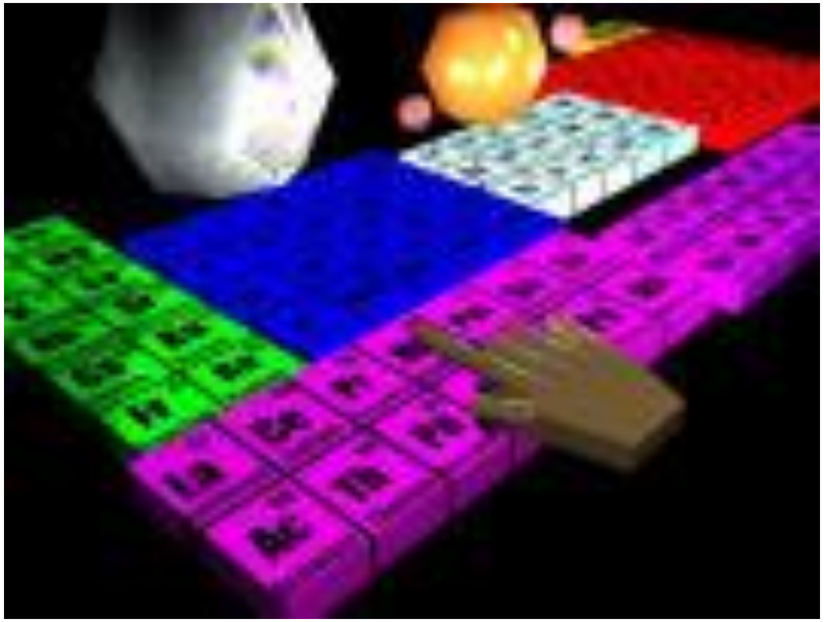
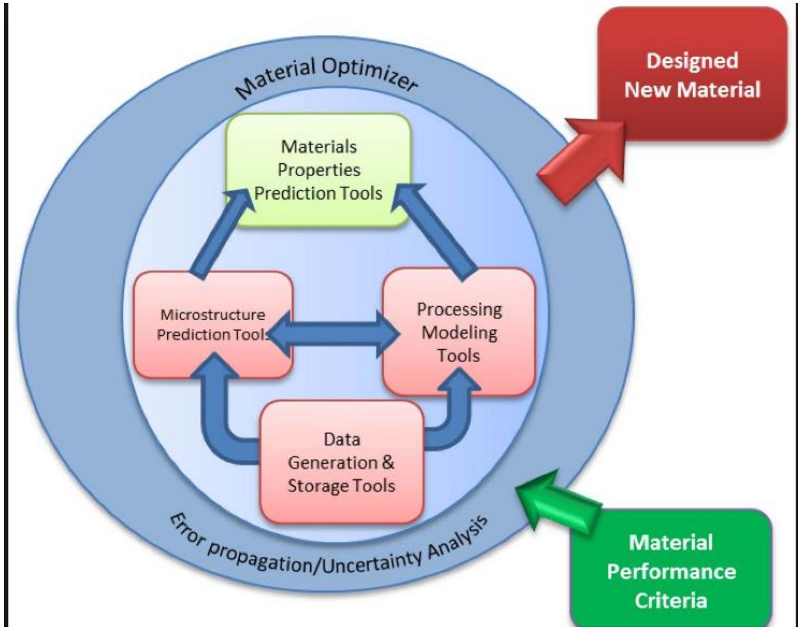
Curso de F-149 – 1S 2017

Desenvolvimento de Novos Materiais (Materials Design)





Aula 7

IFGW

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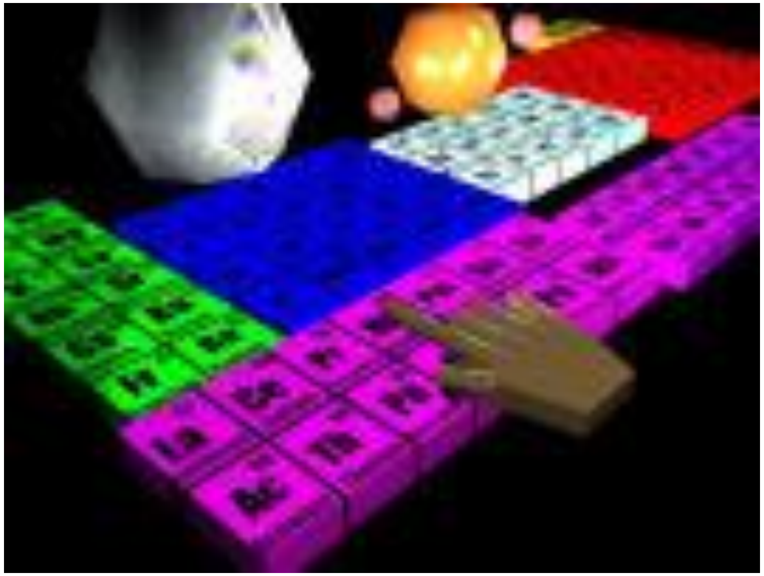
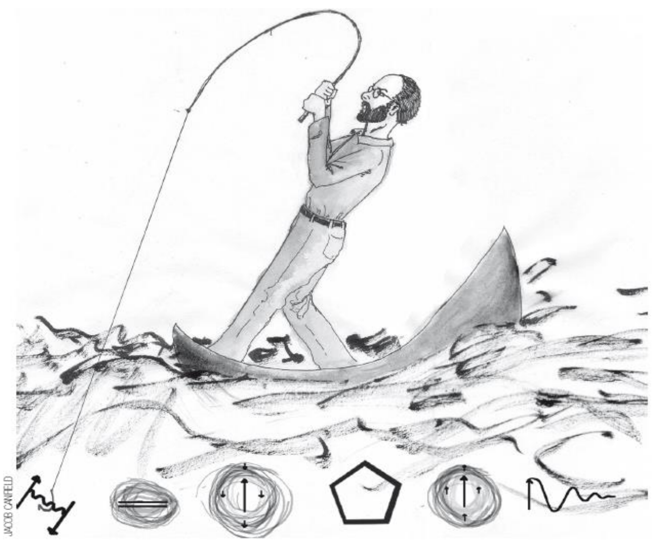
New Materials Design – Rota para novos SC convencionais





Fishing the Fermi sea – P. Canfield.

O Alquimista

Teoria microscópica:

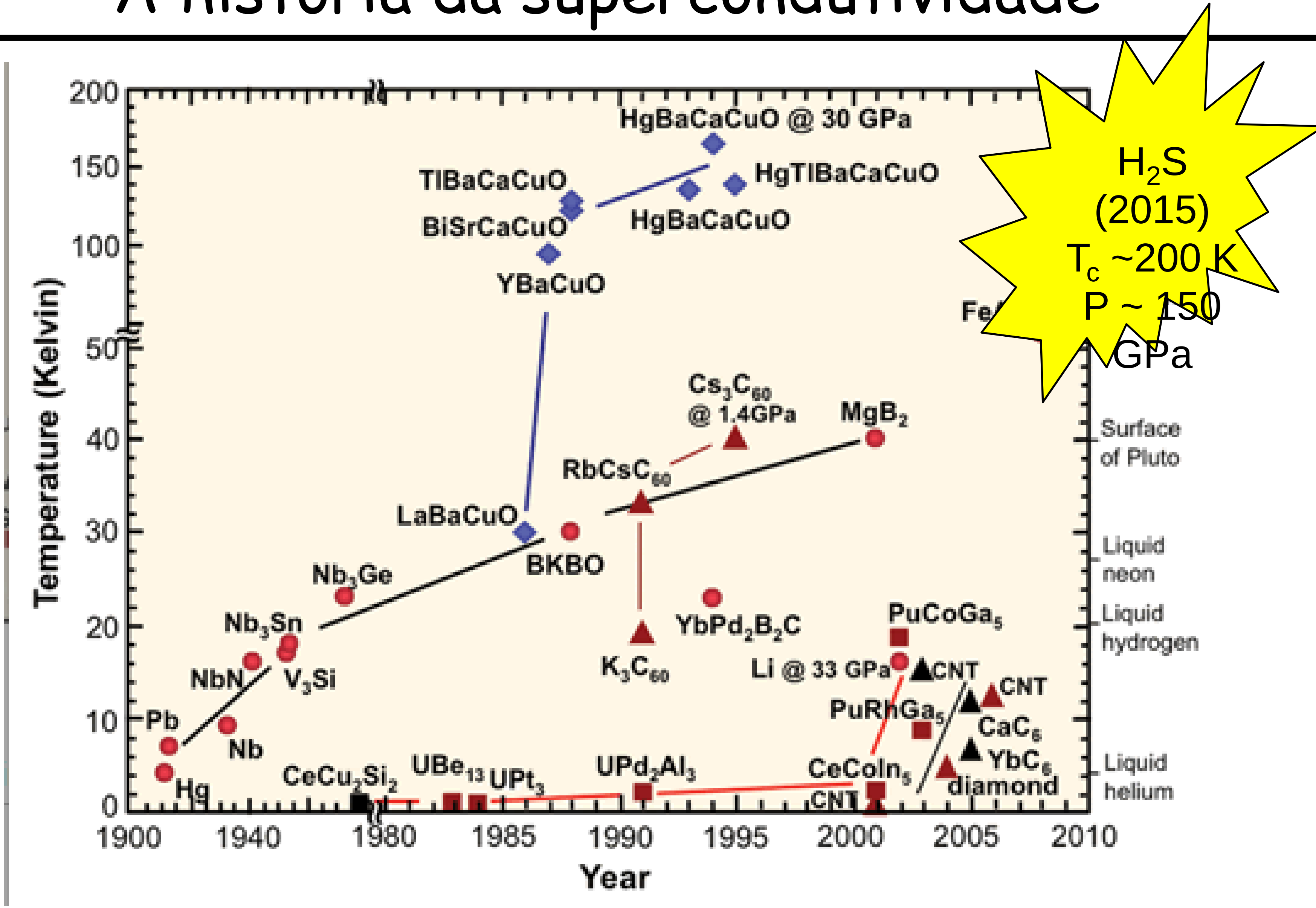
Bardeen, Cooper e Schrieffer

Em 1957, 46 anos após a descoberta da SC, BCS finalmente descobriram a explicação microscópica da SC.

Os 3 receberam o prêmio Nobel de 1972 pela descoberta. John Bardeen é o único a ter recebido 2 Nobel de Física (o primeiro, de 1956, junto com Brattain e Shockley, pela invenção do transistor).

O problema já havia frustrado as tentativas de físicos proeminentes como Bohr, Pauli, Heisenberg, Landau, Bloch, Einstein e Feynman.

A história da supercondutividade



Teoria

❖ Em 1935, F. e H. London propuseram duas equações fenomenológicas:

$$\boldsymbol{E} = \frac{\partial}{\partial t}(\Lambda \boldsymbol{J}_s)$$

$$\boldsymbol{h} = -\, c\, \nabla \times (\Lambda \boldsymbol{J}_s)$$

$$\Lambda = \frac{4\pi \lambda_L{}^2}{c^2} = \frac{m}{n_s e^2} \longrightarrow \text{Parâmetro Fenomenológico}$$

Teoria

- Em 1935, F. e H. London propuseram duas equações fenomenológicas:

$$\boldsymbol{E} = \frac{\partial}{\partial t}(\Lambda \boldsymbol{J}_s)$$

$$\boldsymbol{J} = \sigma \boldsymbol{E}$$

Descreve a condutividade perfeita

$$\boldsymbol{h} = -c\,\nabla \times (\Lambda \boldsymbol{J}_s)$$

$$\nabla \times \boldsymbol{h} = \frac{4\pi \boldsymbol{J}_s}{c}$$

$$\nabla^2 \boldsymbol{h} = \frac{\boldsymbol{h}}{\lambda_L{}^2} \rightarrow$$

Blindagem exponencial do interior do supercondutor para campos magnéticos (com comprimento de penetração λ_L)

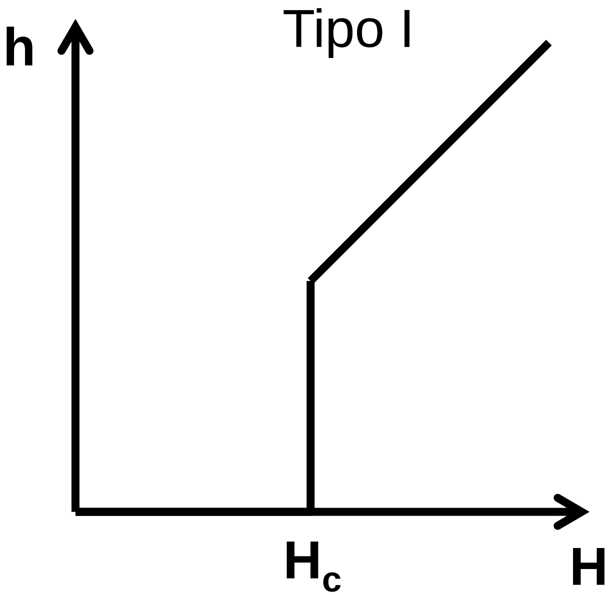
Teoria

❖ Em 1950, teoria Ginzburg-Landau

$$\frac{1}{2m^*}\left(\frac{\hbar}{i}\nabla - \frac{e^*}{c}A\right)^2 \psi + \beta|\psi|^2\psi = -\alpha(T)\psi$$

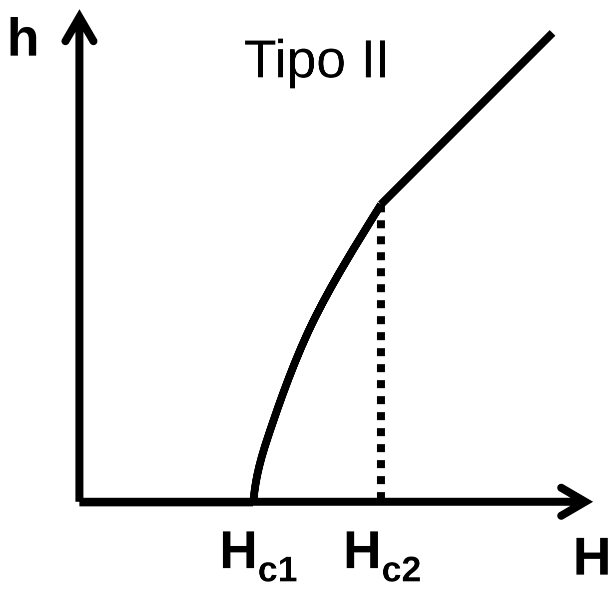
$$\xi(T) = \frac{\hbar}{|2m^*\alpha(T)|^{1/2}}$$

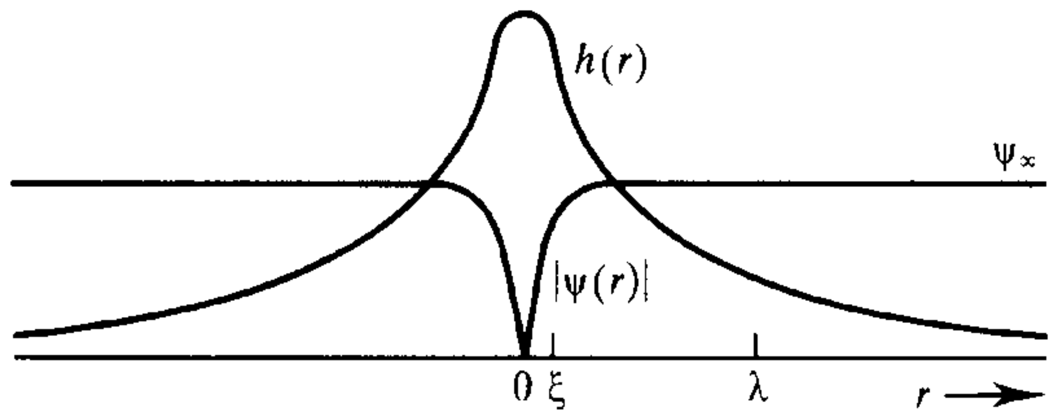
$$\kappa = \frac{\lambda}{\xi} \begin{cases} \kappa < 1/\sqrt{2} & \text{Tipo I} \\ \kappa > 1/\sqrt{2} & \text{Tipo II} \end{cases}$$



Teoria

- Supercondutores tipo II apresentam o estado-misto





TINKHAM, M. Introduction to Superconductivity. 2. ed. New York: Mcgraw-Hill, Inc., 1996.

$$\Phi_0 = \frac{hc}{2e}$$

Teoria

- Em 1956, Cooper demonstrou a possibilidade da formação de um par ligado de elétrons

$$\psi_0(\boldsymbol{r}_1,\boldsymbol{r}_2) = \sum_{\boldsymbol{k}} g_{\boldsymbol{k}} e^{i\boldsymbol{k}\cdot\boldsymbol{r}_1} e^{-i\boldsymbol{k}\cdot\boldsymbol{r}_2}$$

$$\psi_0(\boldsymbol{r}_1-\boldsymbol{r}_2) = \left[\sum_{k>k_F} g_{\boldsymbol{k}} \cos \boldsymbol{k}\cdot(\boldsymbol{r}_1-\boldsymbol{r}_2)\right](|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

- Equação de Schroedinger das duas partículas:

$$E\psi_0 = \left[\sum_{i=1,2} \frac{\boldsymbol{p}_i^2}{2m} + V(\boldsymbol{r}_1,\boldsymbol{r}_2)\right]\psi_0$$

Teoria

$$(E - 2\epsilon_{\boldsymbol{k}})g_{\boldsymbol{k}} = \sum_{k'>k_F} V_{\boldsymbol{kk'}}\, g_{\boldsymbol{k'}}$$

- Considerando um potencial da forma:

$$V_{\boldsymbol{kk'}} = \begin{cases} -V, |\epsilon_{\boldsymbol{k}} - \epsilon_F| \text{ e } |\epsilon_{\boldsymbol{k'}} - \epsilon_F| < \hbar\omega_c \\ 0, \text{ caso contrário} \end{cases}$$

$$\frac{1}{V} = \sum_{k>k_F} (2\epsilon_{\boldsymbol{k}} - E)^{-1}$$

$$\frac{1}{V} = N(E_F) \int_{E_F}^{E_F+\hbar\omega_c} \frac{d\epsilon}{E - 2\epsilon} = \frac{1}{2} N(E_F) ln\left(\frac{2E_F - E + 2\hbar\omega_c}{2E_F - E}\right)$$

- Cooper chegou à energia do par ligado:

$$E \approx 2E_F - 2\hbar\omega_c e^{-\frac{2}{N(E_F)V}}$$

Válido para $N(E_F)V \ll 1$
(acoplamento fraco)

$\omega_c \sim \omega_D\ (frequência\ de\ Debye) \sim \sqrt{\frac{k}{m}}$

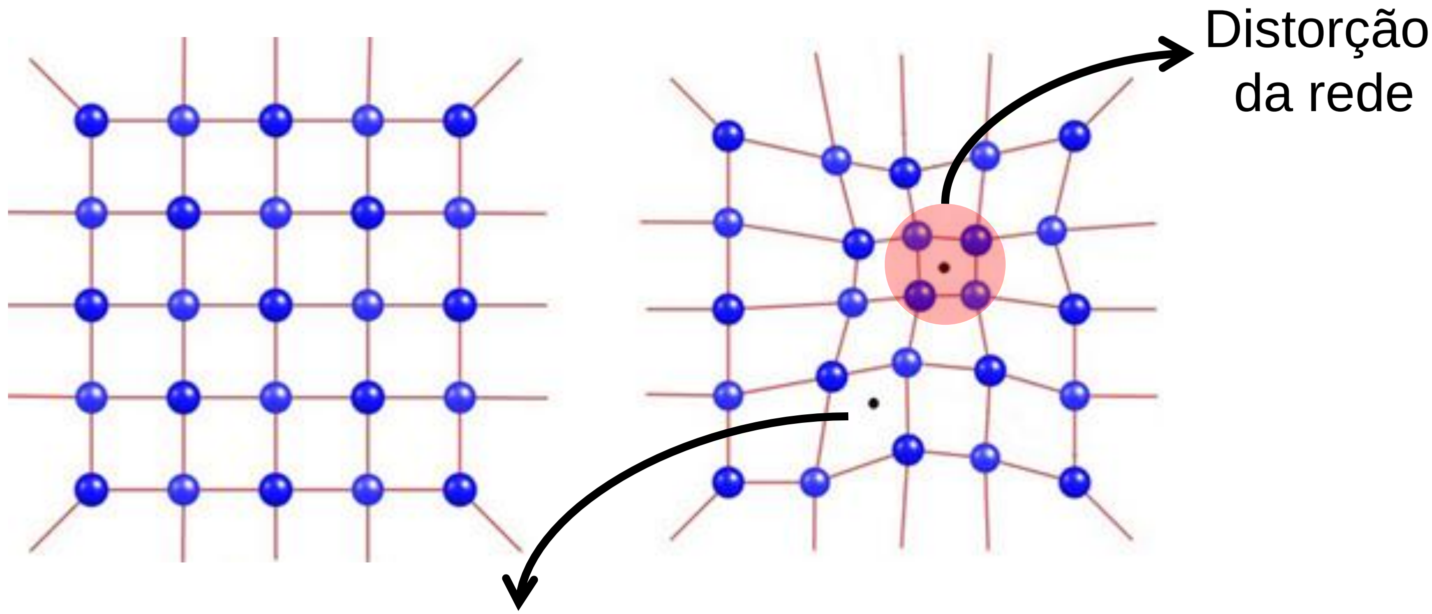
Teoria

- De fato se considerarmos a intereção elétron-elétron efetiva temos:

$$\boldsymbol{q} = \boldsymbol{k} - \boldsymbol{k}'$$

$$V(\boldsymbol{q},\omega) = \frac{4\pi e^2}{q^2 + k_s^2}\left[1 + \frac{\omega_{\boldsymbol{q}}^2}{\omega^2 - \omega_{\boldsymbol{q}}^2}\right]$$

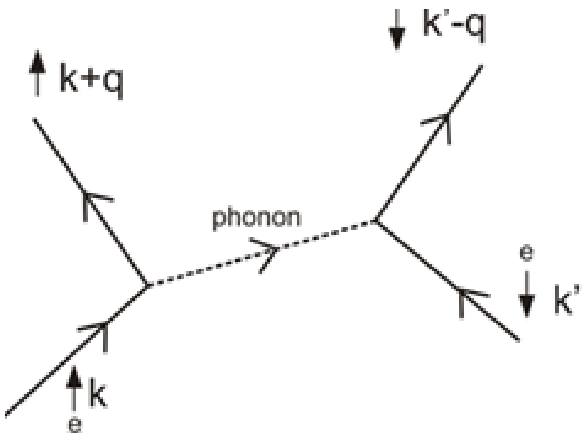
$$\omega = \frac{\epsilon_{\boldsymbol{k}} - \epsilon_{\boldsymbol{k}'}}{\hbar}$$



$T>T_c$ $\quad$ $T<T_c$

Elétron atraído pela concentração de carga +

Teoria



❖ Em 1957, Bardeen, Cooper e Schrieffer expandem a possibilidade do pareamento para N elétrons

$$H = \sum_{\boldsymbol{k}\sigma} \epsilon_{\boldsymbol{k}} n_{\boldsymbol{k}\sigma} + \sum_{\boldsymbol{kl}} V_{\boldsymbol{kl}} c^*_{\boldsymbol{k}\uparrow} c^*_{-\boldsymbol{k}\downarrow} c_{-\boldsymbol{l}\downarrow} c_{\boldsymbol{l}\uparrow}$$

❖ Estado Fundamental

$$|\psi_G\rangle = \prod_{\boldsymbol{k}=\,\boldsymbol{k}_1,\dots,\boldsymbol{k}_M} (u_{\boldsymbol{k}} + \mathrm{v}_{\boldsymbol{k}} c^*_{\boldsymbol{k}\uparrow} c^*_{-\boldsymbol{k}\downarrow}) |\varphi_0\rangle$$

Teoria

- Utilizando o método variacional para determinar os coeficientes

$$\delta\langle\psi_G|H-\mu N_{op}|\psi_G\rangle = 0$$

- Definindo $\xi_{\boldsymbol{k}} = \epsilon_{\boldsymbol{k}} - \mu$, temos

$$\langle\psi_G|H-\mu N_{op}|\psi_G\rangle = 2\sum_{\boldsymbol{k}} \xi_{\boldsymbol{k}}|v_{\boldsymbol{k}}|^2 + \sum_{\boldsymbol{kl}} V_{\boldsymbol{kl}} u_{\boldsymbol{k}} v_{\boldsymbol{k}}^* u_{\boldsymbol{l}}^* v_{\boldsymbol{l}}$$

- Tomando $u_{\boldsymbol{k}} = sen\theta_{\boldsymbol{k}}$ e $v_{\boldsymbol{k}} = cos\theta_{\boldsymbol{k}}$

$$\sum_{\boldsymbol{k}} \xi_{\boldsymbol{k}}(1+cos2\theta_{\boldsymbol{k}}) + \frac{1}{4}\sum_{\boldsymbol{kl}} V_{\boldsymbol{kl}} sen\,2\theta_{\boldsymbol{k}} sen2\theta_{\boldsymbol{l}}$$

Teoria

$$\frac{\partial\langle\psi_G|H-\mu N_{op}|\psi_G\rangle}{\partial\theta_{\boldsymbol{k}}}=0=-2\xi_{\boldsymbol{k}}sen2\theta_{\boldsymbol{k}}+\sum_{\boldsymbol{l}}V_{\boldsymbol{kl}}cos\,2\theta_{\boldsymbol{k}}sen2\theta_{\boldsymbol{l}}$$

$$tan2\theta_{\boldsymbol{k}}=\frac{\sum_{\boldsymbol{l}}V_{\boldsymbol{kl}}\,sen2\theta_{\boldsymbol{l}}}{2\xi_{\boldsymbol{k}}}$$

❖ Definindo:

$$\Delta_{\boldsymbol{k}}=-\sum_{\boldsymbol{l}}V_{\boldsymbol{kl}}u_{\boldsymbol{l}}v_{\boldsymbol{l}}=-\frac{1}{2}\sum_{\boldsymbol{l}}V_{\boldsymbol{kl}}sen2\theta_{\boldsymbol{l}}$$

$$E_{\boldsymbol{k}}=\left(\Delta_{\boldsymbol{k}}^2+\xi_{\boldsymbol{k}}^2\right)^{1/2}$$

$$tan2\theta_{\boldsymbol{k}}=-\frac{\Delta_{\boldsymbol{k}}}{\xi_{\boldsymbol{k}}}$$

$$2u_{\boldsymbol{k}}v_{\boldsymbol{k}}=sen2\theta_{\boldsymbol{k}}=\frac{\Delta_{\boldsymbol{k}}}{E_{\boldsymbol{k}}}$$

$$v_{\boldsymbol{k}}^2-u_{\boldsymbol{k}}^2=cos2\theta_{\boldsymbol{k}}=-\frac{\xi_{\boldsymbol{k}}}{E_{\boldsymbol{k}}}$$

❖ Com isso, temos:

$$\Delta_{\boldsymbol{k}}=-\frac{1}{2}\sum_{\boldsymbol{l}}\frac{\Delta_{\boldsymbol{l}}}{\left(\Delta_{\boldsymbol{l}}^2+\xi_{\boldsymbol{l}}^2\right)^{1/2}}V_{\boldsymbol{kl}}$$

Teoria

❖ Considerando:

$$V_{\boldsymbol{kl}} = \begin{cases} -V, |\xi_{\boldsymbol{k}}| \text{ e } |\xi_{\boldsymbol{l}}| \leq \hbar\omega_c \\ 0, \text{ caso contrário} \end{cases}$$

$$\Delta_{\boldsymbol{k}} = \begin{cases} \Delta, |\xi_{\boldsymbol{k}}| < \hbar\omega_c \\ 0, |\xi_{\boldsymbol{k}}| > \hbar\omega_c \end{cases}$$

❖ Como o gap independe de **k**:

$$\Delta = \frac{V}{2}\sum_{\boldsymbol{l}} \frac{\Delta}{\left(\Delta^2 + \xi_{\boldsymbol{l}}^2\right)^{1/2}} \longrightarrow 1 = \frac{V}{2}\sum_{\boldsymbol{k}} \frac{1}{E_{\boldsymbol{k}}}$$

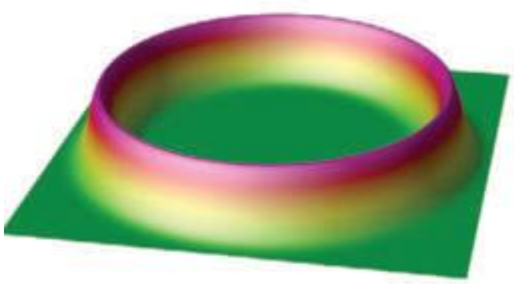
$$\frac{1}{N(E_F)V} = \int_0^{\hbar\omega_c} \frac{d\xi}{(\Delta^2 + \xi^2)^{1/2}} = senh^{-1}\frac{\hbar\omega_c}{\Delta}$$

Teoria

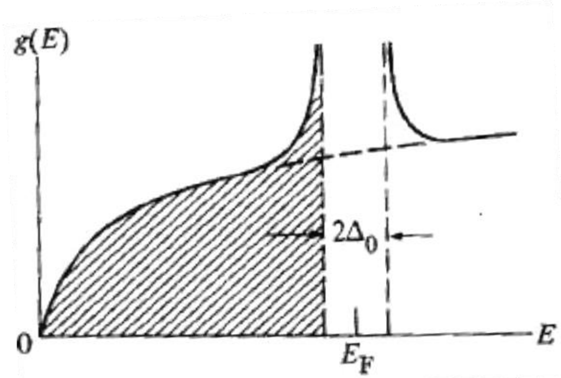
$$\frac{1}{N(E_F)V} = \int_0^{\hbar\omega_c} \frac{d\xi}{(\Delta^2 + \xi^2)^{1/2}} = senh^{-1}\frac{\hbar\omega_c}{\Delta}$$

$$N(E_F)V \ll 1$$

$$\Delta \approx 2\hbar\omega_c e^{-\frac{2}{N(E_F)V}}$$



I. I. Mazin, Nature **464** 183 (2010)



Omar, Ali M., Elementary Solid State Physics, (Pearson Education, 1999), 496-504

Teoria:

❖ Considerando efeitos de temperatura finita:

$$f(E_{\boldsymbol{k}}) = \frac{1}{(1 + e^{\beta E_{\boldsymbol{k}}})} \longrightarrow \Delta_{\boldsymbol{k}} = -\sum_{\boldsymbol{l}} V_{\boldsymbol{kl}} u_{\boldsymbol{l}} v_{\boldsymbol{l}} \longrightarrow 1 = \frac{V}{2} \sum_{\boldsymbol{k}} \frac{tanh(\beta E_k/2)}{E_{\boldsymbol{k}}}$$

❖ A temperatura crítica (T_c) é aquela em que $\Delta(T) \rightarrow 0$, assim $E_{\boldsymbol{k}} \rightarrow |\xi_{\boldsymbol{k}}|$

$$\frac{1}{N(E_F)V} = \int_0^{\hbar\omega_c} \frac{tanh(\beta_c \xi/2) d\xi}{\xi}$$

$$k_B T_c = 1.13 \hbar\omega_c e^{-\frac{1}{N(E_F)V}}$$

$$T_c \sim (0.3 - 0.4)\, \Theta_D$$

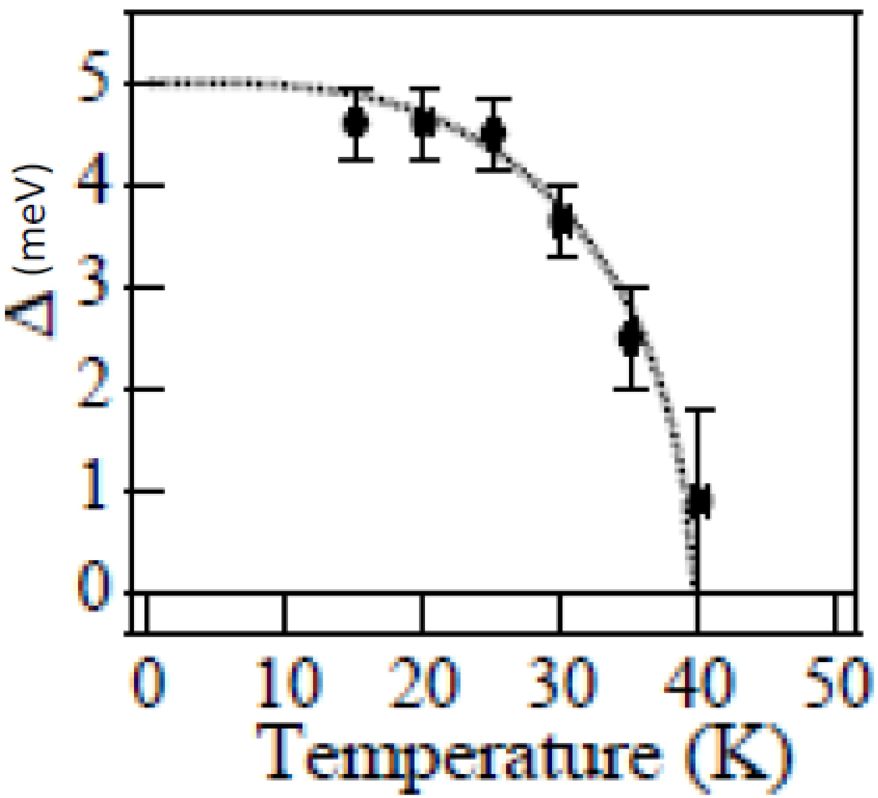
❖ McMillan expandiu essa expressão:

$$k_B T_c = \frac{\hbar\langle\omega\rangle}{1.20} exp\left\{\frac{-1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right\}$$

$$\lambda = \frac{N(E_F)\langle I^2\rangle}{M\langle\omega^2\rangle}$$

W.L. McMillan, Phys. Rev. 167, 331 (1968).

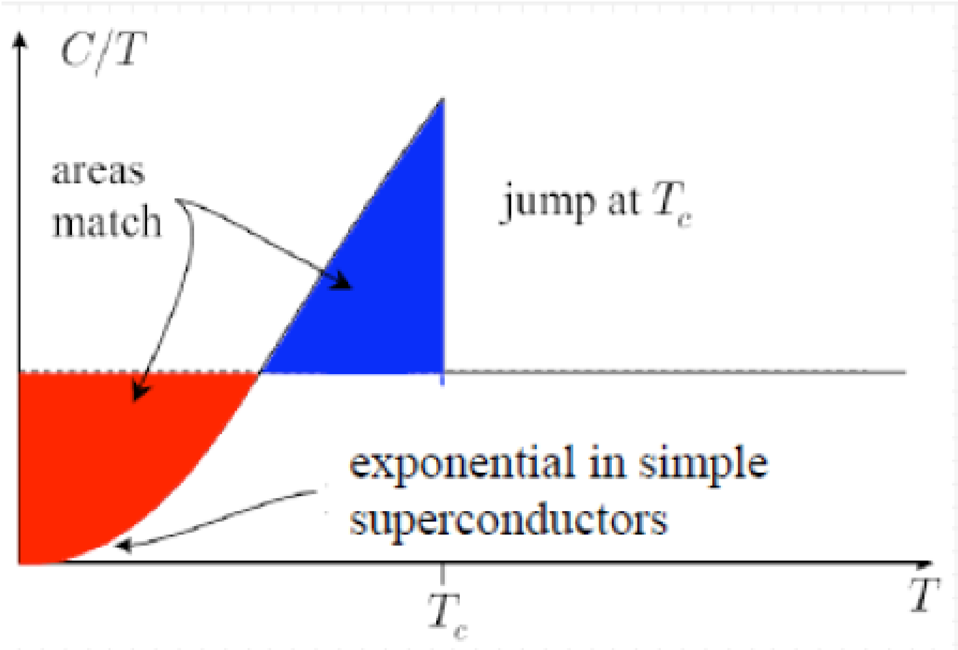
Temperature Dependence of Gap



MgB_2
T_c = 39.5K
Takahashi et al, 2001

Measured directly from Angle Resolved Photoemission Spectroscopy (ARPES)

Specific Heat

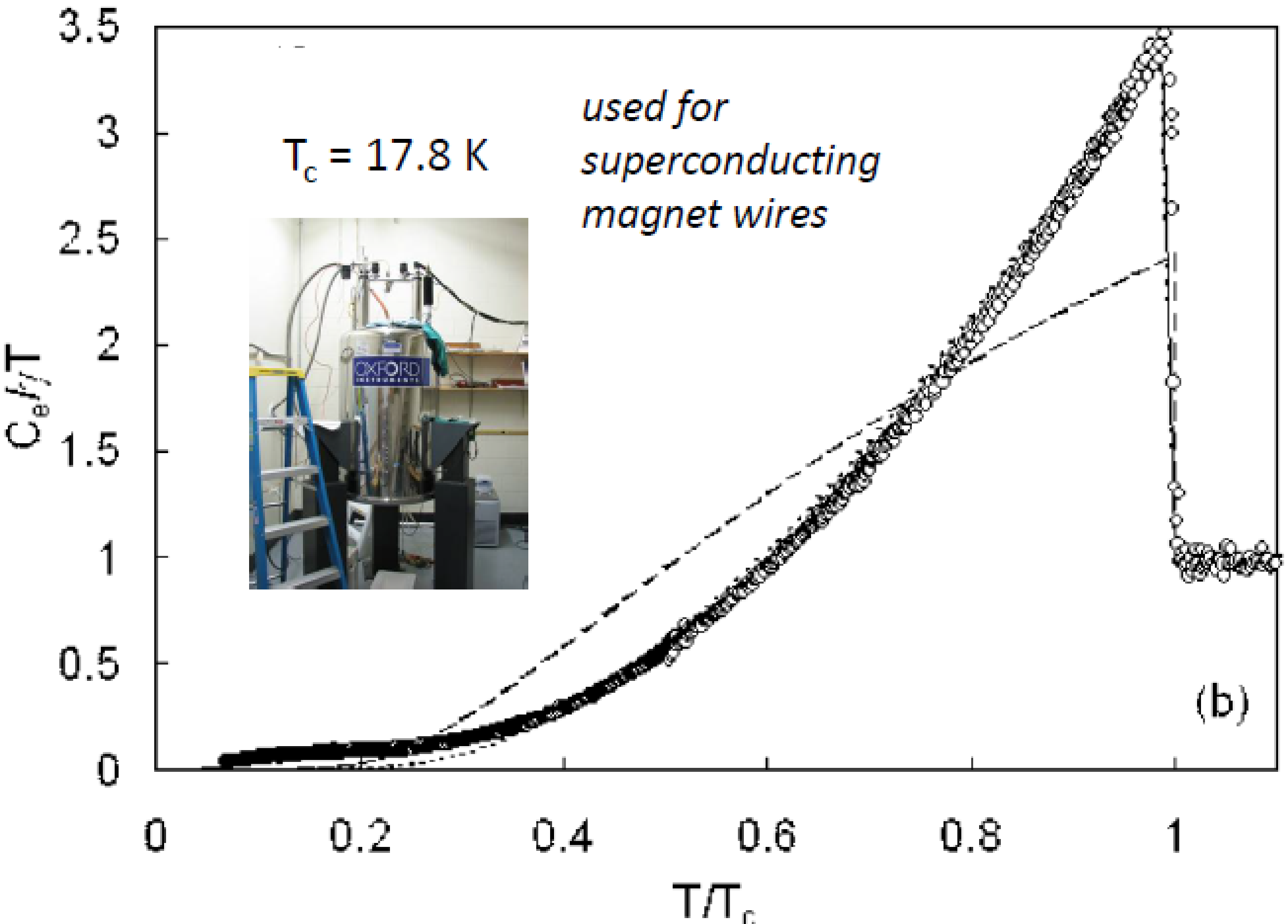


Experiments that probe the Fermi surface can probe the superconducting gap

Electronic specific heat of metal: $C/T \sim N(E_F)$

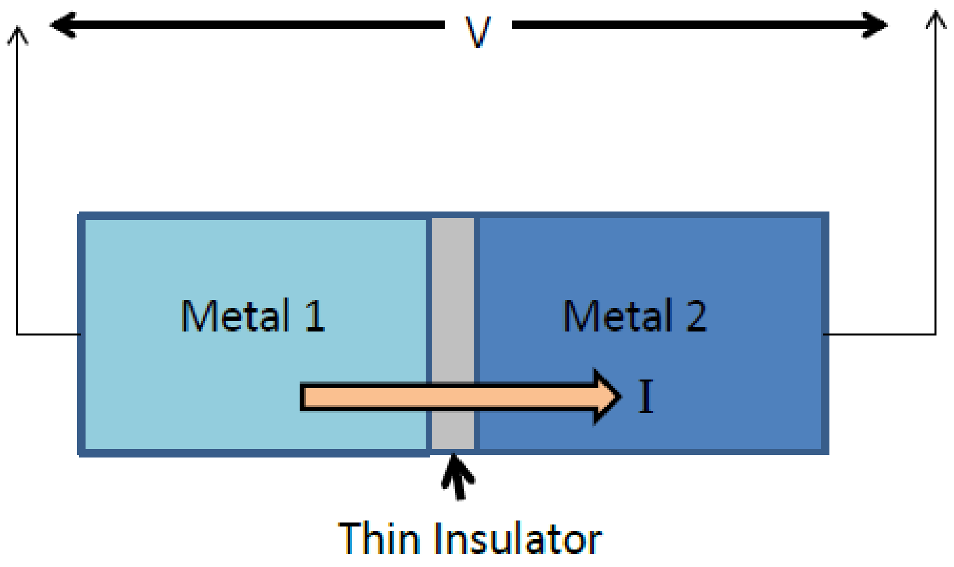
In SC state: $C/T \sim e^{-\Delta/k_B T}$

Example: Nb_3Sn

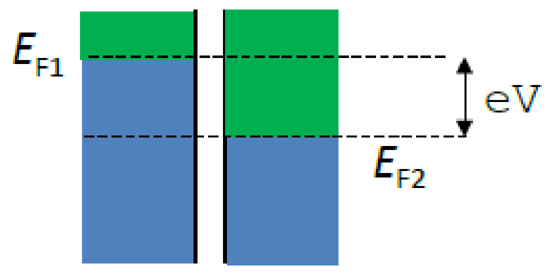


Guritano et al. PRB 2004

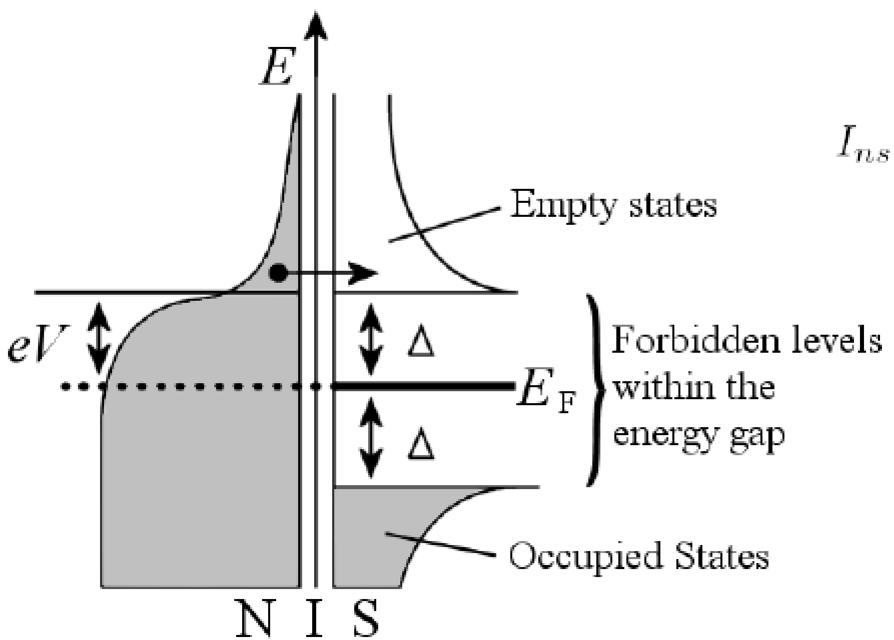
Tunneling: NIN junction



$$I \sim \int N_1(E+eV)N_2(E)[f(E)-f(E+eV)]dE \sim N_1(E_F)N_2(E_F)eV$$



Tunneling: NIS Junction

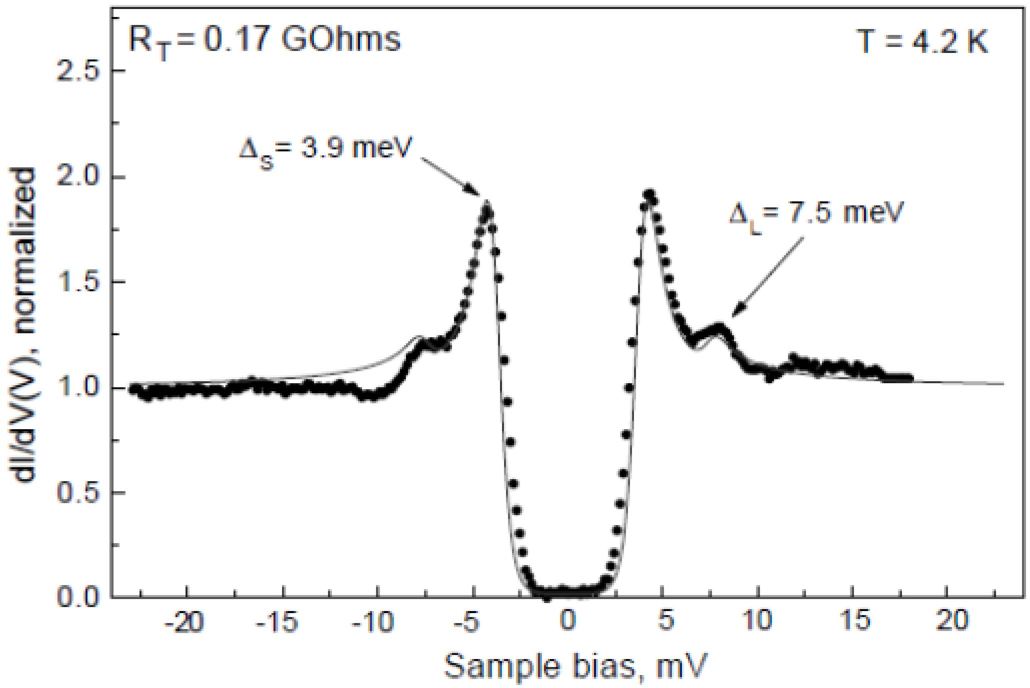


$$I_{ns} \sim N_n(E_F) \int N_s(E)[f(E) - f(E_e V)]dE$$

$$\boxed{\Rightarrow \frac{dI_{ns}}{dV} \sim N_s(eV)}$$

Can probe density of states directly by measuring the differential conductance

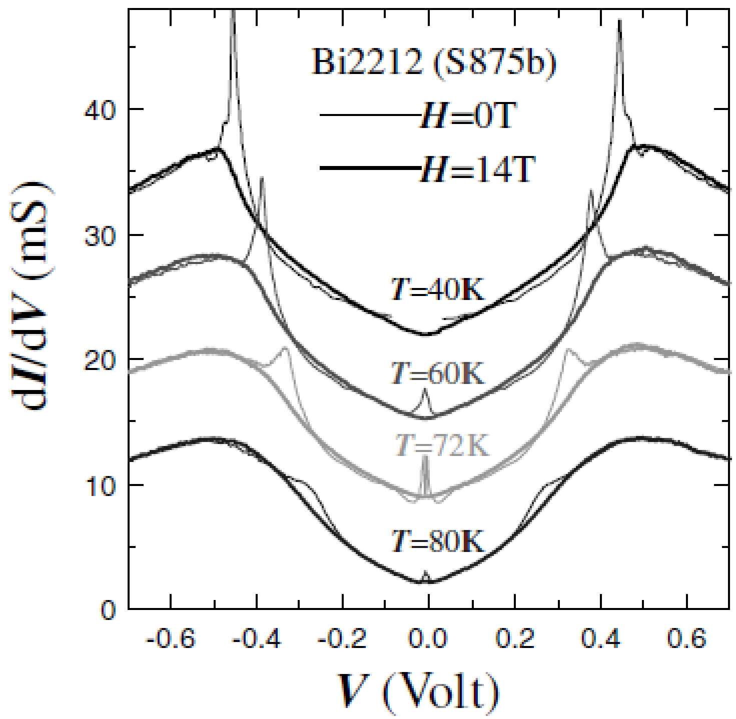
Example: MgB_2



Note the presence of two gaps!

Giubelio et al, EPL (2002)

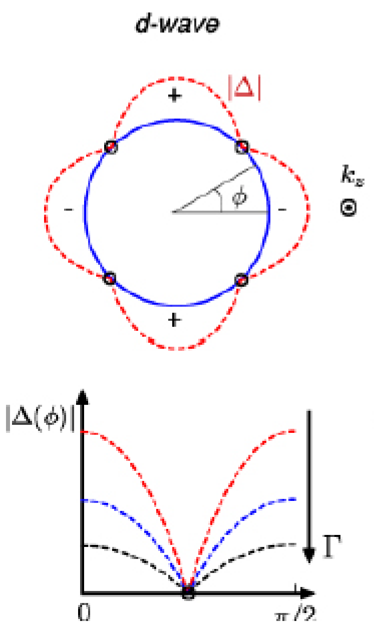
Example: High T_c



Krasnov et al., PRL (2001)

Does not show flat DOS , but something more like a V shape

This is due to the d-wave nature of the superconducting gap



Efeitos de impurezas magnéticas

Teoria de Abrikosov-Gorkov

$$\left|\frac{\Delta T_c}{\Delta c}\right| = \frac{\pi^2}{8}\eta(E_F)\langle J^2(\mathbf{q})\rangle S(S+1),$$

$\eta(E_F)$ é a densidade de estados por spin no nível de Fermi, S é o spin da impureza magnética, J(q) é a interação de troca entre o spin da impureza e o spin dos elétrons do par (que depende de **q)**

SCIENTIFIC REPORTS | 4 : 6252 | DOI: 10.1038/srep06252 3

www.nature.com/scientificreports

Table 1 | Experimental and calculated parameters for $BaFe_{1-x}M_yAs_2$ (this work) and conventional SC (refs. [31, 37])

Sample	c (%)	g_{ESR}	$\|\Delta T_c^{exp}\|$(K)	$T_{c,0}$ (K)	$\langle J^2(\mathbf{q})\rangle^{1/2}_{ESR}$(meV)	$\langle J^2(\mathbf{q})\rangle^{1/2}_{AG}$(meV)
$BaFe_{1.9}Cu_{0.1}As_2$	5	2.08(3)	22	26	1.2(5)	111(10)
$BaFe_{1.88}Mn_{0.12}As_2$	6	2.05(2)	≥26	26	0.7(5)	≥32(3)
$BaFe_{1.895}Co_{0.100}Mn_{0.005}As_2$	0.25	2.06(2)	10	26	0.8(5)	98(9)
$Lu_{1-x}Gd_xNi_2B_2C$	0.5	2.035(7)	≈0.3	15.9	10(4)	11(1)
$Y_{1-x}Gd_xNi_2B_2C$	2.1	2.03(3)	≈0.9	14.6	9(3)	10(1)
$La_{1-x}Gd_xSn_3$	0.4	2.010(10)	≈0.5	6.4	20(2)	≈20(2)

MgB_2: Motivação (2001)

O que faz MgB_2 ser tão especial?

Por que o grande interesse nestes materiais?

Promete que MgB_2 seja um bom candidato à aplicações

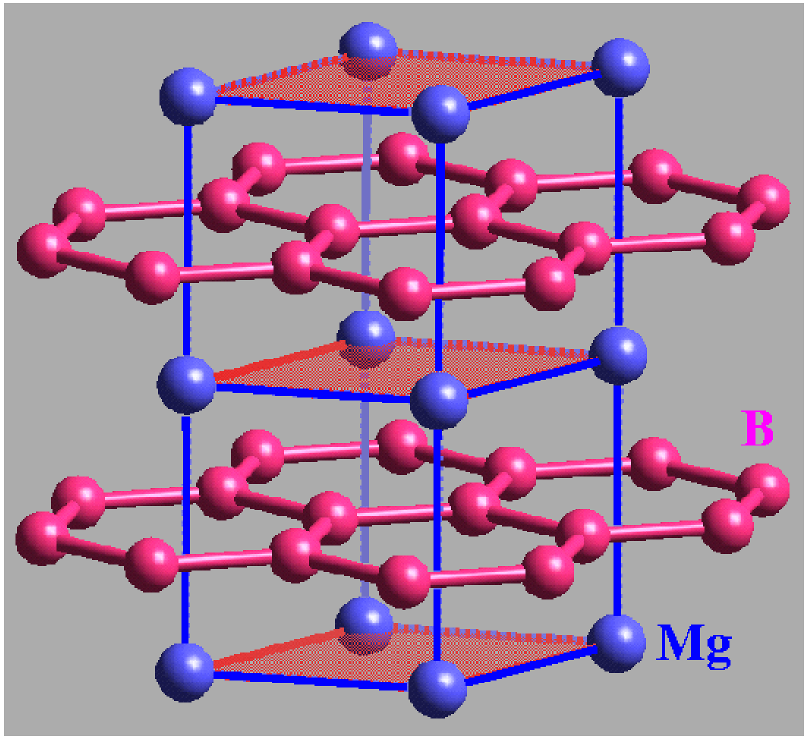
- Alta T_C : 39 K
- Simples estrutura cristalina
- Grande comprimento de coerência ($\xi \approx$
- Alto Campo Crítico: $14\ T \leq H_{c2} \leq$
- Alta densidade de corrente crítica (J_c (4.2 K, 0T) > 10^7 A/cm^2)
- Anisotropia: $\gamma = 1.2 \div 9$
- Custo: Material barato e fácil de obter

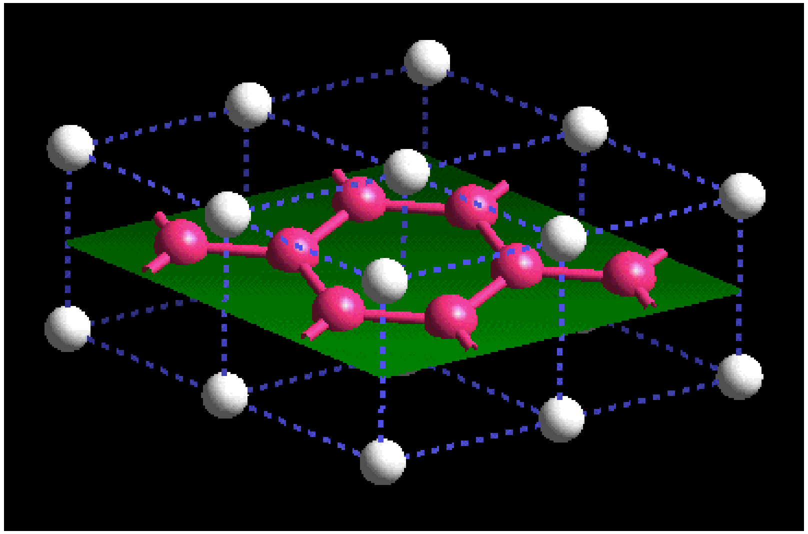
- Sem falar que ele despertou o g<u>de</u> interesse em SC não-óxidos
- Catalizou a descoberta de supercondutividade em muitos outros compostos como por ex. C-S e $MgCNi_3$.

MgB_2: Motivação (2001)

Estrutura hexagonal simples tipo AlB_2

Átomos de Boro formam camadas como no grafite separadas por camadas de átomos de Mg.





Carbono é a chave?

VOLUME 87, NUMBER 14 PHYSICAL REVIEW LETTERS 1 OCTOBER 2001

Indication of Superconductivity at 35 K in Graphite-Sulfur Composites

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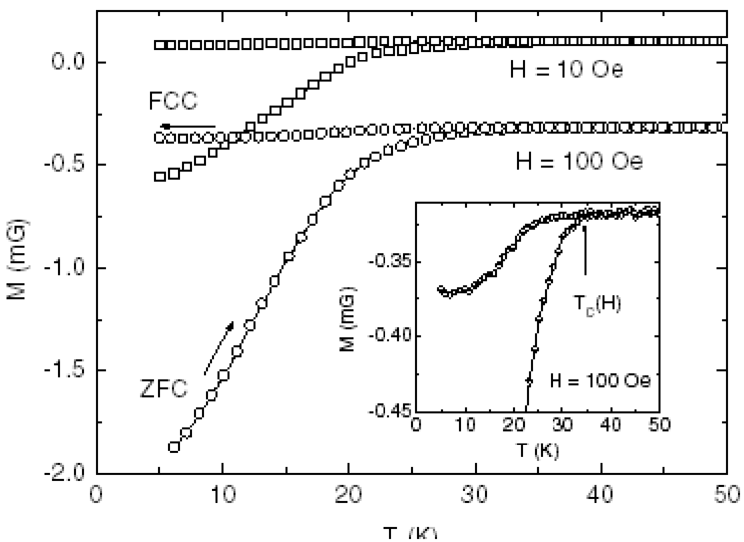
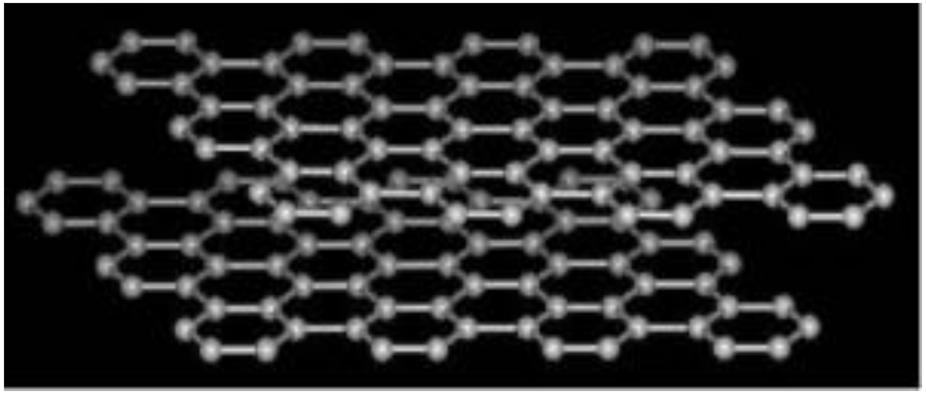
(Received 17 May 2001; published 12 September 2001)

We report magnetization measurements performed on graphite-sulfur composites which demonstrate a clear superconducting behavior below the critical temperature $T_{c0} = 35$ K. The Meissner-Ochsenfeld effect, screening supercurrents, and magnetization hysteresis loops characteristic of type-II superconductors were measured. The results indicate that the superconductivity occurs in a small sample fraction, possibly related to the sample surface.

DOI: 10.1103/PhysRevLett.87.147001 PACS numbers: 74.10.+v, 74.80.–g





Diamantes Supercondutores (2004).

Superconductivity in diamond

E. A. Ekimov[1], V. A. Sidorov[1], E. D. Bauer[2], N. N. Mel'nik[3], N. J. Curro[2], J. D. Thompson[2] & S. M. Stishov[1]

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Diamond is an electrical insulator well known for its exceptional hardness. It also conducts heat even more effectively than copper, and can withstand very high electric fields[1]. With these physical properties, diamond is attractive for electronic applications[2], particularly when charge carriers are introduced (by chemical doping) into the system. Boron has one less electron than carbon and, because of its small atomic radius, boron is relatively easily incorporated into diamond[3]; as boron acts as a charge acceptor, the resulting diamond is effectively hole-doped. Here we report the discovery of superconductivity in boron-doped diamond synthesized at high pressure (nearly 100,000 atmospheres) and temperature (2,500–2,800 K). Electrical resistivity, magnetic susceptibility, specific heat and field-dependent resistance measurements show that boron-doped diamond is a bulk, type-II superconductor below the superconducting transition temperature $T_c \approx 4$ K; superconductivity survives in a magnetic field up to $H_{c2}(0) \geq 3.5$ T. The discovery of superconductivity in diamond-structured carbon suggests that Si and Ge, which also form in the diamond structure, may similarly exhibit superconductivity under the appropriate conditions.

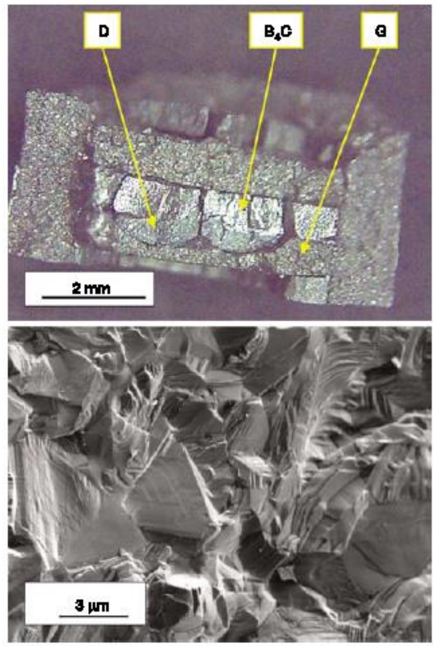
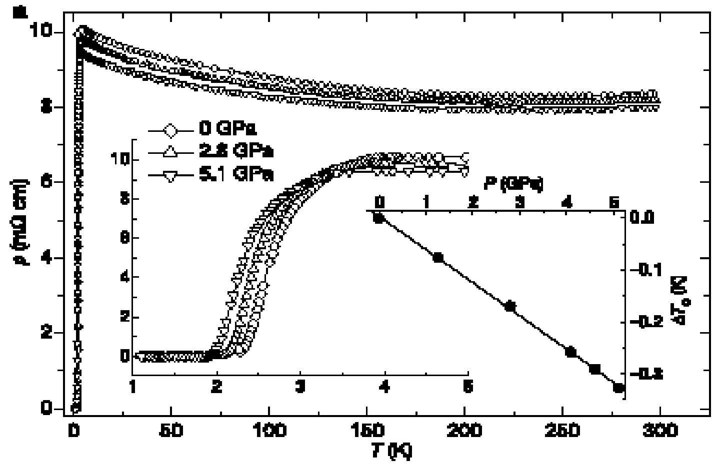
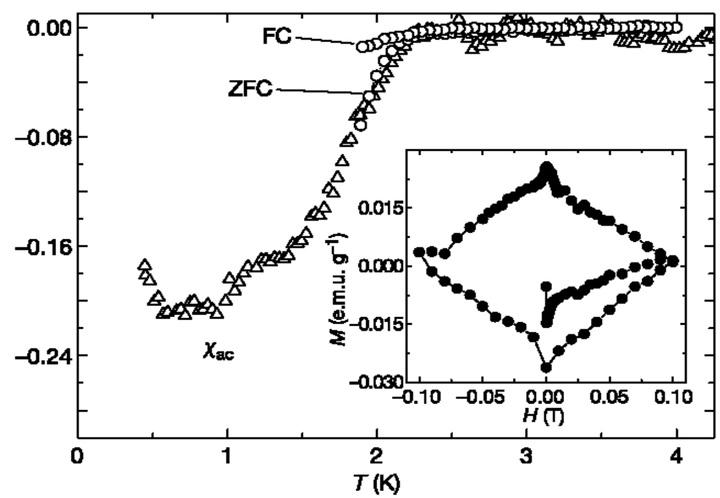


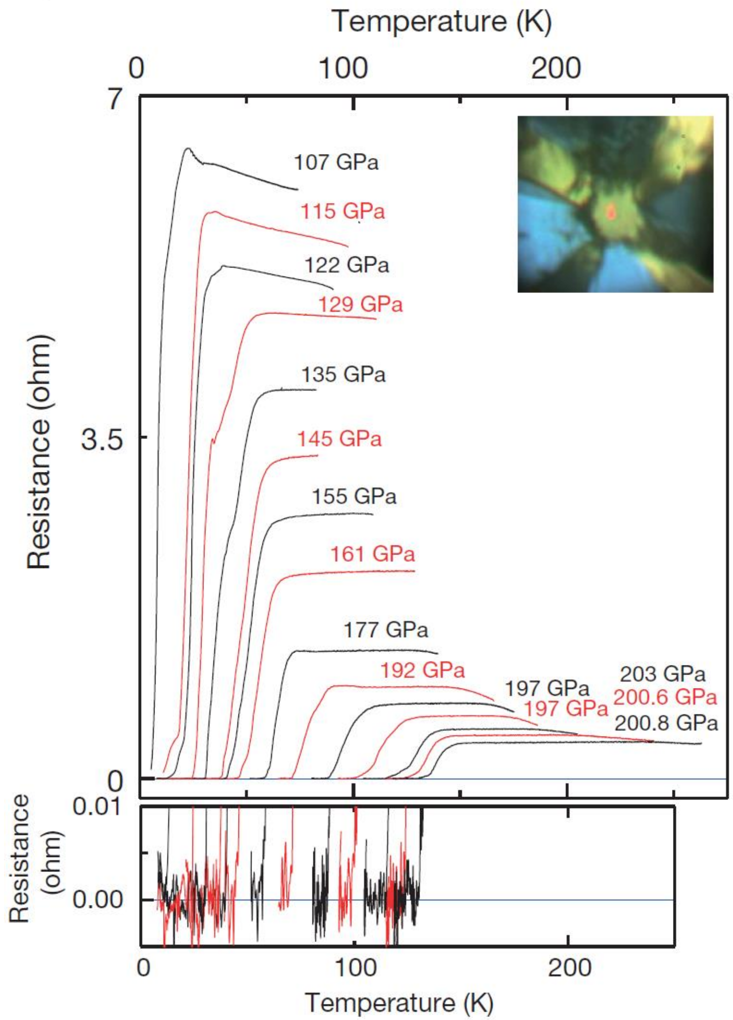
Figure 1 Optical and scanning electron microscopy images of the material. Top, central part of the high-pressure synthesis cell after subjecting graphite and B_4C to high-pressure, high-temperature conditions. D, diamond; G, graphite. Bottom, SEM image of B-doped diamond synthesized at high pressures and temperatures.

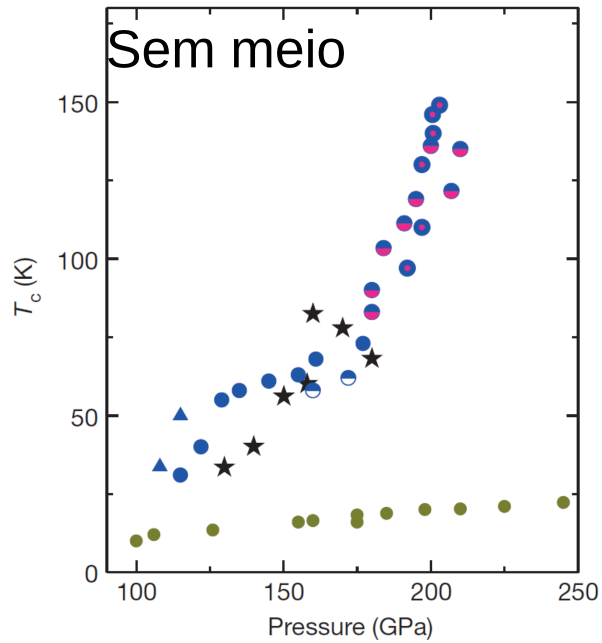
NATURE | VOL 428 | 1 APRIL 2004 | www.nature.com/nature

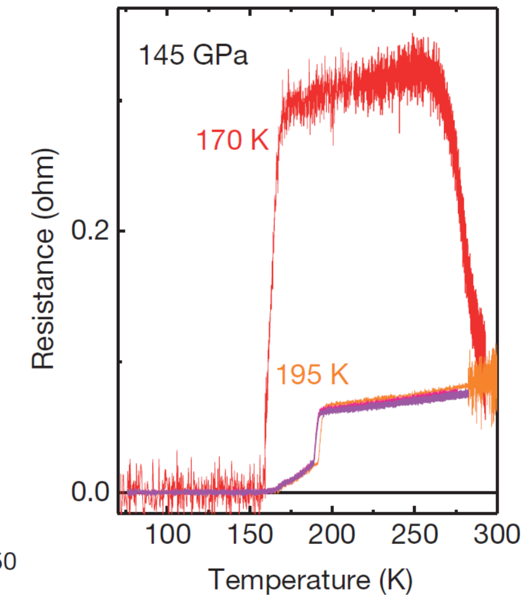




H_2S







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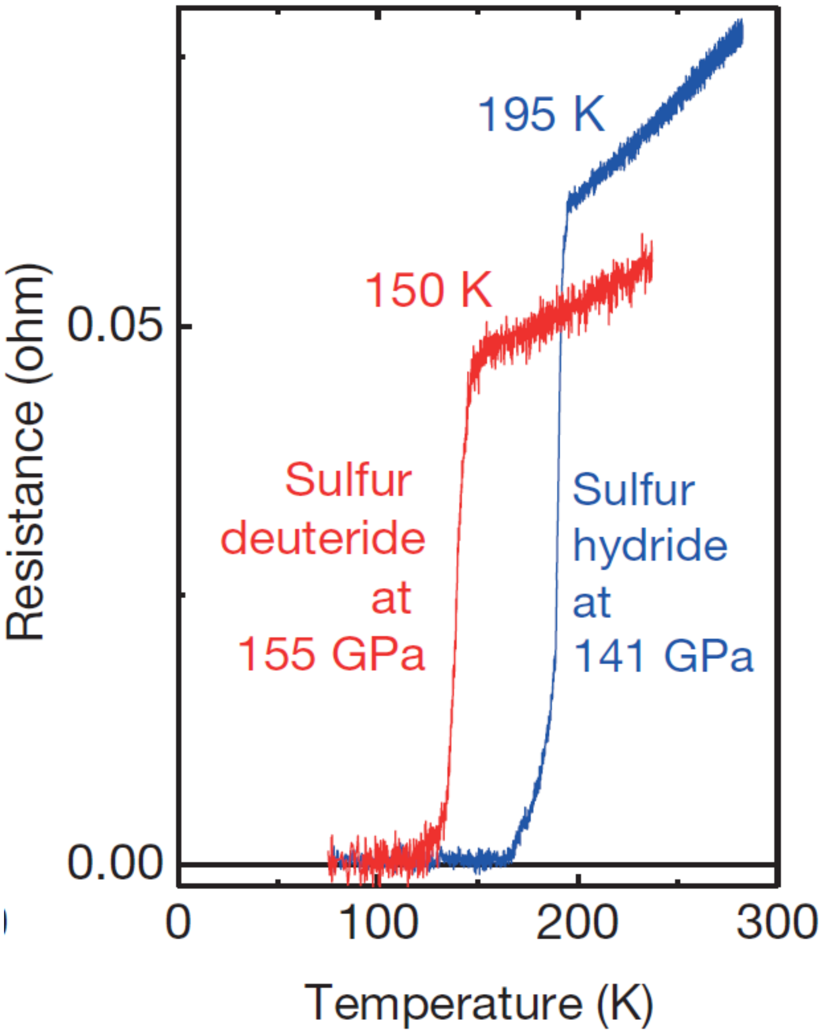
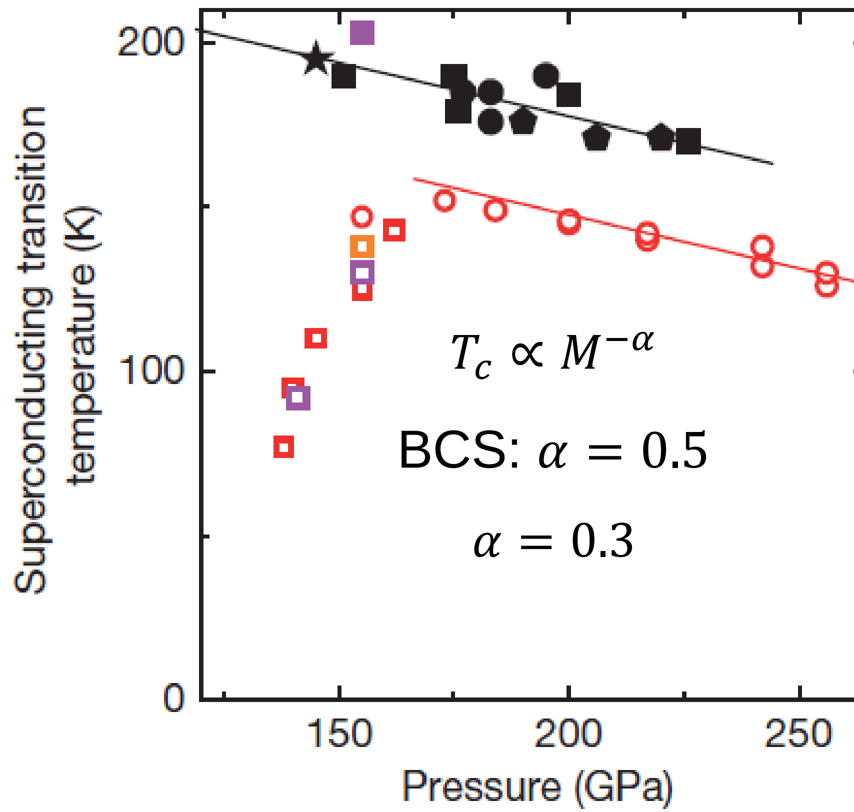
H_2S

- Efeito Isotópico:

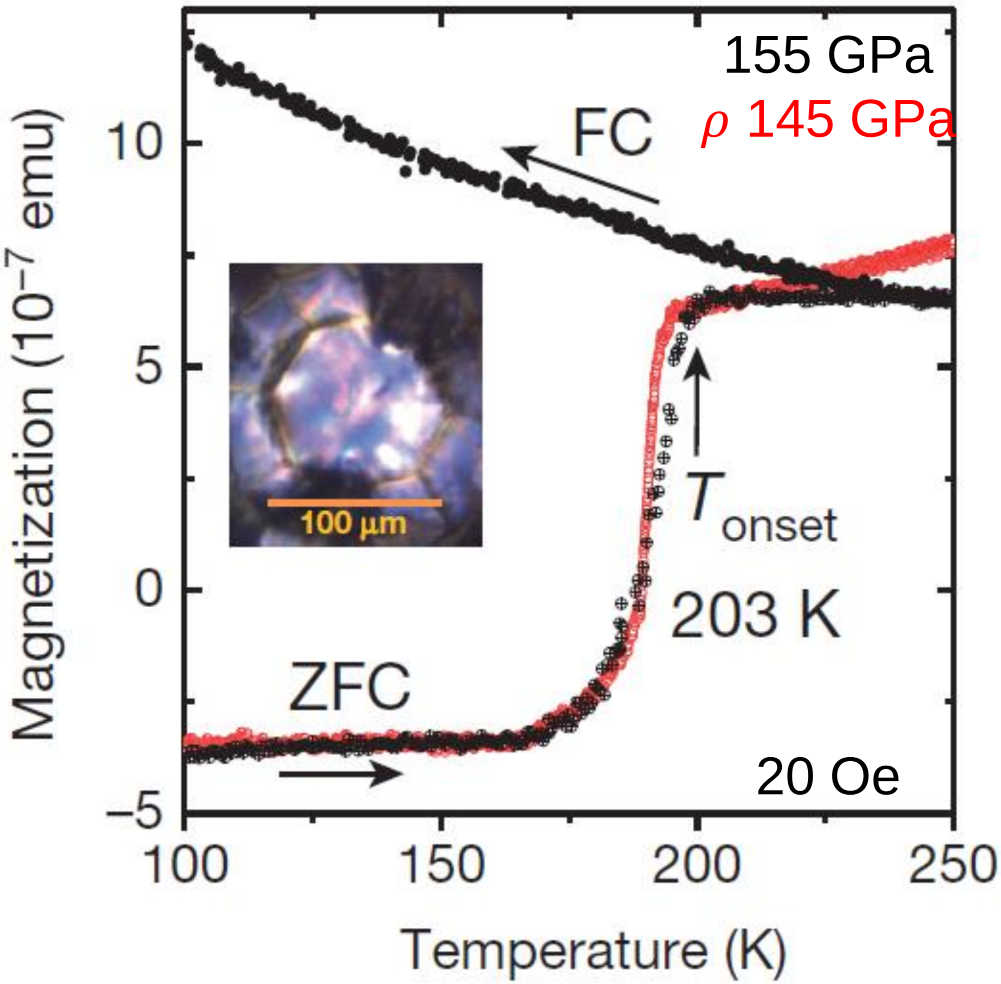


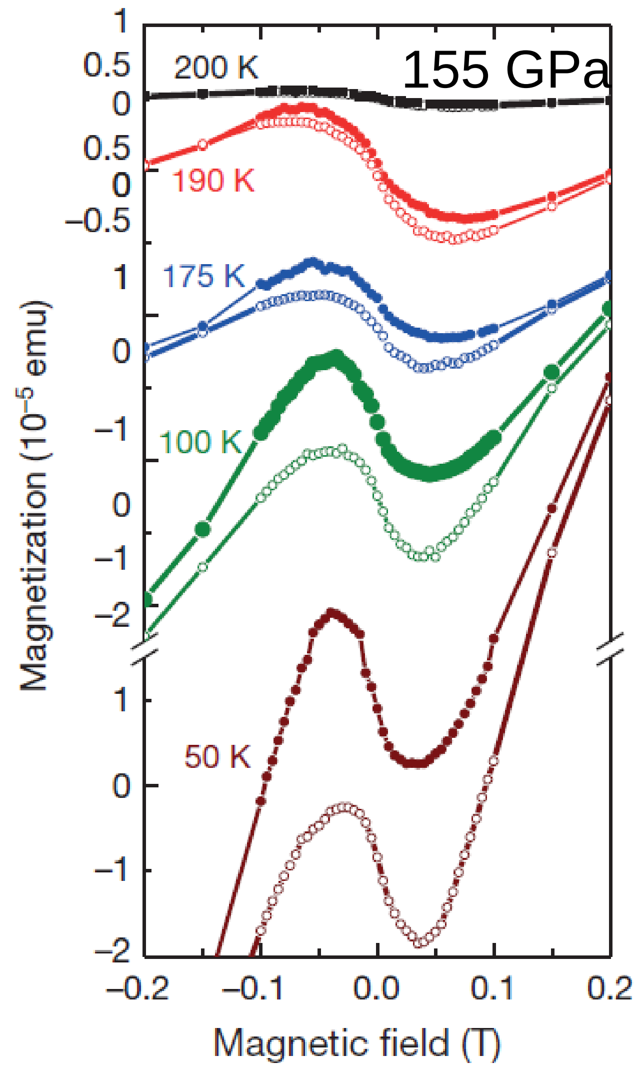


A. P. Drozdov, M. I. Eremets, I. A. Troyan, V. Ksenofontov & S. I. Shylin. *Nature* **525,** 73 (2015)

H_2S

❖ Efeito "Meissner":





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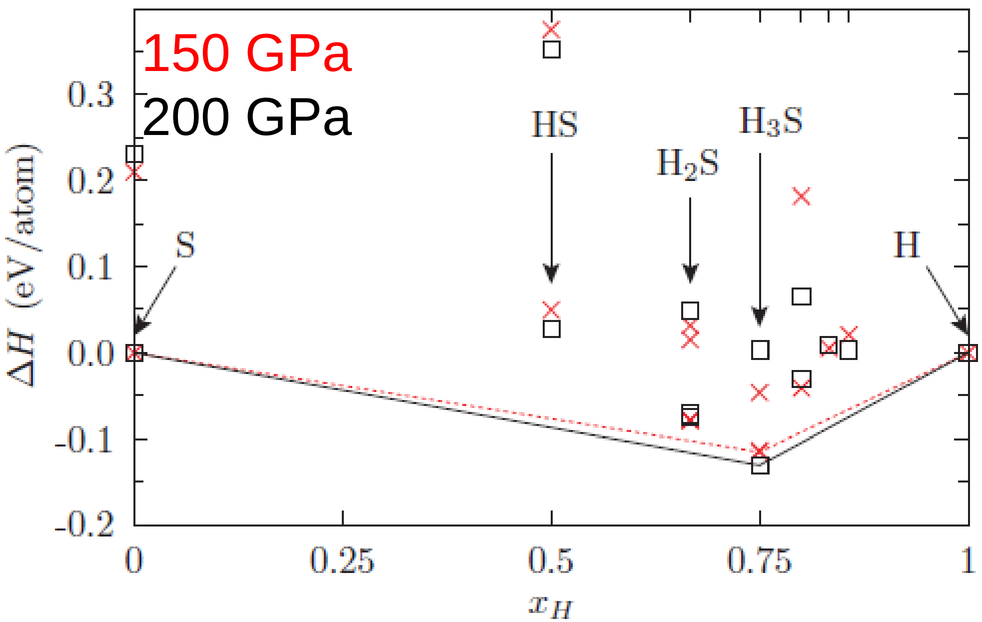
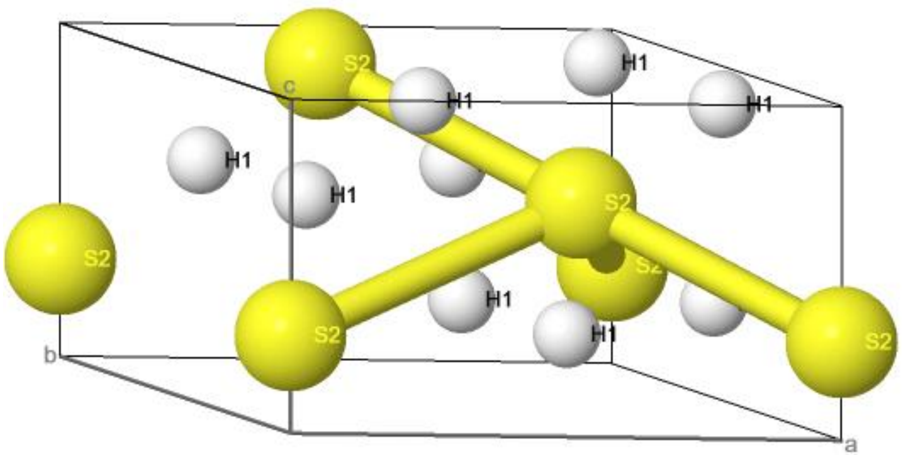
$3H_2S \rightarrow 2H_3S + S$



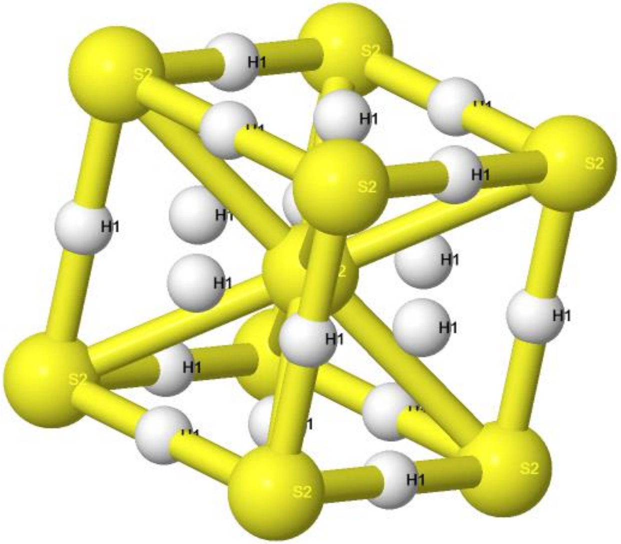
N. Bernstein, C. Stephen Hellberg, M. D. Johannes, I. I. Mazin, and M. J. Mehl, PHYSICAL REVIEW B **91**, 060511(R) (2015)

$3H_2S \rightarrow 2H_3S + S$

R3m - ICSD



Im3m - ICSD



Grupo Pontual	Estrutura	P (GPa)	μ^*	λ	ω_{log} (K)	T_c (K)
R3m	Monoclínica	130	0.1 – 0.13	2.07	1125.1	155 – 166
Im3m	Cúbica	200	0.1 – 0.13	2.19	1334.6	191 – 204

Duan, D. et al. Sci. Rep. **4**, 6968 (2014)

Rota para novos SC convencionais - Resumo

- Átomos leves tenderão a gerar T_C maiores

$$T_c \sim 0.3 - 0.4\ \Theta_D$$

•Materias bem metálicos - alta densidades de estados no nível de Fermi.

•Impossível prever potencial de pareamento

•Não há relação direta com estrutura cristalina, mas estrutura em camadas geraram supercondutores de alta-T_C - exemplos MgB_2 e borocarbides. (soft modes)

• Impurezas Magnéticas atrapalham a SC convencional