High Temperature Superconductivity (HTSC) and

Some unconventional superconductivity

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Sr2Bi2CuO6 Ba₂Tl₂CuO₆ 40K





YBa₂Cu₃O₇

Ζ

90K

Y





La₂CuO₄

40K

Ζ

Critical temperature (T_c), crystal structure, and lattice constants of Representative high-T_c superconductors

Critical temperature (Tc), crystal structure and lattice constants of some high-Tc superconductors						
Formula	Notation	Т _с (К)	No. of Cu-O planes in unit cell	Crystal structure		
YBa ₂ Cu ₃ O ₇	123	92	2	<u>Orthorhombic</u>		
Bi ₂ Sr ₂ CuO ₆	Bi-2201	20	1	<u>Tetragonal</u>		
Bi ₂ Sr ₂ CaCu ₂ O ₈	Bi-2212	85	2	Tetragonal		
Bi ₂ Sr ₂ Ca ₂ Cu ₃ O ₆	Ri-2223	110	3	Tetragonal		
Tl ₂ Ba ₂ CuO ₆	TI-2201	80	1	Tetragonal		
Tl ₂ Ba ₂ CaCu ₂ O ₈	TI-2212	108	2	Tetragonal		
$TI_2Ba_2Ca_2Cu_3O_{10}$	TI-2223	125	3	Tetragonal		
TIBa ₂ Ca ₂ Cu ₄ O ₁₁	TI-1234	122	4	Tetragonal		
HgBa ₂ CuO ₄	Hg-1201	94	1	Tetragonal		
HgBa ₂ CaCu ₂ O ₆	Hg-1212	128	2	Tetragonal		
$HgBa_2Ca_2Cu_3O_8$	Hg-1223	134	3	Tetragonal		

$Y_1Ba_2Cu_3O_{7-x}$ Crystal Structure, with $T_c = 90K$ (1987)



- One of the key feature of the unit cell of YBa₂Cu₃O_{7-x} is the presence of two layers of CuO₂.
- The role of the Y plane is to serve as a spacer between two CuO₂ planes.
- In YBCO, the Cu–O chains are known to play an important role for superconductivity.
- > T_c is maximal near 92 K when $x \approx 0.05$, and the structure is orthorhombic. a > b
- Superconductivity disappears at x ≈ 0.6, where the YBCO structural transform from orthorhombic to tetragonal.

Crystal structures of high-temperature superconductors

- The structure of high-T_c copper oxides or cuprates are often closely related to perovskite structure, and described as a distorted, oxygen deficient, multi-layered perovskite structure.
- One of common features of the crystal structure of oxide SCs is an alternating multi-layer of CuO₂ planes with superconductivity taking place between these layers.

The more layers of CuO_2 , the higher the T_c .

This structure causes a large *anisotropy* in normal conducting and superconducting properties, since electrical currents are carried by holes induced in the oxygen sites of the CuO₂ sheets.

The electrical conduction is highly anisotropic, with a much higher conductivity parallel to the CuO_2 plane than in the perpendicular direction. Along the *c* axis, poor conductivity with *Josephson coupling between CuO₂ planes*.

Generally, critical temperatures depend on the chemical compositions, cations substitutions, and oxygen content.



 $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+x}$, n =1, 2, 3; with T_c of 80K (n =2), and 122K (n =3)

- The crystallographic unit cell of BSCCO-2212 comprising two repeat units offset by (1/2,0,0).
- The other BSCCO family members have very similar structures: 2201 has one less CuO₂ in its top and bottom half and no Ca layer,
- While 2223 has an extra CuO₂ and Ca layer in each half

A small sample of the high-temperature superconductor BSCCO-2223



~ 0.5 cm



FIG. 1. Depictions of the Tl-1212, Tl-1223, Tl-2212, and Tl-2223 crystal structures.

T_c = 108K T_c = 125K

Hg-Ba-Ca-Cu-O superconductor:

- The crystal structure of HgBa₂CuO₄ (Hg-1201), HgBa₂CaCu₂O₆ (Hg-1212), and HgBa₂Ca₂Cu₃O₈ (Hg-1223) is similar to that of TI-1201, TI-1212 and TI-1223, with Hg in place of TI.
- ➤ It is noteworthy that the T_c of the Hg compound (Hg-1201) containing one CuO₂ layer is much larger as compared to the one-CuO₂-layer compound of Tl (Tl-1201).
- ➤ In the Hg-based superconductor, T_c is also found to increase as the CuO₂ layer increases. For Hg-1201, Hg-1212 and Hg-1223, the values of T_c are 94, 128, and the record value at ambient pressure 134 K.
- The T_c of Hg-1223 increases to 153 K under high pressure, and indicates that the T_c of this compound is very sensitive to the structure of the compound.

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HTSC Theory

- P. W. Anderson at Princeton University came up with the first theoretical description of these materials, using the resonating valence bond theory, but a full understanding of these materials is still under developing as today.
- > These superconductors are now known to possess a *d*-wave pair symmetry.
- The first proposal that high-temperature cupurate superconductivity involves

d-wave pairing was made

- --in 1987 by Bickers, Scalapino and Scalettar
- --in 1988 by theories by Inui, Doniach, Hirschfeld and Ruckenstein, using spin-fluctuation theory,
- -- by Gros, Poilblanc, Rice and Zhang, and by Kotliar and Liu identifying d-wave pairing as a natural consequence of the RVB theory.
- The confirmation of the *d*-wave nature of the cuprate superconductors was made by a variety of experiments, including the direct observation of the *d*-wave nodes in the excitation spectrum through
 - -- Angle Resolved Photoemission Spectroscopy
 - -- LT STM
 - -- Observation of a half-integer flux in tunneling experiments on tri-crystal
 - -- Indirectly from the temperature dependence of the penetration depth, specific heat and thermal conductivity.

There have been two representative theories for HTS:

- □ Firstly, it has been suggested that the HTS emerges from antiferromagnetic spin fluctuations in a doped system. According to this theory, the pairing wave function of the cuprate HTS should have a *d*_{x2-y2} symmetry. Thus, determining whether the pairing wave function has *d*-wave symmetry is essential to test the spin fluctuation mechanism.
- Secondly, there was the interlayer coupling model, according to which a layered structure consisting of BCS-type (s-wave symmetry) superconductors can enhance the superconductivity by itself. By introducing an additional tunneling interaction between each layer, this model successfully explained the anisotropic symmetry of the order parameter as well as the emergence of the HTS.
- To solve this unsettled problem, there have been numerous experiments such as photoemission spectroscopy, <u>NMR</u>, <u>specific heat</u> measurements, etc.
- Unfortunately, the results were ambiguous, some reports supported the *d* symmetry for the HTS, whereas others supported the *s* symmetry. This muddy situation possibly originated from the indirect nature of the experimental evidence, as well as experimental issues such as sample quality, impurity scattering, twinning, etc.

Junction experiment supporting the d symmetry

- An experiment based on flux quantization of a tri-crystal of YBa₂Cu₃O₇(YBCO) was proposed to test the symmetry of the order parameter in the HTS. The symmetry of the order parameter could best be probed at the junction interface as the Cooper pairs tunnel across a Josephson junction or weak link.
- It was expected that a half-integer flux, that is, a spontaneous magnetization could only occur for a junction of *d* symmetry superconductors. But, even if the junction experiment is the strongest method to determine the symmetry of the HTS order parameter, the results have been ambiguous. J. R. Kirtley and C. C. Tsuei thought that the ambiguous results came from the defects inside the HTS, so that they designed an experiment where both clean limit (no defects) and dirty limit (maximal defects) were considered simultaneously. In the experiment, the spontaneous magnetization was clearly observed in YBCO, which supported the d symmetry of the order parameter in YBCO.
- □ But, since YBCO is orthorhombic, it might inherently have an admixture of s symmetry. So, by tuning their technique further, they found that there was an admixture of s symmetry in YBCO within about 3%. Also, they found that there was a pure d_{x2-y2} order parameter symmetry in the tetragonal Tl₂Ba₂CuO₆

High T_c Superconductivity Mechanism

- In a high-T_c superconductor, the mechanism is extremely similar to a conventional superconductor, except, in this case, phonons virtually play no role and their role is replaced by spin-density waves.
- As all conventional superconductors are strong phonon systems, all high-T_c superconductors are strong spin-density wave systems, within close vicinity of a magnetic transition to, for example, an antiferromagnet.
- When an electron moves in a high-T_c superconductor, its spin creates a spindensity wave around it. This spin-density wave in turn causes a nearby electron to fall into the spin depression created by the first electron (waterbed effect again). Hence, again, a Cooper pair is formed. When the system temperature is lowered, more spin density waves and Cooper pairs are created, eventually leading to superconductivity.
- Note that in high-T_c systems, as these systems are magnetic systems due to the Coulomb interaction, there is a strong Coulomb repulsion between electrons. This Coulomb repulsion prevents pairing of the Cooper pairs on the same lattice site. The pairing of the electrons occur at nearneighbor lattice sites as a result. This is the so-called *d*-wave pairing, where the pairing state has a node (zero) at the origin.

Resonant Valence Bond (RVB) Theory



The RVB state with valence bond coupling of nearest neighbor electrons

- The resonating valence bond theory (RVB) is a theoretical model that attempts to describe high temperature superconductivity, and in particular the superconductivity in cuprate compounds. It was first proposed by P. W. Anderson and G. Baskaran in 1987.
- The theory states that in copper oxide lattices, electrons from neighboring copper atoms interact to form a valence bond, which locks them in place. With doping, these electrons can act as mobile Cooper pairs and are able to superconduct.
- Anderson observed that the origins of superconductivity in doped cupurates was in the Mott insulator nature of crystalline copper oxide. RVB builds on the Hubbard and t-J models used in the study of strongly correlated materials.

□ The Hubbard model is based on *tight-binding approximation*.

In the tight-binding approximation, electrons are viewed as occupying the standard orbitals of their constituent atoms, and then 'hopping' between atoms during conduction. Mathematically, this is represented as a 'hopping integral' or 'transfer integral' between neighboring atoms, which can be viewed as the physical principle that creates electron bands in crystalline materials, due to overlapping between atomic orbitals. The width of the band depends upon the overlapping amplitude.

$$E_k \sim -\alpha - 2 \gamma$$

- However, the more general band theories do not consider interactions between electrons explicitly. They consider the interaction of a single electron with the potential of nuclei and other electrons in an average way only. By formulating conduction in terms of the hopping integral; however, the Hubbard model is able to include the so-called 'onsite repulsion', which stems from the Coulomb repulsion between electrons at the same atomic orbitals.
- This sets up a competition between the hopping integral, which is a function of the distance and angles between neighboring atoms, and the on-site Coulomb repulsion, which is not considered in the usual band theories. The Hubbard model can therefore explain the transition from metal to insulator in certain transition metal oxides as they are heated by the increase in nearest neighbor spacing, which reduces the 'hopping integral' to the point where the onsite potential is dominant.

Now, consider a 1D chain of hydrogen atoms

In second quantization notation, the *Hubbard Hamiltonian* then takes the form:

$$H = -t \sum_{\langle i,j \rangle,\sigma} (c_{i,\sigma}^{\dagger} c_{j,\sigma} + c_{j,\sigma}^{\dagger} c_{i,\sigma}) + U \sum_{i=1}^{N} n_{i\uparrow} n_{i\downarrow},$$

, where represents nearest-neighbor interaction on the lattice.

The t-J model was first derived in 1977 from the Hubbard model by Józef Spałek. The model describes strongly correlated electron systems. It is used to calculate high temperature superconductivity states in doped antiferromagnets.

The t-J Hamiltonian is:

$$\hat{H} = -t \sum_{\langle ij \rangle \sigma} \left(\hat{a}_{i\sigma}^{\dagger} \hat{a}_{j\sigma} + \hat{a}_{j\sigma}^{\dagger} \hat{a}_{i\sigma} \right) + J \sum_{\langle ij \rangle} (\vec{S}_i \cdot \vec{S}_j - n_i n_j / 4)$$

where

- sum over nearest-neighbor sites i and j,
- fermionic creation and annihilation operators,
- $\sigma\,$ spin polarization,
- t hopping integral

$$J = 4t^2/U$$

- J coupling constant ,
- U coulomb repulsion,
 - n_i, particle number at the site i, and j
 - S_i, spins on the sites i and j.

Iron pnictide superconductors

Iron-based superconductors

- Iron-based superconductors contain layers of iron and a pnictogen—such as arsenic, or phosphorus—or a chalcogen.
- This is currently the family with the second highest critical temperature, behind the cupurates.
- Interest in their superconducting properties began in 2006 with the discovery of superconductivity in LaFePO at 4 K, and gained much greater attention in 2008 after the analogous material LaFeAs(O,F) was found to superconduct at up to 43 K under pressure.
- Simplified doping dependent phase diagrams of iron-based superconductors for both Ln-1111 and Ba-122 materials. The phases shown are the antiferromagnetic/spin density wave (AF/SDW) phase close to zero doping and the superconducting phase around optimal doping.
- The Ln-1111 phase diagrams for La and Sm were determined using muon spin spectroscopy, the phase diagram for Ce was determined using neutron diffraction.



Several families of iron-based superconductors have emerged:

- > LnFeAs(O,F) or LnFeAsO1-x with T_c up to 56 K, referred to as 1111 materials.
- > A fluoride variant of these materials was subsequently found with similar T_c values.
- (Ba,K)Fe2As2 and related materials with pairs of iron-arsenide layers, referred to as 122 compounds. T_c values range up to 38 K.
- These materials also superconduct when iron is replaced with cobalt. LiFeAs and NaFeAs with T_c up to around 20 K. These materials superconduct close to stoichiometric composition and are referred to as 111 compounds.
- FeSe with small off-stoichiometry or tellurium doping.
- Most undoped iron-based superconductors show a tetragonal-orthorhombic structural phase transition followed at lower temperature by magnetic ordering, similar to the cuprate superconductors.
- However, they are poor metals rather than Mott insulators and have five bands at the Fermi surface rather than one.
- The phase diagram emerging as the iron-arsenide layers are doped is remarkably similar, with the superconducting phase close to or overlapping the magnetic phase.
- Strong evidence that the T_c value varies with the As-Fe-As bond angles has already emerged, and shows that the optimal T_c value is obtained with undistorted FeAs₄ tetrahedral.
- The symmetry of the pairing wave function is still widely debated, but an extended s-wave scenario is currently favored.

Historical development of superconductors



Other materials sometimes referred to as high-temperature superconductors

- Magnesium diboride is occasionally referred to as a high-temperature superconductor, because its T_c value of 39 K is above that historically expected for BCS superconductors. However, it is more generally regarded as the highest T_c conventional superconductor, the increased T_c resulting from two separate bands being present at the Fermi level.
- Fulleride superconductors where alkali-metal atoms (Cs, Rb) are intercalated into C60 molecules show superconductivity at temperatures of up to 38 K for Cs₃C60.
- Some organic superconductors and heavy fermion compounds are considered to be high-temperature superconductors because of their high T_c values relative to their Fermi energy, despite the T_c values being lower than for many conventional superconductors. This description may relate better to common aspects of the superconducting mechanism than the superconducting properties.
- In 1964, William A. Little proposed the possibility of high temperature superconductivity in organic polymers. This proposal is based on the exciton-mediated electron pairing, as opposed to phonon-mediated pairing in BCS theory
- Theoretical work by Neil Ashcroft in 1968 predicted that solid metallic hydrogen at extremely high pressure should become superconducting at approximately room-temperature, because of its extremely high speed of sound and expected strong coupling between the conduction electrons and the lattice vibrations. This prediction is yet to be experimentally verified, as the pressure to achieve metallic hydrogen is not known but may be of the order of 500 Gpa.

- **Conventional superconductivity at 190 K at high pressures , A.P. Drozdov, M. I. Eremets*, I. A. Troyan ;** *Max-Planck Institut fur Chemie, Chemistry and Physics at High Pressures Group, Postfach 3060, 55020 Mainz, Germany*
- the Bardeen Cooper Schrieffer (BCS) theory gives a clear guide for achieving high T_c: it should be a favorable combination of high frequency phonons, strong coupling between electrons and phonons, and high density of states.
- These conditions can be fulfilled for metallic hydrogen and covalent hydrogen dominant compounds. Numerous followed calculations supported this idea, and predicted T_c=100-235 K for many hydrides but only moderate T_c of 17 K has been observed experimentally.
- ➤ They found that sulfur hydride transforms at P~90 GPa to metal, and superconductor with T_c increasing with pressure to 150 K at P ≈200 GPa. This is in general agreement with recent calculations of T_c~80 K for H₂S. Moreover we found superconductivity with T_c≈190 K in a H₂S sample pressurized to P>150 GPa at T>220 K.
- This superconductivity likely associates with the dissociation of H₂S, and formation of SH_n (n>2) hydrides. They proved occurrence of superconductivity by the drop of the resistivity at least 50 times lower than the copper resistivity, the decrease of T_c with magnetic field, and the strong isotope shift of T_c in D₂S which evidences a major role of phonons in the superconductivity.
- H₂S is a substance with a moderate content of hydrogen, therefore high T_c can be expected in a wide range of hydrogen–contain materials. Hydrogen atoms seem to be essential to provide the high frequency modes in the phonon spectrum and the strong electron-phonon coupling.

Critical Fields and Critical Currents

■ High T_c suggests a high stabilization energy and high energy gap for the superconducting state, from which follow high H_c (from eq. (9)), and short coherence lengths ξ_0 (from eq. 17).

■ These results lead to extreme type II behavior; high k value in eq. (37b), and very high H_{c2} . At the high temperatures, thermally activated creep of fluxons may limit useable current values.

- 1. In the low temperature limit the London penetration depths are $\lambda_{ab} \approx 140 \ \lambda_c \approx 700 \text{ nm}$,
- 2. $\xi_{ab} \approx 1.5 \text{ nm}$, $\kappa_{ab} = \lambda_{ab} / \xi_{ab} \approx 100$, $\xi_c \approx 0.2 0.6 \text{ nm}$,
- 3. $j_{ab} = 1.2 \times 10^7$ A/cm² in the *ab* plane, and $j_c = 4.2 \times 10^5$ A/cm² in the *c* direction, suggestive of a quasi-2D superconductor with planes connected by Josephson tunneling.
- 4. $H_{c2}(ab) \ge 10^7 \text{ G} = 1000 \text{ T};$

Josephson coupling between CuO₂ planes

In narrow bridges (50 nm) much <u>higher critical current densities have</u> been observed, <u>being limited by the depairing of Cooper pairs</u>. A bridge is narrow if no fluxons form within the volume of the bridge, and the GL parameter ψ may be taken as constant within the bridge. Then (I.10) becomes $\hbar^2 = \frac{d^2\psi}{d^2\psi}$

$$\frac{1}{2m}\frac{1}{dx^2} - \alpha\psi + \beta|\psi|^2\psi = 0, \quad (10) \quad -\alpha + \beta \,|\psi|^2 + \frac{1}{2}mv^2 = 0, \quad (62)$$

where the last term is the kinetic energy of the Cooper pairs, each of mass m. The current density is

$$j = 2e|\psi|^2 \upsilon = (2e|\psi|^2/m^{1/2})(2\alpha - 2\beta|\psi|^2)^{1/2},$$
(63)

which is a maximum with respect to $f = |\psi|^2 / |\psi_0|^2$ when $f_c = \sqrt{(2/3)}$. Here ψ_0 is the GL parameter at zero current. Thus the maximum (depairing) current density is

$$j_c = (4/3\sqrt{3})(e\kappa/m\xi)|\psi_0|^2;$$
(64)

the critical depairing velocity $v_c \approx \kappa/m\xi$. For $\lambda \approx 100$ nm and $\xi \approx 1$ nm, we have $j_c \approx 1.3 \times 10^9$ A/cm² in good agreement with experiment.

Fullerenes

 C_{60} : each molecule has the form of a truncated icosahedron with 20 hexagonal faces and 12 pentagonal faces, like a soccer ball. C_{60} crystallizes in a face-centered cubic structure.



Figure 28 C_{60} fullerene molecules crystallize in a face-centered cubic structure. Courtesy of Steven Louie.

Alkali-fullerene compounds such as K_3C_{60} are superconducting; this one has $T_C = 19.2$ K. The K atoms occupy the octahedral sites in the cubic cell. $RbC_{S_2}C_{60}$ has $T_C = 33$ K.