

APPLIED SUPERCONDUCTIVITY (Superconducting materials)

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CERN, Academic Training, Jan 19 2007

Lecture 3 of 3



Different classes of superconductors (after Buzea and Yamashita).

		<i>T</i> _c (K)	$H_c(0)$ (GAUSS)
Al		1.196	99
Cd		0.56	30
Ga		1.091	51
Hf	1	0.09	
Hg	α (rhomb)	4.15	411
U	β	3.95	339
In		3.40	293
Ir		0.14	19
La	α (hcp)	4.9	798
+	β (fcc)	6.06	1096
Мо		0.92	98
Nb		9.26	1980
Os		0.655	65
Pa		1.4	· · · · · ·
Pb		7.19	803
Re		1.698	198
Ru		0.49	66
Sn		3.72	305
Та		4.48	830
Tc		7.77	1410
Th		1.368	162
Ti	-	0.39	100
Tl		2.39	171
U	α	0.68	
100	γ	1.80	-
V		5.30	1020
W		• 0.012	1
Zn		0.875	53
Zr		0.65	47

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Disorder effect on TC



In the **Tl-Pb-Bi** System, the mass can be held almost constant and the variation of T_C with e/a can be studied in a continuous fashion even up to 9 K



Variation of Transition Temperature with electrons-to-atom ratio in the Tl-Pb-Bi alloy family. *After Dynes and Rowell, Phys. Rev. B* 11,1884 (1975)

Strong Correlations among Superelectrons within a coherence length ξ_0

$$\vec{J}_{s}(\vec{r}) = \int_{\xi_{0}} f(\vec{r}_{1} - \vec{r}) \cdot \vec{A}(\vec{r}_{1}) d\vec{r}_{1}$$

instead of
$$\vec{J}_{s} = -\frac{\vec{A}}{\lambda_{L}^{2} \mu_{0}}$$









$$N(E_{F}) / T_{C} / T_{C} / T_{C} / T_{C} = 1.14\Theta_{D} e^{-\frac{1}{N(E_{F})V - \mu^{*}}}$$

$$\Theta_{\rm D}$$
= Debye Temperature (for TM 250÷450 K)

 $N(E_F)$ = Electronic density of states at the Fermi level

V = attractive potential (phonon-mediated)

 μ^* = coulombian pseudo-potential

Electronic density of states



N(E_F) /

Calore spElectronic specific heat

 $N(E_F)$ can be calculated from:

$$C_e = \gamma \cdot T$$

being

$$\gamma = \frac{\pi^2}{3} \cdot k_B^2 \cdot N(E_F)$$







Matthias empirical rule



It works only for neighbourhood elements in per. table.

Critical Temperature of compounds with NaCl structure

BA	Sc	Y	La	Ti	Zr	Hf	۷	Nb	Та	Cr	Мо	W	Re
В	Sec. 2			1.0	3.4	3.1							
С	<1.38	<1.38		3.42	<0.3	<1.20	0.03 3.2*	12	10.35		14.3	10.0	3.4
N	<1.38	<1.4	1.35	5.49	10.7	8.83	8.5	17.3	6.5	<1.28	5.0	<1.38	
Р	(16) (16)		<1.68					f e tra					
Sb		<1.02	<1.02	연고					sa di sa				
0		121/25	2-1-	2.0			<0.3	1.39					e n Viber Standy
S	<0.33	1.9	0.87		3.3				, the second		4.4		
Se	<0.33	2.5	1.02									1.15	
Te		2.05	1.48		te di	1.10	Vejta Stario M						

 T_{c} = 3.2 K was registered in vanadium carbide after implantation of C⁺ ions s

Critical temperature vs composition for nitride and carbide addition to NbN





A.Nigro, G.Nobile, <u>V.Palmieri</u>, R.Vaglio, "PROPERTIES OF NIOBIUM-TITANIUM NITRIDE SUPERCONDUCTING THIN FILMS", Adv. Cryog. Eng. Mat., vol. 34, (1988) 813



SUPERCONDUCTING THIN FILMS", Adv. Cryog. Eng. Mat., vol. 34, (1988) 813

PdH is a very famous material for the reversal isotope effect and it has low resistivity

And Hydrides of Pd-Ag and Pd-Cu display Tc up to 15K!!!



The A atoms form linear chains parallel to the [100], [010], [001] directions



Nontransition elements	<i>Т</i> _с (К)	Transition elements	T _c (K)
Ti ₃ Sb	6.5	Ti ₃ Ir	4.2
$Zr_{so}Sn_{20}^{a}$	0.92	Ti ₃ Pt	0.5
Zr–Pb	0.76	Zr ₃ Au	0.9
Zr~3Bib	3.4	V.,Re.,	8.4
V–Al ^e	14	V ₅₀ Os ₅₀	5.7
V ₃ Ga	15.9	V ₆₅ Rh ₃₅	$\simeq 1$
V,Si	17.0	$V_{63}Ir_{37}$	1.7
$V_{\sim 3}Ge$	6	$V_{\sim 3}Pd$	0.08
V ₃ Ge ² V ₃ Sn	3.8	V ₃ Ft V ₂ Au	3.7
~79011~21	0.0	, ₇₆ , 10 ₂₄	1.0
V ₇₇ As ₂₃	0.2	Nb ₇₅ Os ₂₅	1.0
V ₇₆ SD ₂₄	0.8	Nb Ir	2.0
Nb ₃ Al	19.1	Nb,Pt	11
Nb ₃ Ga	20.7	Nb_Au	11.5
Nb _{~3} In ^o	9.2	To Dt	0.4
1NO ₈₂ SI ₁₈	4.4	$Ta_{85}Ft_{15}$	0.55
Nb-Si ^c	11-17	x a ~ 80° x a 20	0.55
Nb-Ge ^a	17	Cr ₇₂ Ru ₂₈	3.4
ND-Ge ^e	23	$Cr_{73}Os_{27}$	4.7
Nb-Sh	2	$Cr_{78}Rn_{22}$	0.75
Nb Bib	3	C182118	
T- C-	-	Mo ₄₀ Tc ₆₀	13.4
Ta_3Ge	8 2	Mo Oc	≃15 12.1
$Ta_{3}Sh$	0.7	Mo. Ir.	8.5
14~300	0.7	Mo ₈ ,Pt.,	4.6
Mo ₃ Al	0.58	W D	11
Mo ₃ Ga	0.76	w _{~60} Ke _{~40} °	11
$M_{0,77}SI_{23}$	1.7		
110770023	1.0		

a Rapid quenching b High-pressure synthesis c Film deposition techniques



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Vapor Sn Diffusion



Procedure

- 1) Cavity manufactoring
- 2) Formation of nucleation centers
 of Nb₃Sn (Nb Surface
 Anodization + SnCl₂ Treatment)
- Nb₃Sn film growth in a Sn atmosphere (T = 1050-1250°C,
 - t = dozens of h, p(Sn) ~ 10⁻³mbar)
- 4) Cool down and unwanted phases
 Chemical removal (anodizaton + HF 48%)
 Technique Choice Reasons

Liquid Sn Diffusion?

Bulk Nb substrate dipping Sample Annealing

No nucleation sites on Nb are required

• Fast growth of Nb_3Sn layer

Deasirable uniform thickness

Technique Choice Reasons

Used System



SEM Image

Process T = 1000°C Dipping t = 120' Annealing t = 14h Post annealing: 5h at 500°C



10 µm

Method: "1 step" process

XRD spectrum

Process T = 1000°C, Dipping t = 30', Annealing t = 10h



Method: "1 step" process

A Superconductive Transition Curve



Method: "1 step" process

Francesco Todescato, Thesis 2004, Material Science Dept, Padua University

Synthesis of Niobium Pentakis(dimethilammide)

The reaction happens in two different steps:

First the Me₂NH 50 mL is bubbled for around 90 minutes in LiBu:

 $Me_2NH + LiBu \rightarrow LiNMe_2 + BuH$

Than the butane is evaporated and the product obtained is suspended in pentane and treated by NbCl₅

pentane

$NbCl_{5} + 5LiNMe_{2} \rightarrow Nb(NMe_{2})_{5} + 5LiCl$

 $\begin{array}{c|c} H_{3}C & CH_{3} \\ H_{3}C & N \\ H_{2}C > N & | \\ H_{3}C > N' & | \\ H_{3}C > N' & | \\ H_{3}C & N \\ H_{3}C & CH_{3} \end{array}$

The Ammide is a brrownish powder that sublimes at 130°C



Experimental setup: sputtering



Thin films and new ideas for pushing the limits of RF superconductivity, Legnaro 9-12 October 2006
Thin film grown

Condition of deposition

P base = 1.5×10^{-6} mbar P sputtering = 4.0×10^{-3} mbar



Annealed after sputtering for 3 hours at 975 °C

Thin films and new ideas for pushing the limits of RF superconductivity, Legnaro 9-12 October 2006

Results: X-ray diffraction



Thin films and new ideas for pushing the limits of RF superconductivity, Legnaro 9-12 October 2006

Results: Superconductive characteristic



Thin films and new ideas for pushing the limits of RF superconductivity, Legnaro 9-12 October 2006



Tc vs Si content for sputtered films before and after in situ post-annealing in SiH4 atmosphere



Y. Zhang, V. Palmieri, W. Venturini, F. Stivanello, R. Preciso, LNL-INFN (REP) 157/2000

Molybdenum-Rhenium

Most commonly known as **Moly-Rhenium**, and used extensively throughout many industries -from medicine to defense and pure research to production welding, this material is a less costly alternative to pure rhenium.

Possessing excellent thermal and mechanical properties, **Moly-Rhenium** is used as welding wire, wires for numerous medical applications, components and parts for the aerospace and defense industries, and grids for electronic applications.

Density, g/cm ³	13.52
Melting Point, °C	2550
Thermal Conductivity, W/m at 20°C	36.8
Linear Coefficient of Thermal Expansion, µm/m·K from 20-1000°C	5.7
Ductile Brittle Transition Temperature (DBBT), °C	(-273)-(-173)
Critical Superconducting temperature, K	10.9
Electrical Resistivity, μΩ·m at 20°C	0.220
Elastic Modulus in Tension, GPa	373



Curve **A** - Films sputtered at ~ **500** Å/min onto **1000** °C substrates Curve **B** – Films sputtered at ~ **1000** Å/min onto **1200** °C substrates Curve **C** – Bulk Mo-Re samples

From Blaugher et al

Mo₃₈Re₆₂ (after Testardi)



(The author communicates that the Temperature was 150 C lower than reported in the picture)



Thin Films by Single Target Magnetron Sputtering", IEEE Trans. Mag., 25, 2, (1989) 1972





Magnetic Superconductors

Struttura cristallina di compostiEr-Rh₄B₄



Er-Rh₄B₄





Fig. 1-1. J. Georg Bednorz and K. Alex Müller at IBM's Zurich Research Laboratory.



Fig. 1-2. Dr. Paul Chu, T.L.L. Temple Chair in Science, University of Houston.





Fig. C. President Ronald Reagan receives a lesson in superconductivity from Alan Schriesheim, the director of Argonne National Laboratory (left).



Figure 1.2. The time evolution of the superconducting critical temperature since the discovery of superconductivity in 1911. The solid line shows the T_s evolution of metallic superconductors, and the dashed line marks the T_s evolution of superconducting oxides.



Fig. 1 Crystal structure of the superconductor type Bi₂ $(Sr_{1-y}Ca_y)_3$ Cu_2O_{10-b} developed by Hoechst. Key: green = calcium (Ca), red = copper (Cu), black = oxygen (O), yellow = strontium (Sr), blue = bismuth (Bi). InSnBa₄Tm₄Cu₆O₁₈₊ (As a 1234/1212 intergrowth.)

 $(Hg_{0.8}Tl_{0.2})Ba_{2}Ca_{2}Cu_{3}O_{8.33} \\ HgBa_{2}Ca_{2}Cu_{3}O_{8} \\ HgBa_{2}Ca_{3}Cu_{4}O_{10+} \\ HgBa_{2}(Ca_{1-x}Sr_{x})Cu_{2}O_{6+} \\ HgBa_{2}CuO_{4}+$

 $\begin{array}{l} TI_{2}Ba_{2}Ca_{2}Cu_{3}O_{10} \\ (TI_{1,6}Hg_{0,4})Ba_{2}Ca_{2}Cu_{3}O_{10+} \\ TIBa_{2}Ca_{2}Cu_{3}O_{9+} \\ (TI_{0,5}Pb_{0,5})Sr_{2}Ca_{2}Cu_{3}O_{9} \\ TI_{2}Ba_{2}CaCu_{2}O_{6} \\ (TI_{0,5}Sn_{0,5})Ba_{2}(Ca_{0,5}Tm_{0,5})Cu_{2}O_{x} \\ TIBa_{2}Ca_{3}Cu_{4}O_{11} \\ TIBa_{2}CaCu_{2}O_{7+} \\ TI_{2}Ba_{2}CuO_{6} \end{array}$

 $\begin{array}{l} Sn_{2}Ba_{2}(Ca_{0.5}Tm_{0.5})Cu_{3}O_{x}\\ SnInBa_{4}Tm_{3}Cu_{5}O_{x}\\ Sn_{3}Ba_{8}Ca_{4}Cu_{11}O_{x}\\ Sn_{4}Ba_{4}Tm_{3}Cu_{7}O_{x}\\ Sn_{3}Ba_{4}Y_{2}Cu_{5}O_{x}\\ SnInBa_{4}Tm_{4}Cu_{6}O_{x}\\ Sn_{2}Ba_{2}(Sr_{0.5}Y_{0.5})Cu_{3}O_{8}\\ Sn_{4}Ba_{4}Y_{3}Cu_{7}O_{x}\\ \end{array}$

 $\begin{array}{c} Bi_{1.6}Pb_{0.6}Sr_{2}Ca_{2}Sb_{0.1}Cu_{3}O_{y}\\ Bi_{2}Sr_{2}Ca_{2}Cu_{3}O_{10}\\ Bi_{2}Sr_{2}CaCu_{2}O_{9}\\ Bi_{2}Sr_{2}(Ca_{0.8}Y_{0.2})Cu_{2}O_{8}\\ Bi_{3}Sr_{3}CaCu_{3}O_{8}\\ \end{array}$



 $(Ca_{1-x}Sr_{x})CuO_{2}$

(The First Non-Cuprate High-temperature Superconductor)

A recent preprint by S. Reich and Y. Tsabba (Weizmann Institute) reported experimental evidence suggesting the possibility of superconductivity with Tc ~ 91 K in WO3 crystals with a surface composition of Na0.05WO3

As of October, 2000, Shimon Reich reports that the 91K Tc has been confirmed, but is localized in small islands about 100nm across and 10nm in height on the surface of the material. He also states that, as yet, no other tungsten-bronze compounds have exhibited this kind of high-temperature 2D superconductivity. Rb and Cs surface-doped WO3 only exhibit Tc's ~6K.



YBCO thin films on large area substrates

P.Romano, A. Vecchione, G. Keppel and V. Palmieri

DIODE Sputtering at **950 C at 1 mbar** onto sapphire, and SrTiO3

Distance cathode substrate = 10 mm





Structure of MgB₂ containing graphite-type B layers separated by hexagonal close-packed layers of Mg (After Buzea and Yamashita)



Giorgio Keppel, Thesis 2004, Material Science Dept, Padua University





T-dependence of the order parameter from fit with the one-gap model. $\Delta_{dirty}(T)$ and $\Delta_{3D}(T)$ from fit with the two-gap model. Fit to BCS curves

T-dependence of the order parameter from fit with the one-gap model. Δ_{dirty} (T) and Δ_{3D} (T) from fit with the two-gap model. Fit to BCS curves



(after G. Carapella, N. Martucciello, G. Costabile, C. Ferdeghini, V. Ferrando, and G. Grassano)

Gap parameters from specific heat and spectroscopic experiments:

Technique	$2\Delta_1(0)/k_BT_c$	$2\Delta_2(0)/k_BT_c$	$\gamma_1:\gamma_2$
specific heat	3.8	1.3	0.5:0.5
specific heat	3.9	1.3	0.5:0.5
specific heat	4.4	1.2	0.55:0.45
penetration depth	4.6	1.6	0.60: 0.40
tunneling	4.5	1.9	
Raman	3.7	1.6	
point-contact	4.1	1.7	
photoemission	3.6	1.1	
band structure	4	1.3	0.53: 0.47

(After A. Junod, Y. Wang, .F. Bouquet, P. Toulemonde)

Two fluid model Three fluid model



Equivalent circuit for the admittance of a unit cube of superconductor

High Purity MgB₂ Thin Films

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Supported by ONR, NSF

October 10, 2006 Thin Film RF Workshop Padua, Italy



Reactive Co-Evaporation



- Deposition temperature 550°C
- Good superconducting properties
- Large area and double sided films
- Films stable to moisture

— On various substrates: *r*-plane, *c*-plane, and *m*-plane sapphire, 4H-SiC, MgO, LaAlO₃, NdGaO₃, LaGaO₃, LSAT, SrTiO₃, YSZ, etc.



(Moeckly & Ruby, SC Sci Tech 19, L21 (2006))

MgB₂ Films by Reactive Co-Evaporation



4" MgB₂ film on polycrystalline alumina

(Moeckly & Ruby, SC Sci Tech 19, L21 (2006))

Hybrid Physical-Chemical Vapor Deposition





Figure 4. Periodic Table certain conditions (pressure Periodic Table of elements with critical temperature at film form or charge injected) [Yamashita] at normal pressure, and maximum critical temperature attained under Physicists in Japan have shown that "entirely end-bonded" multi-walled carbon nanotubes can superconduct at temperatures as high as 12 K, which is 30 times greater than for single-walled carbon nanotubes. The discovery has been made by a team led by Junji Haruyama of Aoyama Gakuin University in Kanagawa. The superconducting nanotubes could be used to study fundamental 1D quantum effects and also find practical applications in molecular quantum computing (*Phys. Rev. Lett.* 96 057001).

Ping Sheng and co-workers at Hong Kong University of Science and Technology have found that the nanotubes **exhibit superconducting behaviour below 20 kelvin**, confirming that resistance-free current can flow through pure carbon (Z K Tang *et al* 2001 *Science* 292 2462).

Superconductivity in diamond

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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 fields1. With these physical properties, diamond is attractive for electronic applications², 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 diamond³; 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 $H_{c2}(0) \ge 3.5$ 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 B₄C to high-pressure, high-temperature conditions. D, diamond; G, graphite. Bottom, SEM image of B-doped diamond synthesized at high pressures and temperatures.



Available online at www.sciencedirect.com



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www.elsevier.com/locate/diamond

The superconductivity in boron-doped polycrystalline diamond thick films Z.L. Wang ^a, Q. Luo ^a, L.W. Liu ^a, C.Y. Li ^b, H.X. Yang ^b, H.F. Yang ^a, J.J. Li ^a, X.Y. Lu ^b, Z.S. Jin ^b, L. Lu ^a, C.Z. Gu ^{a,*}

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Available online 14 February 2006

Abstract

Boron-doped polycrystalline diamond thick film was prepared by a hot filament chemical vapor deposition (HFCVD) method. The morphology and structure of the diamond were evaluated by scanning electron microscopy (SEM), X-ray diffraction (XRD) and micro-Raman spectroscopy. The carrier concentration of the boron-doped diamond was 7.3×10^{20} cm⁻³, determined by a Hall measurement system. The transport measurements show that the boron-doped diamond thick film is superconductive and the superconducting transition temperatures are 10 K for T_c onset and 8.3 K for zero resistance, and there is a strong diamagnetic response in the alternating current (AC) magnetic susceptibility of the boron-doped diamond sample below 8.9 K. Such a high T_c value can be attributed to the higher efficiency of doping, contraction of the reconstructed bonds and two-dimensional nature of the surface states for diamond thick films, all together inducing a stronger electron–phonon coupling.

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 - Termine isorizioni: 3 Novembre 2005 Sede del corso: INFN - Laboratori Nazionali di Legnaro e Università di Padova

PROGRAMMA DEL CORSO:

- Vuoto, Alto Vuoto ed UltraAlto Vuoto Materiali Antiusura, Funzionali, Decorativi
- Film sottili, Tecniche PVD e CVD Chimica ed Elettrochimica dei Substrati

- utomazione e Disegno CAD 3D Tecniche di Analisi di Superficio

