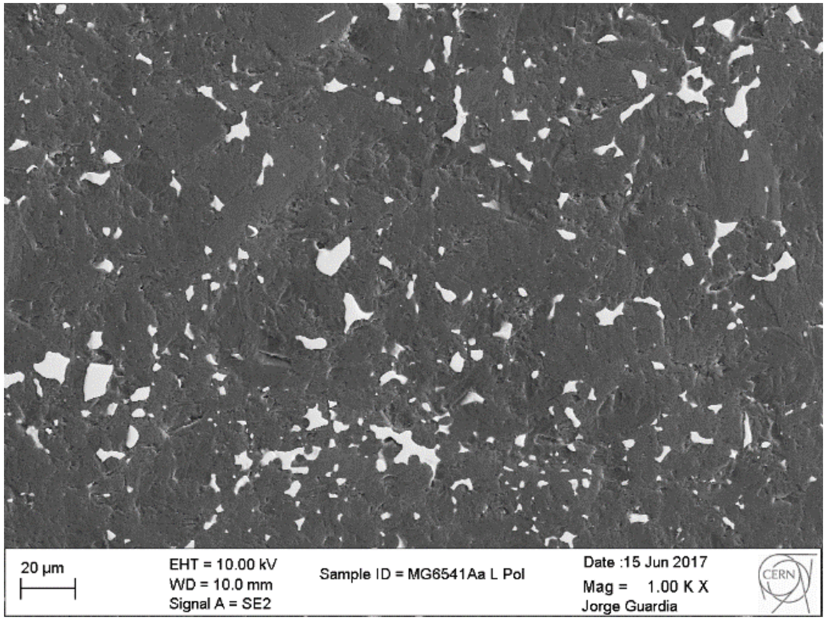
R. B. Matthews, G. M. Jenkins, J. Mat. Sci. 10 (1975) 1976–1990
A. Oya, H. Marsh, J. Mat. Sci. 17 (1982) 309–322
D. John, G. M. Jenkins, J. Mat. Sci. 21 (1986) 2941–2958



- Carbon fibres appear to be dissolved and re-precipitated
  Certain influence in thermophysical properties & radiation hardness

Microstructure

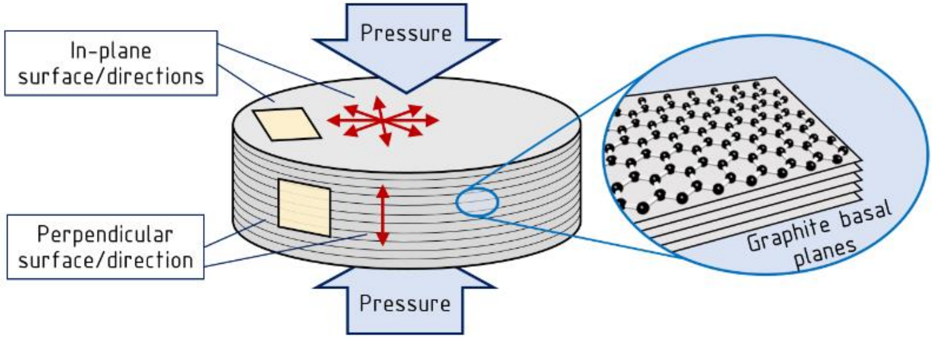
Sintering pressure direction



In-plane polished surface

Perpendicular fracture surface

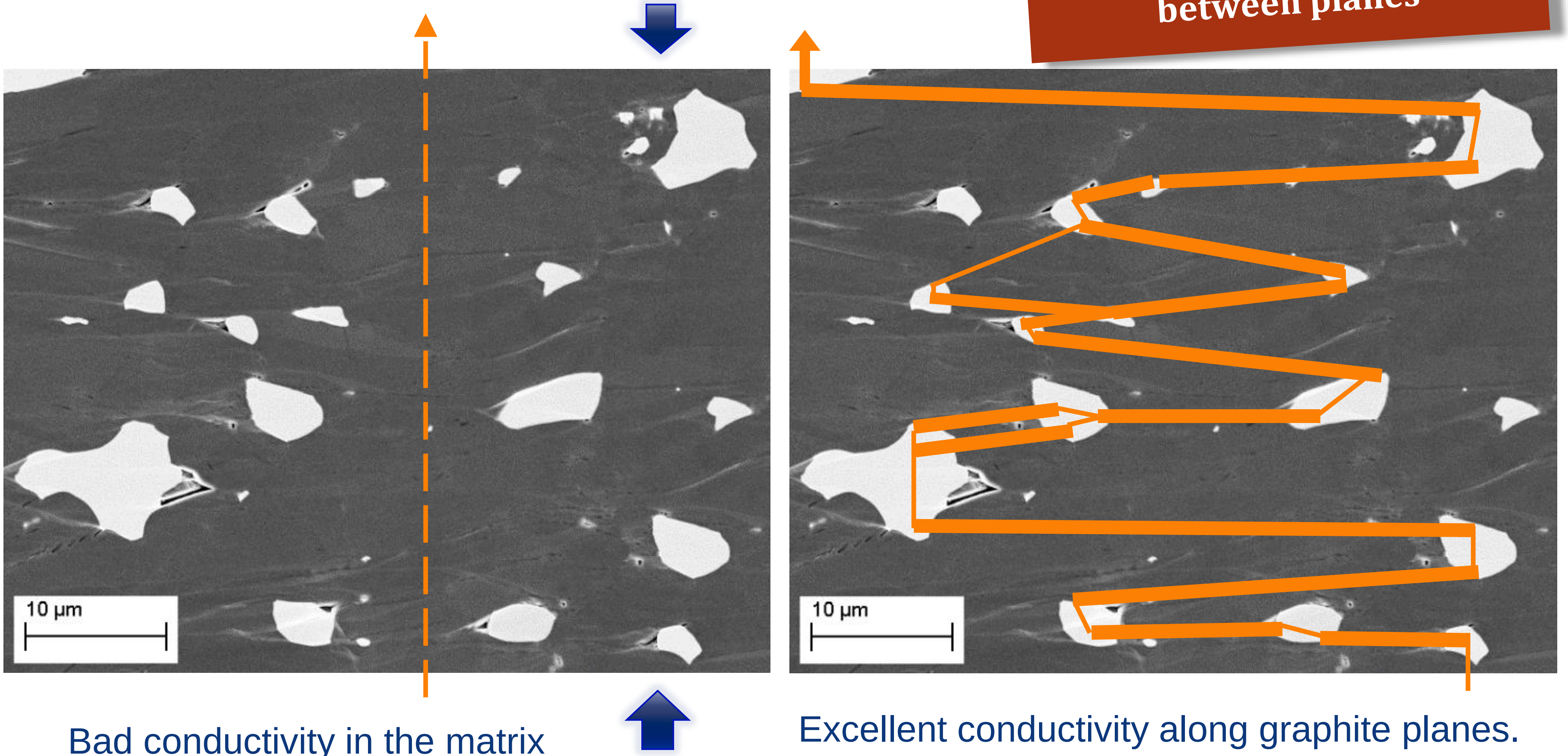
- Carbides: ~5 µm diameter
- Well-connected graphite matrix ~95vol%
- Well-compacted: porosity <0.5 vol.%
- Molybdenum carbide particles reinforce the graphite, holding together the graphite in the weak direction



Through-plane reinforcement

T-plane properties improved by the carbide bridges between planes

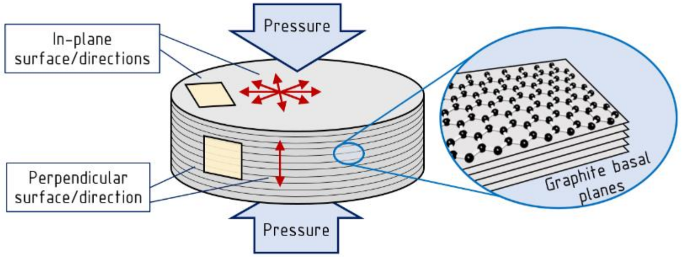
Sintering pressure direction



Bad conductivity in the matrix
(Through-graphite planes)

Excellent conductivity along graphite planes.
Carbide particles bridge between planes

Characterization



	In-plane	Perpendicular
Electrical conductivity [MS/m]	**~1**	~0.08
Thermal Conductivity [W/(mK)]	**700 – 800**	~50
CTE RT÷200 °C [$10^{-6}K^{-1}$]	**1.7 - 2.7**	8 - 12
Flexural Strength [MPa]	60 – 80	10 - 12
Specific Heat [J/(gK)]	0.6 - 0.65	
Density [g/cm^3]	**2.5 – 2.6**	

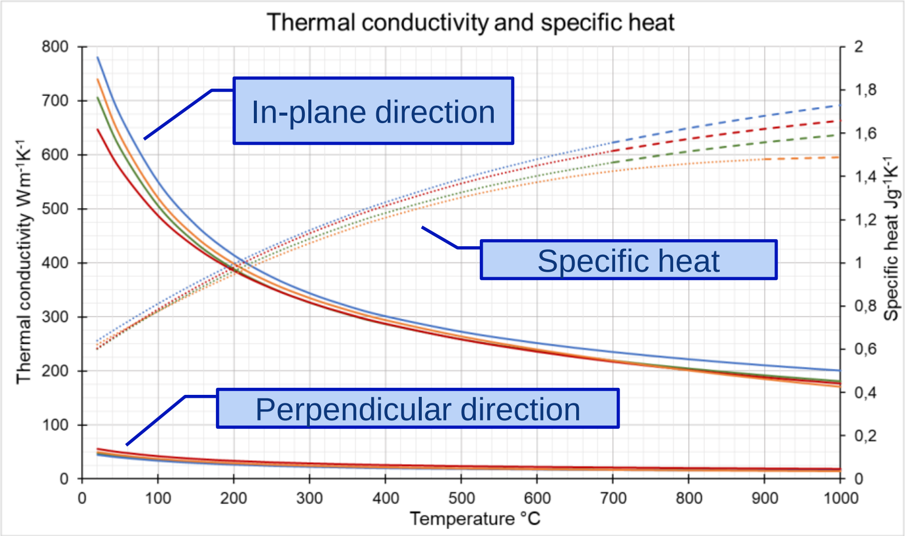
2x Cu

10-15x isotropic graphite

~ isotropic graphite

Si

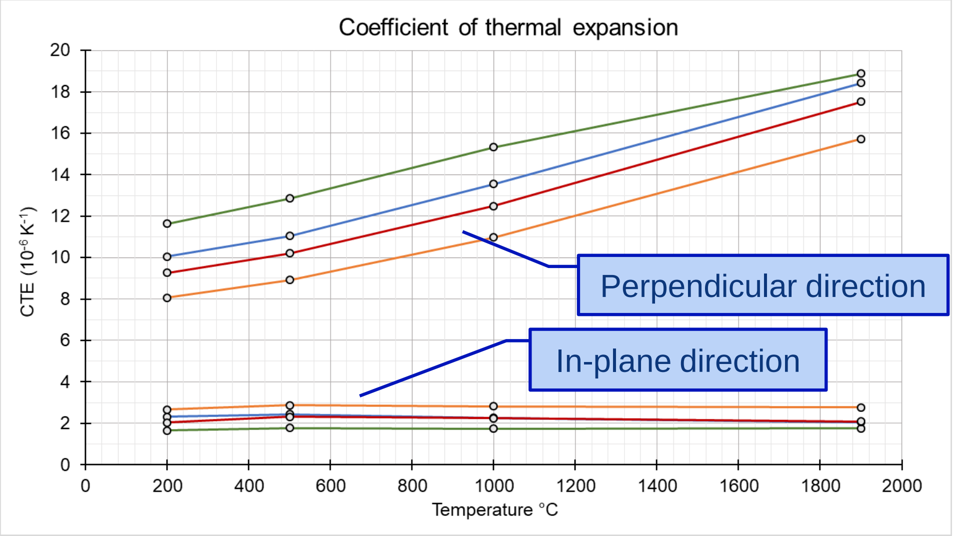
Al



In-plane direction

Specific heat

Perpendicular direction

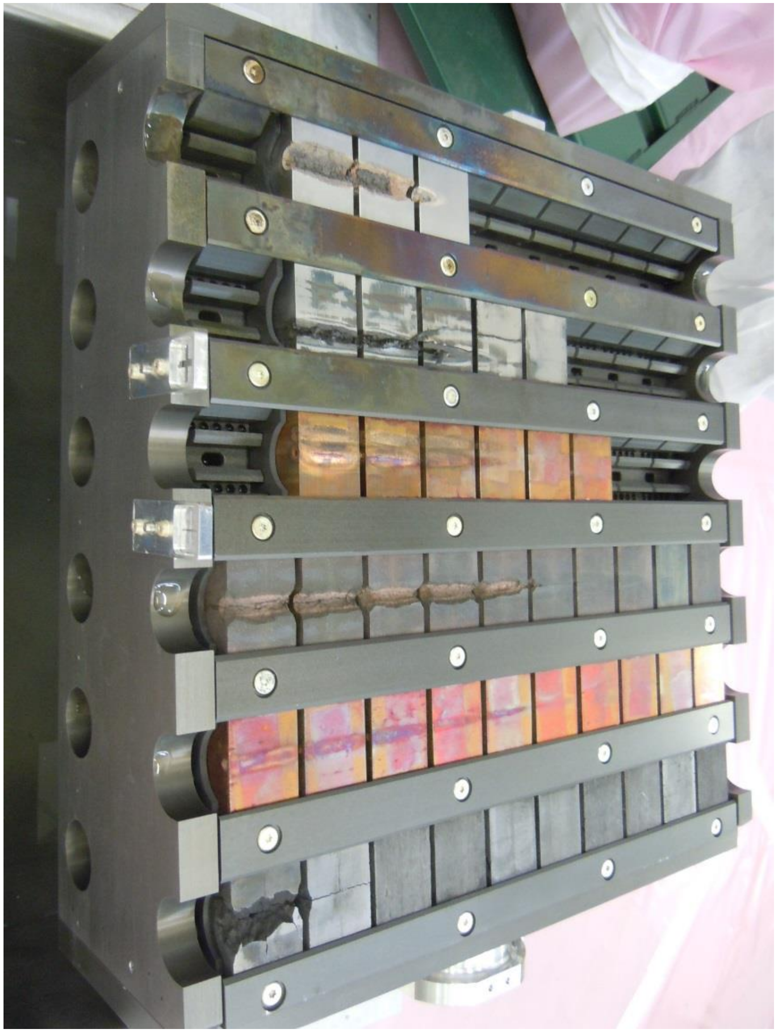


Perpendicular direction

In-plane direction

HiRadMat experiments

HRMT14



W alloy

Mo

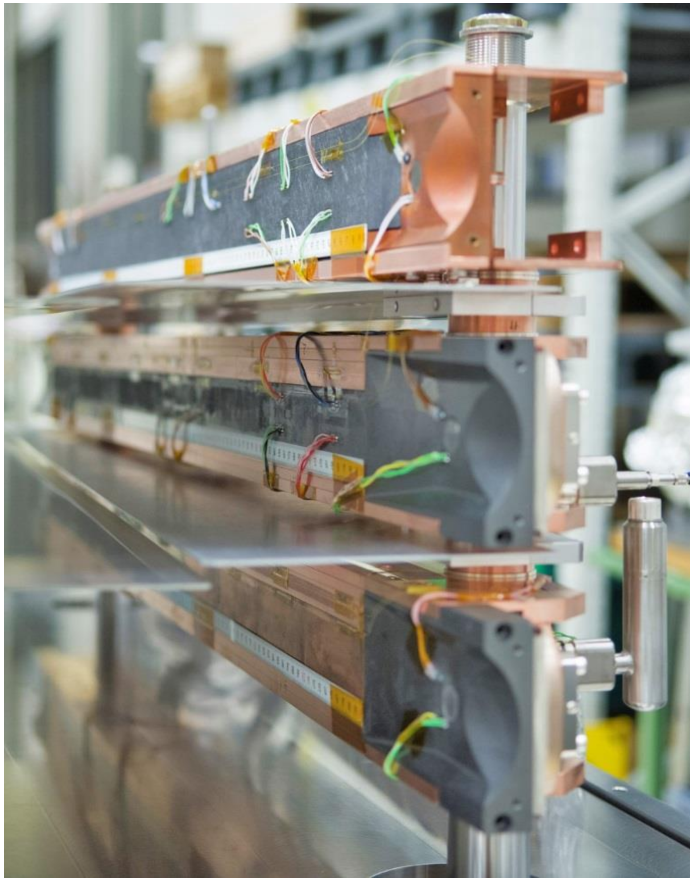
Cu alloy

MoCuCD

CuCD

MoGr
1st gen

HRMT23



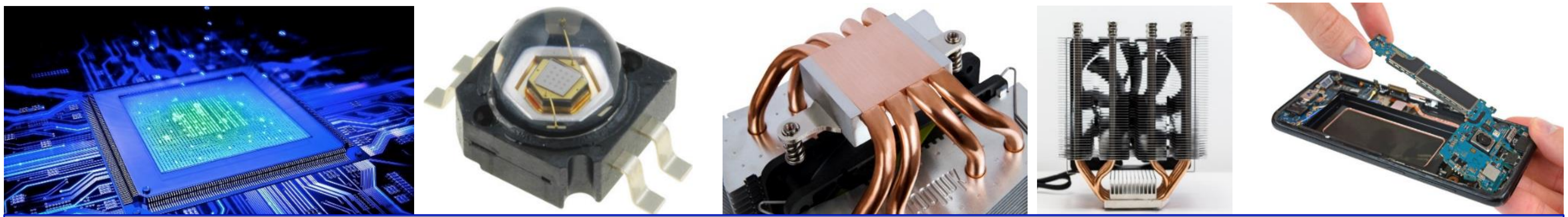
CFC

MoGr

CuCD

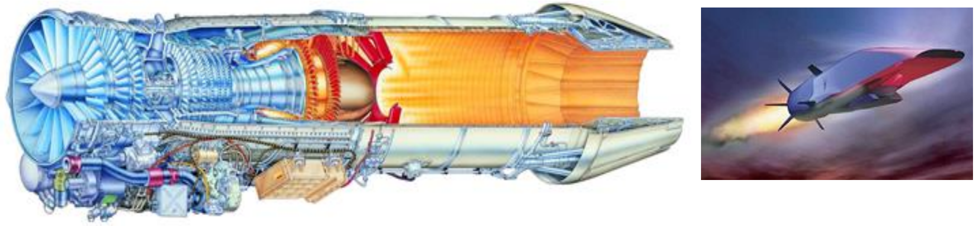
Possible applications outside CERN

Thermal management applications

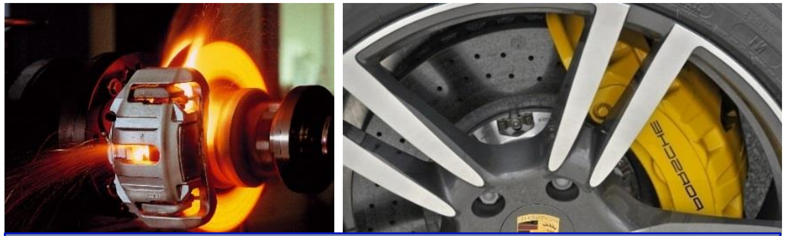


Thermal Management for High Power Electronics

Fusion Engineering



High temperature Aerospace Applications



Advanced Braking Systems

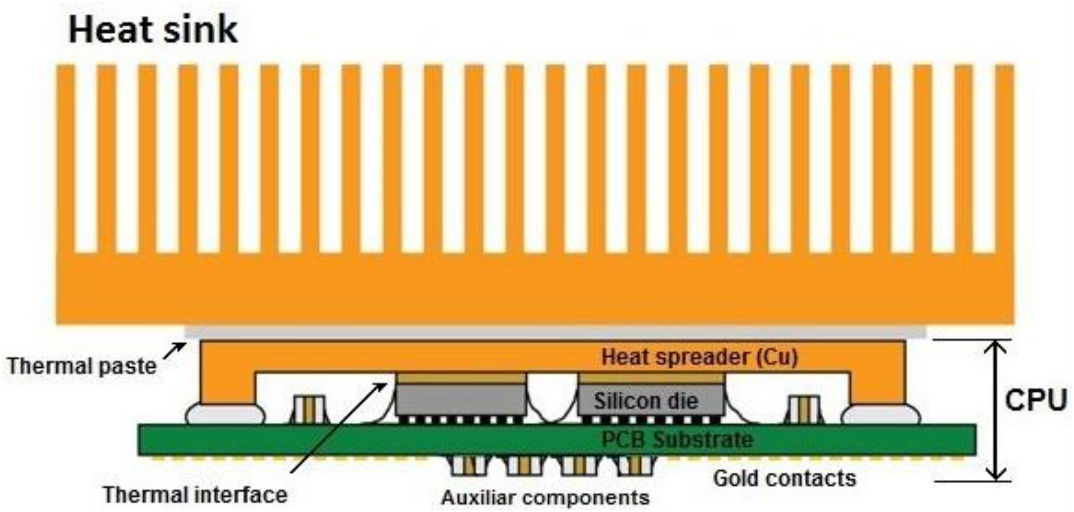
Energy Applications

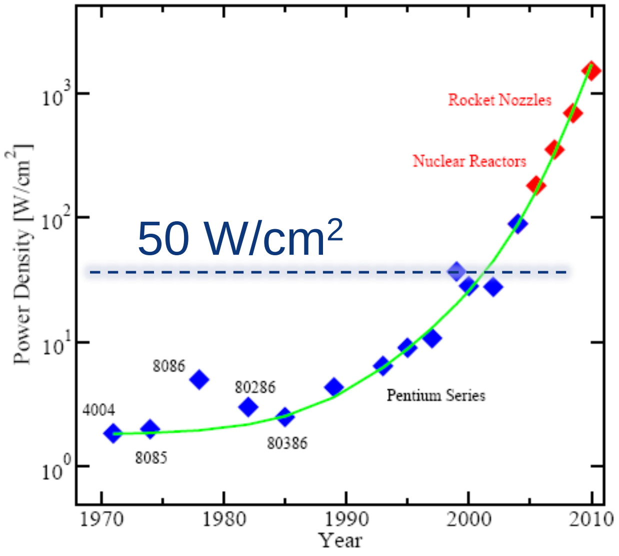
Knowledge transfer group at CERN

http://kt.cern/

Electronics: Microprocessors

Thermal management materials are very relevant for high-power electronic packaging: microprocessors

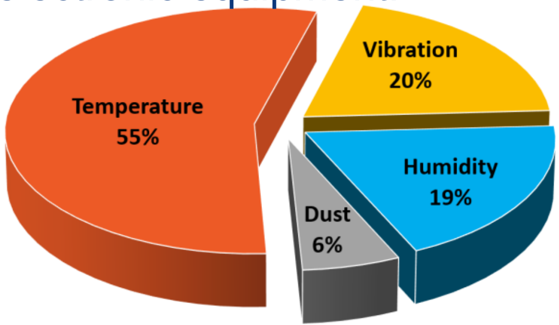




Property (20°C)	Unit	**Silver**	**Copper**	**Gold**	**Aluminium**	Silicon
Density	g/cm^3	10.49	8.89	19.32	2.7	2.33
Melting point	°C	961.8	1084.6	1064.2	660.3	1410
Electrical conductivity	MS/m	62	58.8	43.5	38	10^{-4} - 0.1
Thermal conductivity	W/(mK)	429	404	317	237	148
Specific heat capacity	J/(gK)	0.235	0.385	0.129	0.897	0.705
CTE	$10^{-6}K^{-1}$	18.6	16.8	14.2	23.9	2.53

Need to match CTE to avoid thermal stresses

Sources of stress in electronic equipment:

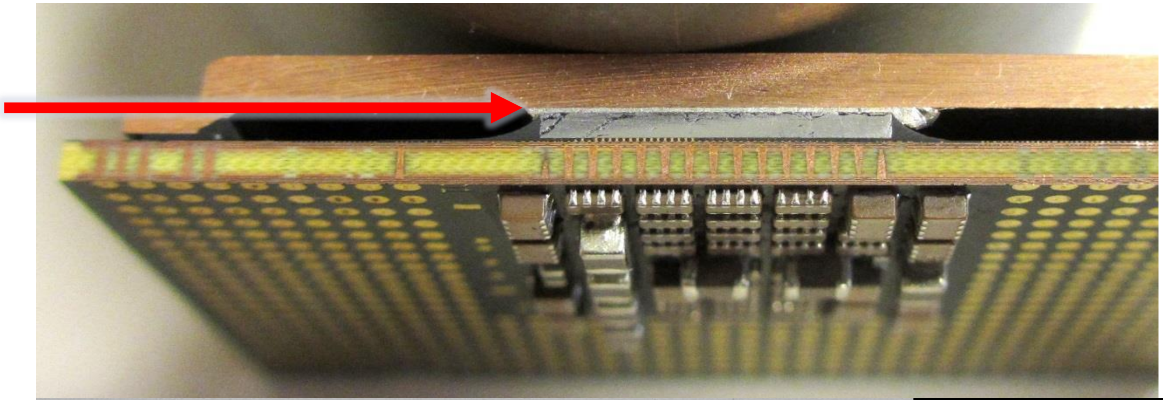


Ref: Michael Pecht. Handbook of Electronic package design. Marcel Dekker INC., 1991

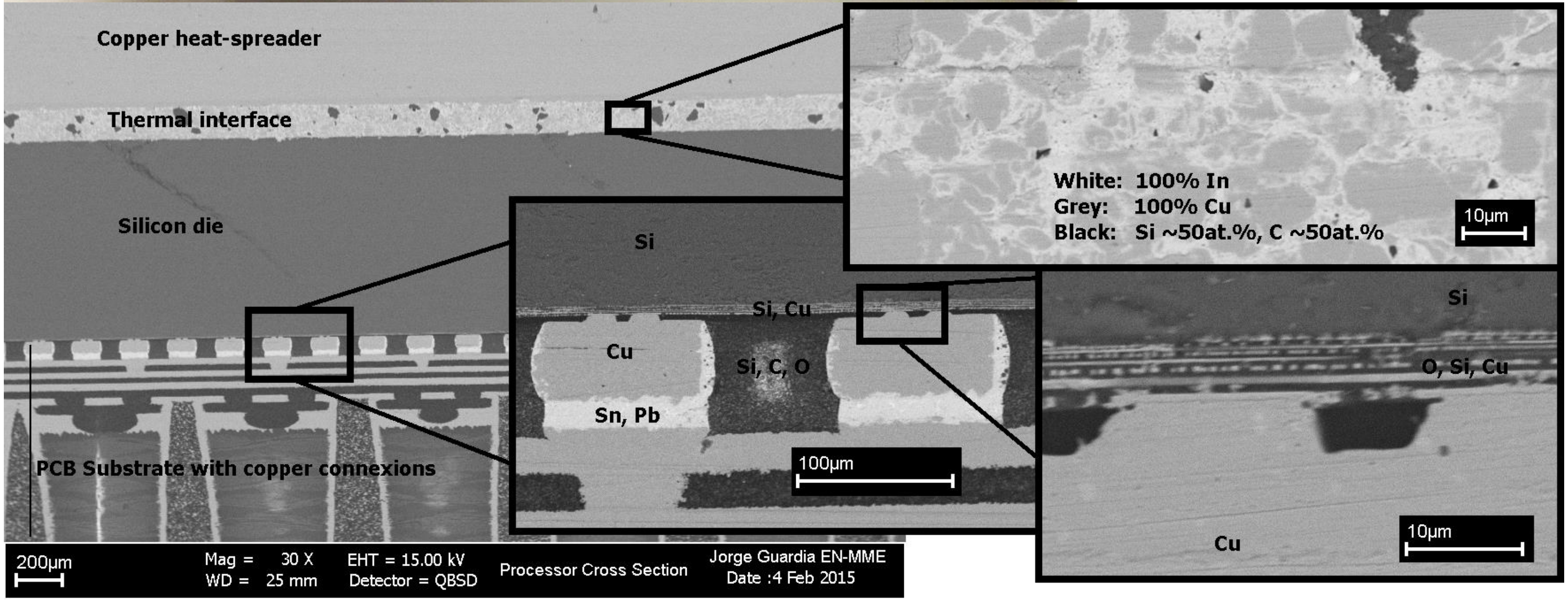
High power density electronic packaging: CPU

Soft thermal interface In-Cu, to “absorb” CTE mismatch

Thermal resistance, power limitation. Target: avoid this interface, replacing copper

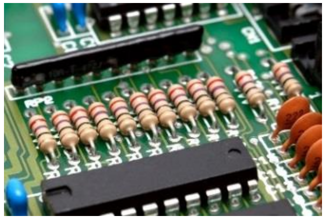


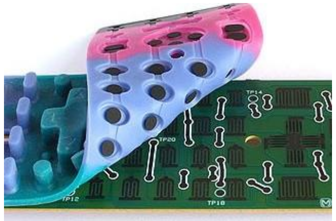
Property (20^{o}C)	Unit	**Indium**
Density	g/cm^3	7.31
Melting point	^{o}C	156.6
Young’s Modulus	GPa	11
Electrical conductivity	MS/m	11.9
Thermal conductivity	W/(mK)	81.6
Specific heat capacity	J/(gK)	0.233
CTE	$10^{-6}K^{-1}$	30

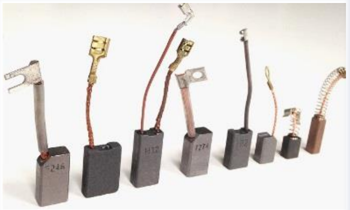


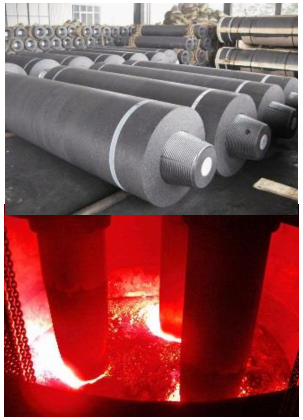
Commercial graphite applications

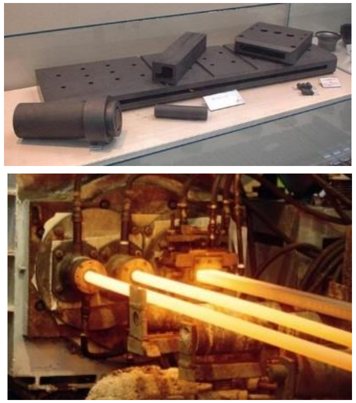
- High operating temperature
- Electrical conductor
- Lithium atoms intercalation
- Oxidation resistance
- Lubricating properties
- High strength and rigidity
- Strong Diamagnetic

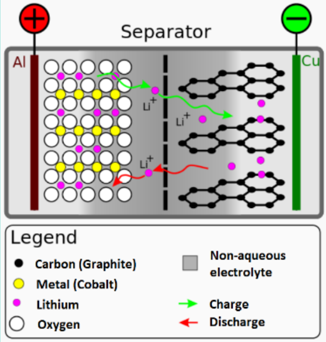


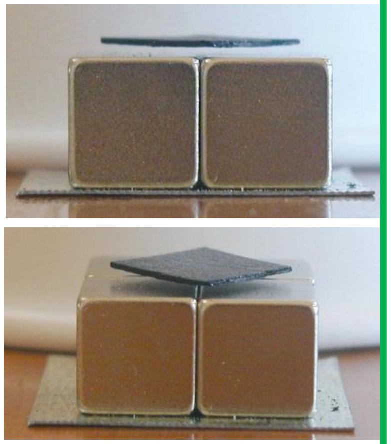












Comparison table

	MoGr		CFC AC150K		Graphite R4550	Glidcop AL-15 (Cu)	IT180 W-alloy	SS-316L
Direction	**In-plane**	**Perp.**	In-plane	Perp.	Isotropic	Isotropic	Isotropic	Isotropic
Density (g×cm^{-3})	**2.5-2.6**		1.89		1.86	8.75	17.94	7.95
Electrical conductivity (MS×m^{-1})	**0.9-1.1**	**0.05-0.07**	0.18-0.24	0.03	0.08	53.8	8.7	1.35
Specific heat at 20°C (J×g^{-1}×K^{-1})	**0.6-0.65**		0.71		0.71	0.39	0.15	0.45
Thermal diff. at 20°C (mm^{2}×s^{-1})	**430-530**	**28-37**	174-227	40	73	106	34	4
Thermal cond. at 20°C (Wm^{-1}K^{-1})	**650-900**	**45-65**	233-304	54	100	365	91	14
CTE 20-200°C (x10^{-6} K^{-1})	**1.7-2.7**	**8-12**	-0.8	11	4.2	18.5	5.3	15
Flexural strength (MPa)	**60-80**	**10-12**	105-140	10	60	375 (Tens.)	683 (Tens.)	515 (Tens.)
Elastic modulus (GPa)	**60-85**	**4-5**	~90	~5	11.5	128	360	195
Flexural strain to rupture (%)	**0.18-0.26**	**0.45-0.72**	0.14-0.2	0.43	0.72	27 (Tens.)	3 (Tens.)	40 (Tens.)

Main limitations

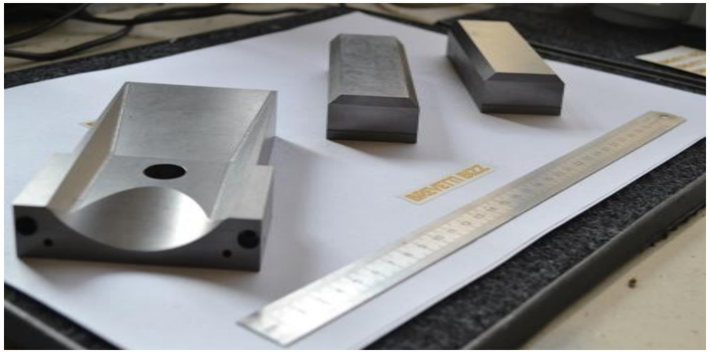
- Higher cost compared to Cu. Around 30 times more per cm^3
  - Cu ~ 0.13 eur/cm^3
  - MoGr ~ 5 eur/cm^3 (estimation of the production of one sintered plate)
  - PG ~ 10 eur/cm^3
  - HOPG >100 eur/cm^3
  - Nb ~ 6 eur/cm^3
  - W-alloy ~ 9 eur/cm^3

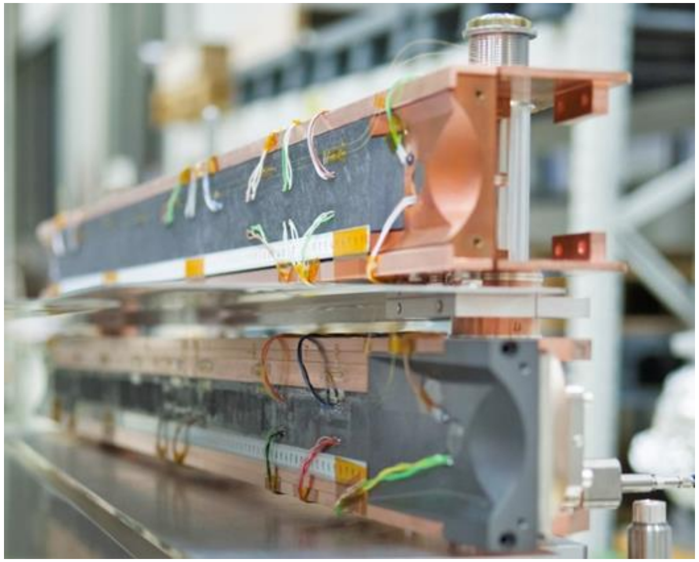
- Anisotropy: properties in the through-plane direction are lower by a factor ~10 wrt in-plane. However, oriented graphites (PG, HOPG) show factors >200.

- It belongs to brittle materials family, similarly to commercial graphite.

Conclusions

- A family of **graphite-matrix** composite materials containing **molybdenum carbide** particles (MoGr) successfully developed for CERN future HL-LHC collimators
- Produced by **spark plasma sintering** assisted by **molten metal-carbon liquid phase**
- **Production parameters,** physical mechanisms (**catalytic graphitization)** studied
- **Characterization, microstructural & phase analysis** performed. Transversely isotropic material
- Material of interest for other **thermal management applications** such as electronics or aerospace
    - Low CTE$_{20\text{-}200\ °C}$: ~$2.5×10^{-6}$ K^{-1} (≈Silicon)
    - High thermal conductivity: ~800 W $m^{-1}K^{-1}$
    - Low density: ~2.5 g cm^{-3}
    - Electrical conductivity: ~0.9 MS m^{-1}





Acknowledgements

- A. Bertarelli, F. Carra, N. Mariani, S. Bizzaro, R. Arenal
- S. Redaelli (LHC collimation project leader)
- M. Guinchard, O. Sacristán-de-Frutos and L. Bianchi (thermo-mechanical measurements lab at CERN)
- J. Busom-Descarrega, A.T. Perez-Fontenla (metallurgy lab at CERN)

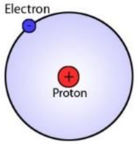
The research leading to these results has received funding from the European Commission under the FP7 Research Infrastructures project EuCARD-2, grant agreement No 312453. This project has received funding from the European Union's Horizon 2020 Research and Innovation programme under Grant Agreement No 730871. Research supported by the High Luminosity LHC project.

Thank you for your attention!

Backup slides

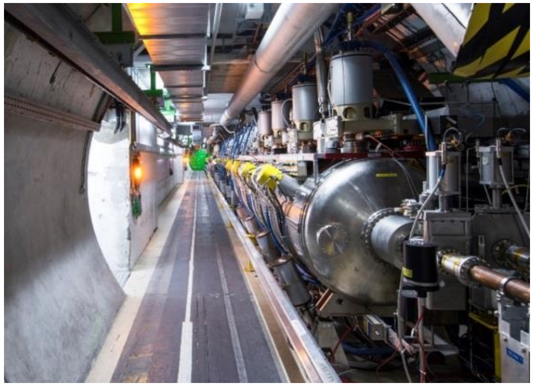
LHC particle accelerator operation

H: $1s^1$

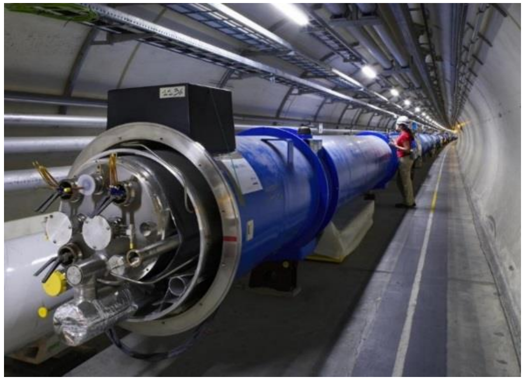


1. Hydrogen gas is ionized. H nucleus = one proton.
2. Protons are accelerated, firstly in a linear accelerator.
3. Several stages in different accelerators with increasing size

   (BOOSTER, PS, SPS) ⟶ LHC
4. Beam = separated bunches of $1.3 \cdot 10^{11}$ protons. ≈ Speed of light: circulate the 27km 10,000 times per second.
5. Two beams circulate in opposite directions. Collisions at the experiments. Products of collisions are detected, measured and characterized



Radio-frequency cavity: acceleration



Superconducting dipole magnet: bending trajectory

HRMT36 (oct. 2017)

The acquisition system featured:

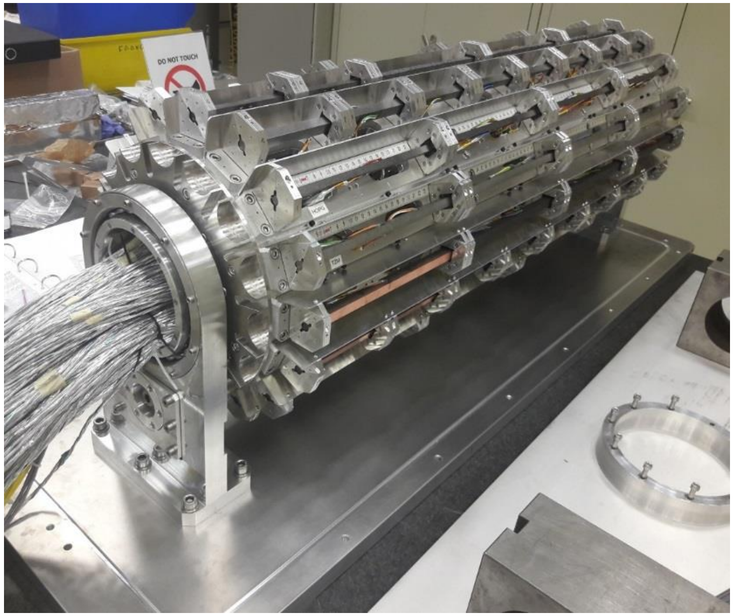
•335 electrical strain gauges placed depending on the material and on the deposited energy distribution (longitudinal/transverse strain);

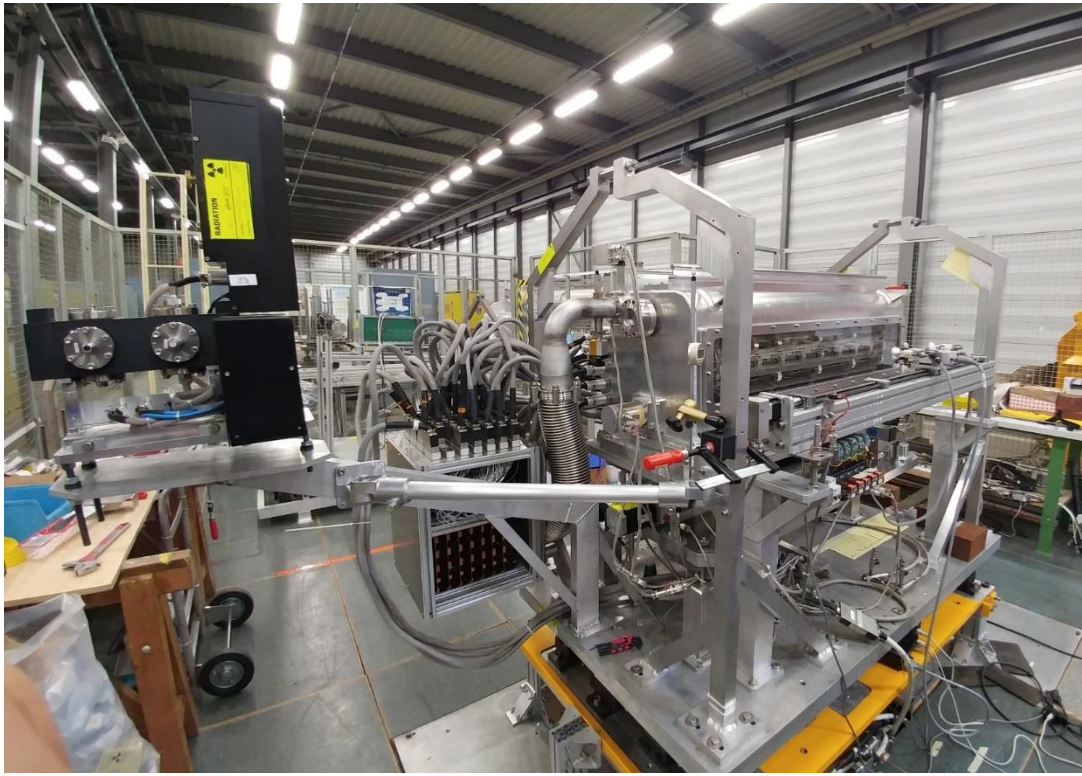
•112 electrical temperature probes (**total of 894 wires**);

•1 laser-doppler vibrometer (speed of spec. top faces);

•1 Rad-hard camera (side-mounted);

- Al vessel hosting 16 target stations on a rotatable barrel. Total of 18 materials
- Specimens of simple geometry (slender bars, length 120 or 247 mm)
- Mainly square cross section (8×8 to 12×11.5 mm^2)





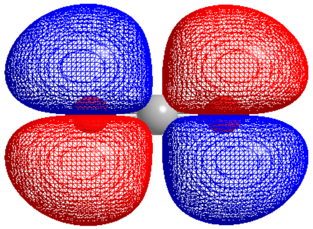
Introduction: Classification of materials

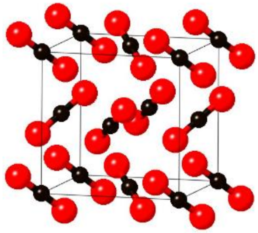
According to electronic band theory:

- Insulators
- Semiconductors
- Semimetals
- Metals

E_F: Fermi energy level
50% probability of being occupied by an electron
→Largest mobility

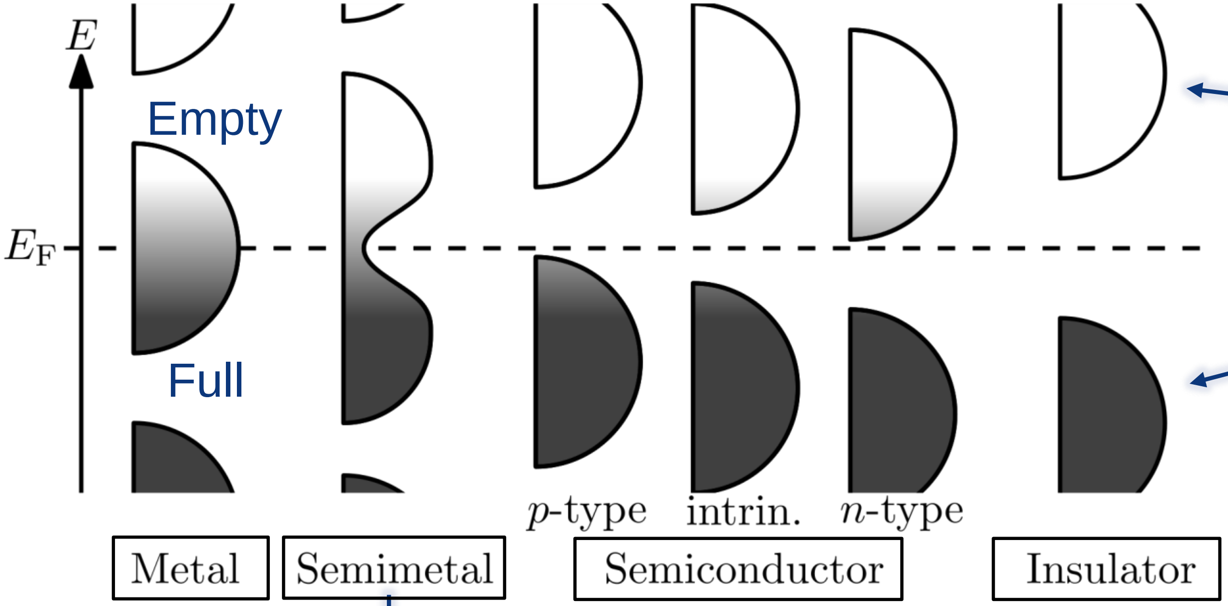
Solid CO_2





CO_2 electronic orbital (Full)
Full valence band → insulator

Electrons can freely move within a band if it is not full.

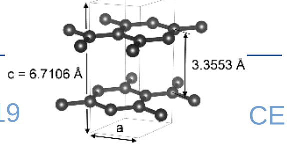


Conduction band:
Vacant electronic states

Valence band:
Where electrons are normally present (T=0 K)

E_F inside one partially filled band

Graphite

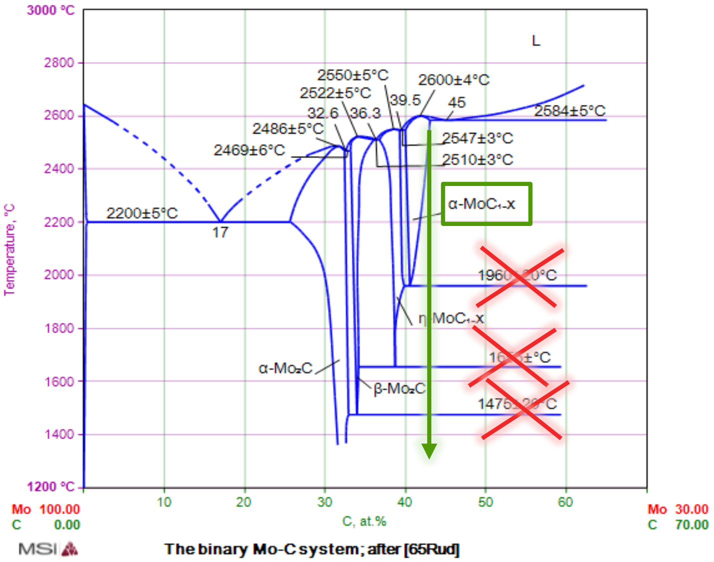


Valence band is full but close to conduction band
Band gap < 4 eV

Valence band is full and far to C.B.

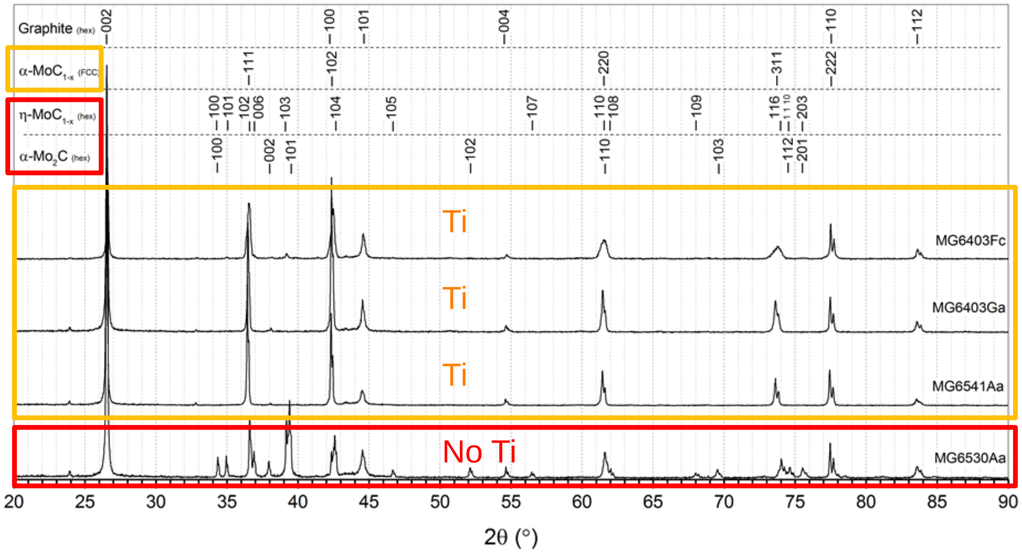
Carbide phases, titanium addition

- **Titanium** doping → α-MoC_{1-x} **phase stabilizer**



The binary Mo-C system; after [65Rud]

X-Ray Diffraction (XRD)



- If **no Ti** is added, there are hexagonal/orthorhombic carbides
- with If **Ti** is added, there is only FCC carbide (same structure as TiC)
- FCC α-MoC_{1-x} carbide stable from RT to melting point → thermal stability, radiation hardness
- **Graphite matrix** with very high quality. C-spacing: 3.36 Å

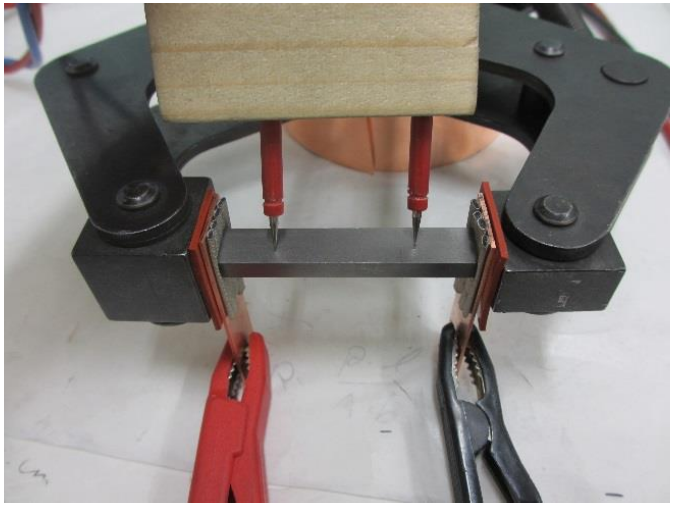
Thermo-mechanical characterization

Mechanical Measurements Lab at CERN

- Archimedes scale: density
- Differential Scanning Calorimeter: heat capacity
- Laser Flash Analysis: thermal diffusivity
- Dilatometer: CTE
- Universal testing machine: 4-point bending test
- Spectrum analyser (IET): Elastic constants

- Electrical resistivity measurement

Eddy-current device



4-wire method (ASTM C611-98)