# Superconductivity

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## **Discovery of Superconductivity**

An infinitely high electrical conductivity is unthinkable because (1) a crystal without a certain degree of disorder is inconceivable according to the second law of thermodynamics, and (2) even in the absence of phonon and defect scattering, electron-electron scattering will still cause resistance. However, in the year 1911, Kamerlingh Onnes discovered that the electrical resistance of mercury (Hg) approaches an unmeasurably small value when it is cooled below 4.2 K. This phenomenon is called *superconductivity*.

He

Ne

Ar

Kr

Xe

Rn



#### **Magnetic Responses**



Vanishing resistance implies that the magnetic flux  $B \cdot S$  through the closed loop may not alter after cooling and after switching off the external field  $B_{ext}$ .

#### **Meissner-Ochsenfeld Effect**

Because of the Meissner-Ochsenfeld effect, the magnetic state of a superconductor can be described as ideal diamagnetism. Persistent surface currents maintain a magnetization  $M = -H_{ext}$  in the interior, and this magnetization is exactly opposite to the applied magnetic field  $H_{ext}$ .



If the magnetic field strength  $H_{ext}$  is further increased, then at a critical field strength  $H_c$  it is energetically more favorable for the material to convert to the normally conducting phase, in which the magnetic field penetrates the material. The phase boundary between superconducting and normally conducting states corresponds to the critical magnetic field  $H_c$  (*T*).

#### **Types of Superconductivity**



Pure specimens of many materials exhibit this behavior; they are called type I superconductors or, formerly, soft superconductors. The values of  $H_c$  are always too low for type I superconductors to have application in coils for superconducting magnets. Type II or hard superconductors, usually alloys, have superconducting electrical properties up to a field denoted by  $H_{c2}$ . Between the lower critical field  $H_{c1}$  and the upper critical field  $H_{c2}$  the flux density  $B \neq 0$  and the superconductor is threaded by flux lines and is said to be in the vortex state.

### **Change on Specific Heat**

The transition of a metal from its normal state to a superconducting state has nothing to do with a change of crystallographic structure. What actually occurs in the transition is a thermodynamic change of state, or phase transition, which is clearly manifest in other physical quantities. The specific heat as a function of temperature, for example, changes discontinuously at the transition temperature  $T_c$ . The specific heat  $c_n$  of a normally conducting metal is composed of a lattice-dynamical part  $c_{nl}$  and an electronic part  $c_{ne}$  as



$$c_{\rm n} = c_{\rm es} + c_{\rm nl} = \gamma T + \beta T^3$$

At the transition to the superconducting state the lattice dynamical part  $c_{nl}$  remains constant and the electronic part  $c_{es}$  must be replaced by a component which decreases exponentially, so for  $T < T_c$ 

$$c_{\rm es} = \gamma TS \ e^{-A/kT}$$

## **Superconducting Energy Gap**

The energy gap of superconductors is of entirely different origin and nature than the energy gap of insulators. In an insulator the energy gap is caused by the electron-lattice interaction. This interaction ties the electrons to the lattice. In a superconductor the important interaction is the electron-electron interaction which orders the electrons in **k** space with respect to the Fermi gas of electrons. The energy gap decreases continuously to zero as the temperature is increased to the transition temperature  $T_{cr}$  indicating a second-order phase transition.



	Tab	le 3 Ei	nergy g	aps in s	uperco	nductor	s, at <i>T</i> :	= 0		AI	Si
$E_g(0)$ in $10^{-4}$ eV. $E_g(0)/k_BT_c$ .								3.4 3.3			
Sc	Ti	v	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge
		16. 3.4							2.4 3.2	3.3 3.5	
Y	Zr	Nb	Мо	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn (w)
		30.5 3.80	2.7 3.4	1		1			1.5 3.2	10.5 3.6	11.5 3.5
La fcc	Hf	Та	w	Re	Os	Ir	Pt	Au	Hg (a)	TI	Pb
19. 3.7		14. 3.60	-			1		1	16.5 4.6	7.35 3.57	27.3 4.38

### **Isotope Effect**

It has been observed that the critical temperature of superconductors varies with isotopic mass. In mercury  $T_c$  varies from 4.185 K to 4.146 K as the average atomic mass M varies from 199.5 to 203.4 atomic mass units. The transition temperature changes smoothly when we mix different isotopes of the same element. The experimental results within each series of isotopes may be fitted by a relation of the form  $M^{\alpha}T_c$  = constant. From the dependence of  $T_c$  on the isotopic mass we learn that lattice vibrations and hence electron-lattice interactions are deeply involved in superconductivity. The original BCS model gave the result  $T_c \propto \theta_{\text{Debye}} \propto M^{-1/2}$ , so that  $\alpha = \frac{1}{2}$ , but the inclusion of coulomb interactions between the electrons changes the relation.

Substance	α	Substance	α
Zn	$0.45 \pm 0.05$	Ru	$0.00 \pm 0.05$
Cd	$0.32 \pm 0.07$	Os	$0.15\pm0.05$
Sn	$0.47\pm0.02$	Мо	0.33
Hg	$0.50\pm0.03$	Nb <sub>3</sub> Sn	$0.08\pm0.02$
Pb	$0.49 \pm 0.02$	Zr	$0.00\pm0.05$

Experimental values of  $\alpha$  in  $M^{\alpha}T_{c}$  = constant, where M is the isotopic mass.

## **Free Energies**



The free energy density  $F_N$  of a nonmagnetic normal metal is approximately independent of the intensity of the applied magnetic field  $B_a$ . At a temperature  $T < T_c$  the metal is a superconductor in zero magnetic field, so that  $F_s(T, 0)$  is lower than  $F_N(T, 0)$  by

$$\Delta F \equiv F_N(0) - F_S(0) = B_{ac}^2 / 8\pi$$

with

 $F_{\rm S}(B_{\rm a})-F_{\rm S}(0)=B_{\rm a}^2/8\pi$  ; and  $F_{\rm N}(B_{\rm ac})=F_{\rm N}(0)$  .

At a finite *T*, the normal and superconducting phases are in equilibrium when the magnetic field is such that their free energies F = U - TS are equal. Experimental curves of the free energies of the two phases for aluminum are shown in the left.

## **London Theory**

The London equations are a set of phenomenological equations in an attempt to describe the Meissner effect.

Newton's law (inertial response) for applied electric field

We know B = 0 inside superconductors

## **London Penetration Depth**

In the pure superconducting state the only field allowed is exponentially damped into the bulk from an external surface.



An applied magnetic field  $B_a$  will penetrate a thin film fairly uniformly if the thickness is much less than  $\lambda_L$ ; thus in a thin film the Meissner effect is not complete. In a thin film the induced field is much less than  $B_a$ , and there is little effect of  $B_a$ . It follows that the critical field  $H_c$  of thin films in parallel magnetic fields will be very high.

#### **Coherence Length**

The coherence length  $\xi$  is a measure of the distance within which the superconducting electron concentration cannot change drastically in a spatially varying magnetic field. Any spatial variation in the state of an electronic system requires extra kinetic energy. A modulation of an eigenfunction increases the kinetic energy because the modulation will increase the integral of  $d^2\varphi/dx^2$ .

Assume a strongly modulated wavefunction  $\varphi(x) = 2^{-1/2}(e^{i(k+q)x} + e^{ikx})$ , then

$$\varphi^* \varphi = \frac{1}{2} (e^{-i(k+q)x} + e^{-ikx}) (e^{i(k+q)x} + e^{ikx}) = 1 + \cos qx \quad \text{. The kinetic energy is}$$
$$\int dx \; \varphi^* \left( -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \right) \varphi = \frac{1}{2} \left( \frac{\hbar^2}{2m} \right) [(k+q)^2 + k^2] \cong \frac{\hbar^2}{2m} k^2 + \frac{\hbar^2}{2m} kq$$

The increase of energy required to modulate is  $\hbar^2 kq/2m$ . If this increase exceeds the energy gap  $E_g$ , superconductivity will be destroyed. The critical value  $q_0$  of the modulation wavevector is given by  $\frac{\hbar^2}{2m}k_Fq_0 = E_g$ 

Define an **intrinsic coherence length**  $\xi_0 = 1/q_0$ , then

$$\xi_0 = \hbar^2 k_F / 2mE_g = \hbar v_F / 2E_g$$

## **λ** and ξ

The coherence length  $\xi$  and the actual penetration depth  $\lambda$  depend on the mean free path  $\ell$  of the electrons measured in the normal state; the relationships are indicated in figure below. They describe the structure of the transition layer between normal and superconducting phases in contact. In impure materials and in alloys the coherence length  $\xi$  is shorter than  $\xi_0$ . When the superconductor is very impure, with a very small  $\ell$ , then  $\xi \simeq (\xi_0 \ell)^{1/2}$  and  $\lambda \simeq \lambda_L (\xi_0 / \ell)^{1/2}$ , so that  $\lambda/\xi = \lambda_L/\ell$ . This is the "dirty superconductor" limit.



Metal	Intrinsic Pippard coherence length $\xi_0$ , in $10^{-6}$ cm	London penetration depth $\lambda_L$ , in $10^{-6}$ cm	$\lambda_L/\xi_0$
Sn	23.	3.4	0.16
Al	160.	1.6	0.010
Pb	8.3	3.7	0.45
Cd	76.	11.0	0.14
Nb	3.8	3.9	1.02
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### **Ginzburg-Landau Equation**

We introduce the **order parameter**  $\psi(\mathbf{r})$  with the property that  $\psi^*(\mathbf{r})\psi(\mathbf{r}) = n_s(\mathbf{r})$ , the local concentration of superconducting electrons. The free energy density  $F_s(\mathbf{r})$  in a superconductor, near the transition temperature, as a function of the order parameter can be written as

$$F_{S}(\mathbf{r}) = F_{N} - \alpha |\psi|^{2} + \frac{1}{2}\beta |\psi|^{4} + (1/2m)|(-i\hbar\nabla - qA/c)\psi|^{2} - \int_{0}^{B_{a}} \mathbf{M} \cdot d\mathbf{B}_{a}$$

- **1.**  $F_N$  is the free energy density of the normal state.
- **2.**  $-\alpha |\psi|^2 + \frac{1}{2}\beta |\psi|^4$  is a typical Landau form for the expansion of the free energy in terms of an order parameter that vanishes at a second-order phase transition.
- **3.** The term in  $|\text{grad } \psi|^2$  represents an increase in energy caused by a spatial variation of the order parameter. It has the form of the kinetic energy in quantum mechanics. Here q = -2e for an electron pair.
- **4.** The term  $-\int \mathbf{M} \cdot d\mathbf{B}_a$ , with the fictitious magnetization  $\mathbf{M} = (\mathbf{B} \mathbf{B}_a)/4\pi$ , represents the increase in the superconducting free energy caused by the expulsion of magnetic flux from the superconductor.

#### **Coherence Length**

Minimize the total free energy  $\int dV F_s(\mathbf{r})$  with respect to variations in  $\psi(\mathbf{r})$ , then  $\delta \int dV F_s = \int dV \delta \psi^* [-\alpha \psi + \beta |\psi|^2 \psi + (1/2m)(-i\hbar \nabla - q\mathbf{A}/c)^2 \psi] + \text{c.c.}$ 

This integral is zero if the term in brackets is zero:

$$[(1/2m)(-i\hbar\nabla - q\mathbf{A}/c)^2 - \alpha + \beta |\psi|^2]\psi = 0$$

This is Ginzburg-Landau equation; it resembles a Schrödinger equation for  $\psi$ . The intrinsic coherence length  $\xi$  can be defined from the GL equation with **A** = 0 and neglecting  $\beta |\psi|^2$ , in one dimension the above GL equation becomes

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = \alpha\psi, \quad \psi = C\exp(ix/\xi), \text{ and } \xi \equiv (\hbar^2/2m\alpha)^{1/2}$$

Consider the situation representing the boundary of a type I superconductor and a normal metal. Retain the nonlinear term  $\beta |\psi|^2$  in the GL equation:

 $\begin{aligned} -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} - \alpha\psi + \beta|\psi|^2\psi &= 0 \ , \ \text{with boundary conditions } \psi(0) = 0, \ \psi(\infty) = \psi_0 \,, \\ \text{then} \qquad \psi(x) &= (\alpha/\beta)^{1/2} \text{tanh}(x/\sqrt{2}\xi) \end{aligned}$ 

#### **Penetration Depth**

Deep inside the superconductor the free energy is a minimum when

$$|\psi_0|^2 = lpha / eta$$
 , so  $F_S = F_N - lpha^2 / 2eta = F_N - H_c^2 / 8\pi$  ,  $H_c = (4\pi lpha^2 / eta)^{1/2}$ 

 $F_s$  is the stabilization free energy density of the superconducting state at the thermodynamic critical field  $H_c$ .

Consider the penetration depth of a weak magnetic field ( $B \ll H_c$ ) into a superconductor. We assume that  $|\psi|$  in the superconductor is equal to  $|\psi_0|$ , the value in the absence of a field. Then the equation for the supercurrent flux reduces to  $\mathbf{j}_S(\mathbf{r}) = -(q^2/mc)|\psi_0|^2\mathbf{A}$ ,

which is just the London eq.  $\mathbf{j}_{S}(\mathbf{r}) = -(c/4\pi\lambda^{2})\mathbf{A}$ , with the penetration depth

$$\lambda = \left(\frac{mc^2}{4\pi q^2 |\psi_0|^2}\right)^{1/2} = \left(\frac{mc^2\beta}{4\pi q^2\alpha}\right)^{1/2}$$

The dimensionless ratio  $\kappa \equiv \lambda/\xi$  of the two characteristic lengths, the penetration depth  $\lambda$  and coherence length  $\xi$ , is an important parameter in the theory of superconductivity. Then  $mc (\beta)^{1/2}$ 

$$\kappa = \frac{mc}{q\hbar} \left(\frac{\beta}{2\pi}\right)^{1}$$

### **Upper Critical Field**

At the onset of superconductivity  $|\psi|$  is small and the GL equation can be written as:

$$\frac{1}{2m}(-i\hbar\nabla - q\mathbf{A}/c)^{2}\psi = \alpha\psi, \quad \text{or with } \mathbf{A} = B(0, x, 0)$$
$$-\frac{\hbar}{2m}\left(\frac{\partial^{2}}{\partial x^{2}} + \frac{\partial^{2}}{\partial z^{2}}\right)\psi + \frac{1}{2m}\left(i\hbar\frac{\partial}{\partial y} + \frac{qB}{c}x\right)^{2}\psi = \alpha\psi$$

We look for a solution in the form  $\exp[i(k_y y + k_z z)]\varphi(x)$  and find

$$\begin{split} (1/2m)[-\hbar^2 d^2/dx^2 + \hbar^2 k_z^2 + (\hbar k_y - qBx/c)^2]\varphi &= \alpha\varphi\\ \downarrow \\ (1/2m)[-\hbar^2 d^2/dx^2 + (q^2 B^2/c^2)x^2 - (2\hbar k_y qB/c)x]\varphi &= E\varphi \ , \ E &= \alpha - (\hbar^2/2m) \ (k_y^2 + k_z^2) \\ \text{with } X &= x - x_0, \ x_0 = \hbar k_y qB/2mc, \end{split}$$

$$-\left[\frac{\hbar^2}{2m}\frac{d^2}{dX^2} + \frac{1}{2}m(qB/mc)^2X^2\right]\varphi = (E + \hbar^2k_y^2/2m)\varphi$$

This is the equation for an harmonic oscillator.

The largest value of the magnetic field *B* for which solutions exist is given by the lowest eigenvalue, which is

 $\frac{1}{2}\hbar\omega = \hbar q B_{\text{max}}/2mc = \alpha - \hbar^2 k_z^2/2m$ , where  $\omega$  is the oscillator frequency qB/mc. With  $k_z$  set equal to zero, $B_{\text{max}} \equiv H_{c2} = 2\alpha mc/q\hbar$ .

In terms of the thermodynamic critical field  $H_c$  and the GL parameter  $\kappa = \lambda/\xi$ :

$$H_{c2} = \frac{2\alpha mc}{q\hbar} \cdot \frac{H_c}{(4\pi\alpha^2/\beta)^{1/2}} = \sqrt{2} \frac{mc}{\hbar q} \sqrt{\frac{\beta}{2\pi}} H_c = \sqrt{2}\kappa H_c$$

When  $\lambda/\xi > 1/\sqrt{2}$ , a superconductor has  $H_{c2} > H_c$  and is said to be of type II.

In terms of the flux quantum  $\Phi_0 = 2\pi \hbar c/q$  and  $\xi^2 = \hbar^2/2m\alpha$ :

$$H_{c2} = \frac{2mc\alpha}{q\hbar} \cdot \frac{q\Phi_0}{2\pi\hbar c} \cdot \frac{\hbar^2}{2m\alpha\xi^2} = \frac{\Phi_0}{2\pi\xi^2}$$

This says at the upper critical field ( $H_{c2}$ ) the flux density is equal to one flux quantum per area  $2\pi\xi^2$ , consistent with a fluxoid lattice spacing of the order of  $\xi$ .

## **BCS Theory of Superconductivity**

The basis of a quantum theory of superconductivity was laid by the classic 1957 papers of Bardeen, Cooper, and Schrieffer, which includes:

1. An attractive interaction manifests between electrons.



The central feature of the BCS state is that the one-particle orbitals are occupied in pairs: if an orbital with wavevector **k** and spin up is occupied, then the orbital with wavevector  $-\mathbf{k}$  and spin down is also occupied. If  $\mathbf{k}\uparrow$  is vacant, then  $-\mathbf{k}\downarrow$  is also vacant. The pairs are called **Cooper pairs** and have spin zero as well as many attributes of bosons.

#### **Electron Lattice Interaction**



An electron moving through a conductor will attract nearby positive charges in the lattice. This deformation of the lattice causes another electron, with opposite spin, to move into the region of higher positive charge density. The two electrons then become correlated. Because there are a lot of such electron pairs in a superconductor, these pairs overlap very strongly and form a highly collective condensate.

In this "condensed" state, the breaking of one pair will change the energy of the entire condensate, not just a single pair. The energy required to break any single pair is related to the energy required to break *all* of the pairs. The electrons stay paired together and flow as a whole will not experience resistance. Thus, the collective behavior of the condensate is a crucial ingredient necessary for superconductivity.

- **2.** The electron-lattice-electron interaction leads to an energy gap of the observed magnitude.
- **3.** The penetration depth and the coherence length emerge as natural consequences of the BCS theory.
- **4.** The criterion for the transition temperature of an element or alloy involves the electron density of orbitals  $D(\epsilon_F)$  of one spin at the Fermi level and the electron-lattice interaction U, which can be estimated from the electrical resistivity because the resistivity at room temperature is a measure of the electron-phonon interaction. For  $UD(\epsilon_F) \ll 1$  the BCS theory predicts

 $T_c = 1.14\theta \exp[-1/UD(\epsilon_F)]$ 

where  $\theta$  is the Debye temperature and U is an attractive interaction.

**5.** Magnetic flux through a superconducting ring is quantized and the effective unit of charge is 2e rather than e.

#### **EM Field Intensity Approximation**

Let  $\psi(\mathbf{r})$  be the particle probability amplitude. We suppose that the pair concentration  $n = \psi^* \psi$  = constant. Then, we can write

$$\psi = n^{1/2} e^{i \, \theta(\mathbf{r})} \; ; \qquad \psi^* = n^{1/2} e^{-i \, \theta(\mathbf{r})}$$

From the Hamilton equations of mechanics,

$$\mathbf{v} = \frac{1}{m} \left( \mathbf{p} - \frac{q}{c} \mathbf{A} \right) = \frac{1}{m} \left( -i\hbar\nabla - \frac{q}{c} \mathbf{A} \right)$$

so that the electric current density is

$$\mathbf{j} = q \boldsymbol{\psi}^* \mathbf{v} \boldsymbol{\psi} = \frac{nq}{m} \left( \hbar \nabla \theta - \frac{q}{c} \mathbf{A} \right) \ .$$

We can thus obtain

$$\mathbf{\nabla} \times \mathbf{j} = -\frac{nq^2}{mc} \mathbf{B}$$
, the London equation.

We recall that the Meissner effect is a consequence of the London equation, which we have here derived.

## **Flux Quantization in a Superconducting Ring**



The flux through the ring is the sum of the flux  $\Phi_{ext}$  from external sources and the flux  $\Phi_{sc}$  from the superconducting currents which flow in the surface of the ring;

$$\Phi = \Phi_{ext} + \Phi_{sc}.$$

The Meissner effect tells us that **B** and **j** are zero in the interior. So, we will have  $\hbar c \nabla \theta = q \mathbf{A} \ .$ 

The change of phase on going around the ring is  $\oint_C \nabla \theta \cdot dl = \theta_2 - \theta_1 = 2\pi s \ , \text{ where } s \text{ is an integer.}$ 

By the Stokes theorem,

$$\oint_C \mathbf{A} \cdot dl = \int_C (\operatorname{curl} \mathbf{A}) \cdot d\boldsymbol{\sigma} = \int_C \mathbf{B} \cdot d\boldsymbol{\sigma} = \Phi \implies \Phi = (2\pi\hbar c/q)s$$

By setting q = -2e, the quantum of flux in a superconductor (*fluxoid*) is  $\Phi_0 = 2\pi \hbar c/2e \approx 2.0678 \times 10^{-7} \text{ gauss cm}^2$ 

## Type II Superconductors ( $\xi < \lambda$ )

There is no difference in the mechanism of superconductivity in type I and type II superconductors. Both types have similar thermal properties at the superconductor-normal transition in zero magnetic field. But the Meissner effect is entirely different.



### **Vortex State in Type II Superconductor**

There is no chemical or crystallographic difference between the normal and the superconducting regions in the vortex state. The vortex state is stable when the penetration of the applied field into the superconducting material causes the surface energy to become negative. A type II superconductor is characterized by a vortex state stable over a certain range of magnetic field strength; namely, between  $H_{c1}$  and  $H_{c2}$ .



#### **Types of Superconductors**

penetration depth  $\lambda$ ; coherence length  $\xi$ ; mean free path  $\ell$  $\xi \simeq (\xi_0 \ell)^{1/2}$  and  $\lambda \simeq \lambda_L (\xi_0 / \ell)^{1/2}$ 







 $\lambda >> \xi$ 

 elemental superconductors predicted in 1950s by Abrikosov

	ξ (nm)	λ (nm)	$T_{c}(K)$	$H_{c2}(T)$
Al	1600	50	1.2	.01
Pb	83	39	7.2	.08
Sn	230	51	3.7	.03

	ξ (nm)	λ (nm)	$T_{c}(K)$	$H_{c2}(T)$
Nb <sub>3</sub> Sn	11	200	18	25
YBCO	1.5	200	92	150
MgB <sub>2</sub>	5	185	37	14

## **Single Particle Tunneling**

If the insulating barrier is sufficiently thin (less than 10 or 20 Å) there is a significant probability that an electron which impinges on the barrier will pass from one metal to the other: this is called **tunneling**.



Two metals, A and B, separated by a thin layer of an insulator  $C \sim 10$  Å.





Preparation of an Al/Al<sub>2</sub>O<sub>3</sub>/Sn sandwich

(a) Linear current-voltage relation for junction of normal metals separated by oxide layer; (b) current-voltage relation with one metal normal and the other metal superconducting.

### **Supercurrent Tunneling**

In the superconductor there is an energy gap centered at the Fermi level. At absolute zero no current can flow until the applied voltage is  $V = E_g / 2e = \Delta/e$ . The gap  $E_g$  corresponds to the break-up of a pair of electrons in the superconducting state, with the formation of two electrons, or an electron and a hole, in the normal state. The current starts when  $eV = \Delta$ .



The density of states and the current-voltage characteristic for a tunneling junction.

## **Josephson Superconductor Tunneling**

The tunneling of superconducting electron pairs from a superconductor into another superconductor has produced many remarkable effects:

**Dc Josephson effect.** A dc current flows across the junction in the absence of any electric or magnetic field.

Ac Josephson effect. A dc voltage applied across the junction causes rf current oscillations across the junction. This effect has been utilized in a precision determination of the value of  $e/\hbar$ . Further, an rf voltage applied with the dc voltage can then cause a dc current across the junction.

**Macroscopic long-range quantum interference.** A dc magnetic field applied through a superconducting circuit containing two junctions causes the maximum supercurrent to show interference effects as a function of magnetic field intensity.

#### **Dc Josephson Effect**

Let  $\psi_1$  be the probability amplitude of electron pairs on one side of a junction, and let  $\psi_2$  be the amplitude on the other side, and both superconductors be identical. Apply the time-dependent Schrödinger equation  $i\hbar\partial\psi/\partial t = \Re\psi$  to the two amplitudes gives

$$i\hbar \frac{\partial \psi_1}{\partial t} = \hbar T \psi_2 \; ; \qquad i\hbar \frac{\partial \psi_2}{\partial t} = \hbar T \psi_1 \; .$$

Here  $\hbar T$  represents the effect of the electron-pair coupling or transfer interaction across the insulator. Let  $\psi_1 = n_1^{1/2} e^{i \theta_1}$  and  $\psi_2 = n_2^{1/2} e^{i \theta_2}$ . Then

$$\frac{\partial \psi_1}{\partial t} = \frac{1}{2} n_1^{-1/2} e^{i\theta_1} \frac{\partial n_1}{\partial t} + i\psi_1 \frac{\partial \theta_1}{\partial t} = -iT\psi_2 ;$$

$$\frac{\partial \psi_2}{\partial t} = \frac{1}{2} n_2^{-1/2} e^{i \theta_2} \frac{\partial n_2}{\partial t} + i \psi_2 \frac{\partial \theta_2}{\partial t} = -iT\psi_1$$

We thus obtain, with  $\delta \equiv \theta_2 - \theta_1$ ,

$$\begin{split} &\frac{1}{2}\frac{\partial n_1}{\partial t} + in_1\frac{\partial \theta_1}{\partial t} = -iT(n_1n_2)^{1/2}e^{i\delta} \\ &\frac{1}{2}\frac{\partial n_2}{\partial t} + in_2\frac{\partial \theta_2}{\partial t} = -iT(n_1n_2)^{1/2}e^{-i\delta} \end{split}$$

Separate and equate the real and imaginary parts and we get

$$\begin{aligned} \frac{\partial n_1}{\partial t} &= 2T(n_1n_2)^{1/2}\sin\delta \; ; \qquad \frac{\partial n_2}{\partial t} &= -2T(n_1n_2)^{1/2}\sin\delta \\ \frac{\partial \theta_1}{\partial t} &= -T\left(\frac{n_2}{n_1}\right)^{1/2}\cos\delta \; ; \qquad \frac{\partial \theta_2}{\partial t} &= -T\left(\frac{n_1}{n_2}\right)^{1/2}\cos\delta \end{aligned}$$

$$\implies \qquad \frac{\partial \theta_1}{\partial t} = \frac{\partial \theta_2}{\partial t} \quad ; \qquad \frac{\partial n_2}{\partial t} = -\frac{\partial n_1}{\partial t}$$

$$J = J_0 \sin \delta = J_0 \sin (\theta_2 - \theta_1)$$

With no applied voltage a dc current will flow across the junction (shown in the right), with a value between J and -J according to the value of the phase difference  $\delta \equiv \theta_2 - \theta_1$ .

This is the **dc Josephson effect**.



#### **Ac Josephson Effect**

Let a dc voltage *V* be applied across the junction. We can do this because the junction is an insulator. An electron pair experiences a potential energy difference qV on passing across the junction, where q = -2e. We can say that a pair on one side is at potential energy -eV and a pair on the other side is at eV. The equations of motion:  $i\hbar \partial \psi_1 / \partial t = \hbar T \psi_2 - eV \psi_1$ ;  $i\hbar \partial \psi_2 / \partial t = \hbar T \psi_1 + eV \psi_2$ Let  $\psi_1 = n_1^{1/2} e^{i\theta_1}$  and  $\psi_2 = n_2^{1/2} e^{i\theta_2}$ . Then

$$\frac{1}{2}\frac{\partial n_1}{\partial t} + in_1\frac{\partial \theta_1}{\partial t} = ieVn_1\hbar^{-1} - iT(n_1n_2)^{1/2}e^{i\delta}; \quad \frac{1}{2}\frac{\partial n_2}{\partial t} + in_2\frac{\partial \theta_2}{\partial t} = -ieVn_2\hbar^{-1} - iT(n_1n_2)^{1/2}e^{-i\delta}$$

Separate and equate the real and imaginary parts and we get

 $\partial n_1 / \partial t = 2T(n_1 n_2)^{1/2} \sin \delta$  and  $\partial \theta_1 / \partial t = (eV/\hbar) - T(n_2/n_1)^{1/2} \cos \delta$ 

 $\partial n_2/\partial t = -2T(n_1n_2)^{1/2}\sin\delta$  and  $\partial \theta_2/\partial t = -(eV/\hbar) - T(n_1/n_2)^{1/2}\cos\delta$ 

With *n*1  $\simeq$  *n*2, we have  $\partial(\theta_2 - \theta_1)/\partial t = \partial \delta/\partial t = -2eV/\hbar$ 

The superconducting current is given by  $J = J_0 \sin \left[ \delta(0) - (2eVt/\hbar) \right]$ 

The current oscillates with frequency  $\omega = 2eV/\hbar$  . A dc voltage of 1  $\mu$ V produces a frequency of 483.6 MHz.

#### **Macroscopic Quantum Interference**

The phase difference  $\theta_2 - \theta_1$  around a closed circuit which encompasses a total magnetic flux  $\Phi$  is given by  $\theta_2 - \theta_1 = (2e/\hbar c)\Phi$ .

We consider two Josephson junctions in parallel:

Let the phase difference between points 1 and 2 taken on a path through

junction a be  $\delta_a$ . When taken on a path through junction b, the phase difference is  $\delta_b$ . In the absence of a magnetic field these two phases must be equal.



Now let the flux  $\Phi$  pass through the interior of the circuit, then

$$\delta_b - \delta_a = (2e/\hbar c)\Phi, \quad \text{ or } \quad \delta_b = \delta_0 + \frac{e}{\hbar c}\Phi \ ; \quad \delta_a = \delta_0 - \frac{e}{\hbar c}\Phi \ .$$

The total current is the sum of  $J_a$  and  $J_b$ , which is

$$J_{\text{Total}} = J_0 \left\{ \sin \left( \delta_0 + \frac{e}{\hbar c} \Phi \right) + \sin \left( \delta_0 - \frac{e}{\hbar c} \Phi \right) \right\} = 2(J_0 \sin \delta_0) \cos \frac{e\Phi}{\hbar c}$$

The current varies with  $\Phi$  and has maxima when

$$e\Phi/\hbar c = s\pi$$
,  $s = integer$ 

The periodicity of the current is shown below. The short period variation is produced by interference from the two junctions. The longer period variation is a diffraction effect and arises from the finite dimensions of each junction—this causes  $\Phi$  to depend on the particular path of integration.



The field periodicity is 39.5 and 16 mG for A and B, respectively. Approximate maximum currents are 1 mA (A) and 0.5 mA (B). The junction separation is 3 mm and junction width 0.5 mm for both cases. The zero offset of A is due to a background magnetic field.

### **High-Temperature Superconductors**

High-temperature superconductors (abbreviated high- $T_c$  or HTS) are operatively defined as materials that behave as superconductors at the boiling point of liquid nitrogen (77K), one of the simplest coolants in cryogenics.

The first high-temperature superconductor was discovered in 1986, by IBM researchers Bednorz and Müller, who were awarded the Nobel Prize in Physics in 1987 "for their important break-through in the discovery of superconductivity in ceramic materials".

The main class of high-temperature superconductors are in the class of copper oxides. The second class of high-temperature superconductors in the practical classification is the class of iron-based compounds.

Some extremely-high pressure super-hydride compounds are usually categorized as high-temperature superconductors, which is not suitable for practical applications. The current  $T_c$  record holder is carbonaceous sulfur hydride (H<sub>2</sub>S + CH<sub>4</sub> at 267 GPa) at 287K.

#### **Structure of YBCO Cuprate**

Cuprates are layered materials, consisting of superconducting layers of copper oxide, separated by spacer layers. Their superconducting properties are determined by electrons moving within weakly coupled copper-oxide  $(CuO_2)$  layers. Neighboring layers contain ions such as lanthanum, barium, yttrium, or other atoms which act to stabilize the structure and dope electrons or holes onto the copper-oxide layers. The unit cell of  $YBa_2Cu_3O_7$  (YBCO) consists of three perovskite unit cells, which is pseudocubic, nearly orthorombic. The structure has a stacking of different layers: (CuO) (BaO) (CuO<sub>2</sub>) (Y) (CuO<sub>2</sub>) (BaO) (CuO). One of the key feature of this unit cell is the presence of two layers of  $CuO_2$ .





perovskite unit cells: A<sup>2+</sup>B<sup>4+</sup>(X<sup>-2</sup>)<sub>3</sub>

## **Phase Diagram of Cuprates**

The undoped "parent" or "mother" compounds are Mott insulators with long-range antiferromagnetic order at sufficiently low temperatures. Certain aspects common to all materials have been identified.

- The antiferromagnetic low-temperature state of undoped materials and the 350 superconducting state that emerges 300 upon doping, primarily the  $d_{x^2-y^2}^2$  orbital 250 state of the Cu<sup>2+</sup> ions, suggest that  $\stackrel{()}{\underset{}{\leftarrow}}_{200}$ electron-electron interactions are more 150 significant than electron-phonon interactions in cuprates, making the superconductivity unconventional. 0
- Presence of a pseudogap phase appears up to at least optimal doping.
- The weak isotope effects observed for most cuprates.



Phase diagram of cuprate superconductors: Both standard cuprate super-conductors, YBCO and BSCCO, are notably **hole-doped**.

## Problems

**1. Structure of a vortex.** (a) Find a solution to the London equation that has cylindrical symmetry and applies outside a line core. In cylindrical polar coordinates, we want a solution of

$$B - \lambda^2 \nabla^2 B = 0$$

that is singular at the origin and for which the total flux is the flux quantum:

$$2\pi \int_0^\infty d\rho \,\rho B(\rho) = \Phi_0$$

The equation is in fact valid only outside the normal core of radius  $\xi$ . (b) Show that the solution has the limits

$$\begin{split} B(\rho) &\simeq (\Phi_0/2\pi\lambda^2) \ln(\lambda/\rho) \ , \qquad (\xi \ll \rho \ll \lambda) \\ B(\rho) &\simeq (\Phi_0/2\pi\lambda^2)(\pi\lambda/2\rho)^{1/2} \exp(-\rho/\lambda) \ . \qquad (\rho \gg \lambda) \end{split}$$

### Problems

**2.** Diffraction effect of Josephson junction. Consider a junction of rectangular cross section with a magnetic field *B* applied in the plane of the junction, normal to an edge of width *w*. Let the thickness of the junction be *T*. Assume for convenience that the phase difference of the two superconductors is  $\pi/2$  when B = 0. Show that the dc current in the presence of the magnetic field is

$$J \approx J_0 \frac{\sin(wTBe/\hbar c)}{(wTBe/\hbar c)} \ .$$

**3.** *Meissner effect in sphere*. Consider a sphere of a type I superconductor with critical field  $H_c$ . (a) Show that in the Meissner regime the effective magnetization M within the sphere is given by  $-8\pi M/3 = B_a$ , the uniform applied magnetic field. (b) Show that the magnetic field at the surface of the sphere in the equatorial plane is  $3B_a/2$ . (It follows that the applied field at which the Meissner effect starts to break down is  $2H_c/3$ .) Reminder: The demagnetization field of a uniformly magnetized sphere is  $-4\pi M/3$ .