

(References: de Gannes chapters 1-3, Tinkham chapter 1)

Statements refer to “classic” (pre-1970) superconductors (Al, Sn, Pb, alloys...). Most but not all statements apply also to HTS, fullerenes, heavy-fermions, organics...

1. Definition of superconductivity

The superconducting state differs qualitatively from the normal (non-superconducting) state in 3 major respects:

- (a) d.c. conductivity (in zero magnetic field & for small enough current) effectively infinite (seen either in voltage-drop experiments, or in persistence of current in rings)
- (b) simply connected sample expels weak magnetic field (Meissner effect): perfect diamagnet, i.e.  $\mathbf{B} = 0$ . [convention for  $\underline{H}$ ,  $\underline{B}$  later]
- (c) Peltier coefficient\* vanishes, i.e. electrical current not accompanied by heat current (contrary to usual behavior in normal phase).

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These three phenomena set in essentially discontinuously at a critical temperature  $T_c$  which may be anything from  $\sim 1$  mK to  $\sim 25$ K (higher for HTS, etc.) For most elements & alloys,  $T_c \sim$  a few K. (Note: this is  $\sim 3$ -4 orders of magnitude below  $T_F$  and  $\sim 1$ -2 below  $\theta_D$ ) Onset is abrupt: no reliable way of telling, from  $N$ -state bulk measurements, whether superconductivity will set in at all, let alone at what temperature. (but cf. proximity-effect measurements on Cu etc.). For new HS compounds, at a pressure of 200 GPa,  $T_c$  can exceed 200K.

2. Occurrence

Superconductivity appears to occur only in materials which in the normal phase (i.e. above  $T_c$ ) are metals or (occasionally, under extreme conditions) semiconductors: There is no clear case in which, as  $T$  is lowered, the system goes from an insulating to a  $S$  state<sup>†</sup>. In the case of the classic superconductors,  $N$  state is almost always a “textbook” metal (see (3) below).

However, the correlation between  $N$ -state conductivity  $\sigma$  and the occurrence of superconductivity is negative: the best  $N$ -state conductors (Cu, Ag, Au) do not become superconducting (at least down to 10 mK, and there is some reason to believe

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\*Peltier coefficient  $\Pi$  is defined as ratio of heat current to electric current for  $\nabla T=0$ : see Ziman, P. Th. Solids, pp. 201-2.

<sup>†</sup>Theoretically such a transition is predicted to be possible under extreme conditions. The experimental evidence is unconvincing for the classic superconductors and ambiguous for HTS: M.V. Sadovskii, Phys. Rev. 282, 226 (1997).

they never will). In the periodic table of the elements, superconductivity occurs mainly in the middle: see AM p. 726, table 34.1, or Kittel (3<sup>rd</sup> edition), p. 338, table 2. Many intermetallic compounds, e.g. Nb<sub>3</sub>Sn, V<sub>3</sub>Ga, often with high  $T_c$  (~20K).

Superconductivity is not destroyed by nonmagnetic impurities, in fact  $T_c$  sometimes increases with alloying & there are thousands of superconducting alloys, including some with very high (20-25K)  $T_c$ . But magnetic impurities (i.e. impurities carrying electrons with nonzero total spin) are rapidly fatal: e.g. pure Mo is superconducting with  $T_c \sim 1$ K, but a few ppm of Fe drives  $T_c$  to zero. No known case among classic superconductors where superconductivity coexists with any form of magnetic ordering. (but situation in “exotics” more complicated)

Isotope effect: in most though not all cases of classic superconductivity,  $T_c \propto M^{-1/2}$ . (crucial clue to mechanism)

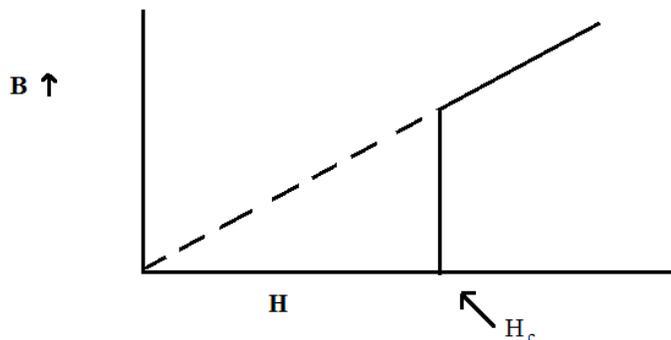
### 3. Normal state of superconductors

Almost all the classic superconductors are, above  $T_c$ , “textbook” normal metals: i.e.  $C_v \sim T$ ,  $\chi \sim \text{const.}$ ,  $\rho \sim \text{const.} + f(T)$  ( $f(T) \sim T$  for  $T \gg \theta_D$ ),  $\kappa/\sigma T = \text{const.}$ , etc.

### 4. Magnetic behavior of superconducting phase

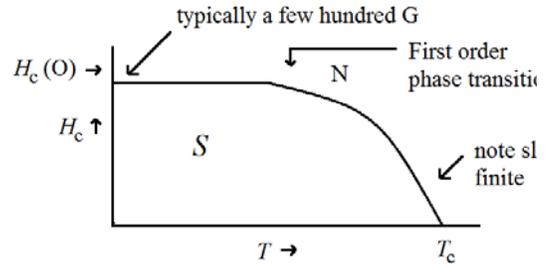
For a given material, the magnetic behavior is in general a function of the shape of the sample: the simplest case to analyze is a (large) long cylinder parallel to the external field. In this case, there are 2 types of behavior, type-I and type-II. Most pure elemental superconductors are type-I (exception: pure Nb): compounds and alloys tend to be type-II, and this is the case for virtually all the highest- $T_c$  materials.

(a) **Type-I:** At any given  $T < T_c(0)$ , if we gradually raise  $H$ , system remains perfectly superconducting up to a definite critical field  $H_c(T)$ , at which point it goes over discontinuously (by a first-order transition) to the normal phase and readmits the magnetic field completely. In terms of the  $B(H)$  relation\*:



\*It is conventional in the theory of superconductivity to define  $\mathbf{H}$  as the field due to external sources, and  $\mathbf{B}$  as the total local field averaged over a few atomic distances. Thus,  $\mathbf{B} = \mu_0 \mathbf{H} + \mathbf{M}$  where  $\mathbf{M}$  is the average magnetization due to macroscopic circulating currents. (Atomic-scale variations usually not considered)

The shape of  $H_c(T)$  is approximately  $\rightarrow$  [actually more curved at low  $T$ ] and is well fit by the formula  $(1-(T/T_c)^2)$



The reason for the existence and behavior of the critical field  $H_c(T)$  is a straightforward thermodynamic one: the  $S$  state has a negative (condensation) energy relative to the  $N$  state, but since it excludes the magnetic field entirely, this costs an (extra) energy

$$dE_{mag} = -\mathbf{M} \cdot d\mathbf{H}_{ext} \Rightarrow E_{mag} = + \frac{1}{2}\mu_0 H_{ext}^2 V \quad (\text{SI units})$$

since  $\mathbf{M}$  is oppositely directed to  $\mathbf{H}_{ext}$  (diamagnetism). ( $B = 0 \Rightarrow \mathbf{M} = -\mu_0 \mathbf{H}$ ) (This is essentially the energy necessary to “bend” the field lines so as to avoid the sample) (levitation). In the normal phase, excluding small atomic-level magnetic effects, the extra energy is zero. Thus it becomes energetically advantageous to switch to the  $N$  phase at the point

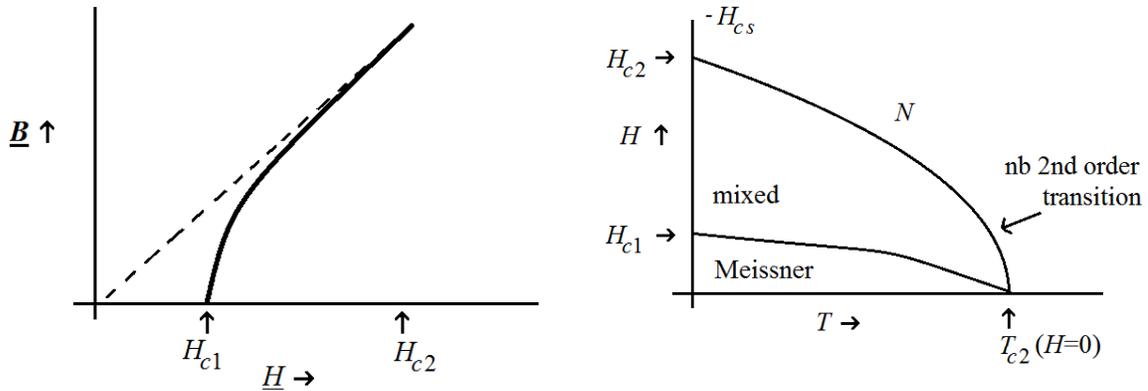
$$G_n(T) - G_s(T) = \frac{1}{2} \mu_0 H^2 \equiv \frac{1}{2}\mu_0 H_c^2(T) \quad [\Rightarrow \text{transition 1}^{st} \text{ order}]$$

and this is a useful method of measuring the  $LHS$ . (See below (5)).

Above analysis is for a “large” sample. Actually, there is a characteristic length  $\lambda$  (cf. below) over which field penetrates. Thus, for sample sizes  $< \lambda$ , we expect the thermodynamic critical field to be higher, and this is indeed seen.

Note also that for samples of less convenient shape may get a break-up into  $N$  and  $S$  regions (intermediate state: distinguish from “mixed” state, below).

- (b) Type-II: start with  $T < T_c(H = 0)$ , turn up field  $H$ . For sufficiently small field behaves as type-I, i.e. expels flux completely (“Meissner state”). Above a “lower critical field”  $H_{c1}$ , flux begins to penetrate, so  $\mathbf{M}$  is negative but  $|\mathbf{M}| < \mu_0 \mathbf{H}$ , so  $B > 0$ . As  $\mathbf{H}$  further increased,  $\mathbf{M}$  becomes smaller until at an “upper critical field”  $H_{c2}$  it vanishes (in the bulk) & system switches to normal state. Apart from this, in the “mixed” state between  $H_{c1}$  and  $H_{c2}$  system behaves in a typically superconducting way (though cf below for resistive behavior).



Anticipate: in mixed state, magnetic field punching through in form of vortices (cores effectively normal), while bulk remains superconducting.

Can define  $H_c(T)$  for type-II as above from  $G_n - G_s$ . Then, to an order of magnitude  $H_{c1} \cdot H_{c2} \sim H_c^2$ . Typically  $H_{c1} \sim$  a few  $G$ ,  $H_{c2} \sim$  several  $T$ . (30T for  $V_3Ga$ )

### 5. Resistance

One can make one simple statement about the d.c. resistance  $R$  of a superconductor: For any bulk type-I superconductor when the field (including that generated by the current) is everywhere less than  $H_c(T)$ , or for a bulk type-II superconductor when it is less than  $H_{c1}(T)$ , the effective resistance is zero. It is also true that for a type-I superconductor, those parts which are in a field  $< H_c(T)$  have local resistivity zero: however, because any current will generate a spatially varying field, the total resistance even of a thin wire is a quite complicated function of current\*. For a single wire (dimensions  $\ll \lambda$ ) in zero external magnetic field the resistance is zero up to a critical current  $I_c(T)$  defined by Silsbee's rule, i.e.

$$I_c(T) = H_c(T)a/2, \quad a = \text{radius of wire}$$

As  $I$  is increased beyond  $I_c(T)$ , the resistance jumps discontinuously to a value  $\sim 0.7 - 0.8$  of the normal-state value, and for  $I \gg I_c(T)$  approaches the latter.

For type-II superconductors situation is even more complicated, because in general in the mixed phase even local resistivity is not zero, (due to the possibility of flux flow). A formula which often describes the behavior in this region quite well is (cf. Tinkham section 5.5.1)

$$\rho/\rho_n \cong B/\mu_0 H_{c2}$$

[effect of pinning]

\* See Tinkham section 3-5.

Again, in a thin wire resistance first develops when  $I_c = H_{c2}(T)a/2$  and tends to the normal value asymptotically as  $I \rightarrow \infty$ .

The above all refers to d.c. resistance. The a.c. resistance is nonzero even when all regions of the superconductor are in the Meissner phase: generally speaking,  $R$  increases as some power of  $\omega$

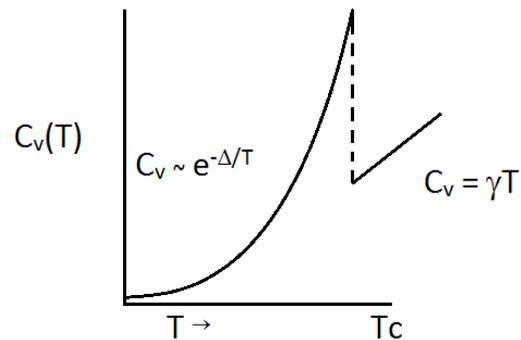
6. Microscopic properties of the superconducting phase

(a) Specific heat  $C_v$ . (after subtraction of phonon terms)

This is  $\propto T$  in the  $N$  phase. There is a jump<sup>†</sup> at  $T_c$ , such that  $\Delta C_v / C_v^{(n)} \cong 1.4$  (or sometimes a little greater, up to 2.65 for Pb). For  $T \ll T_c$   $C_v$  drops below the  $N$  state value, and as  $T \rightarrow 0$  follows

$$C_v|_{T \rightarrow 0} \sim \exp - \Delta / \kappa T$$

where  $\Delta$  is a constant of the order of  $k_B T_c$ .



A very useful relation between the specific heat and the thermodynamic critical field  $H_c(T)$  can be obtained by differentiating twice the relation  $G_n - G_s = 1/2 \mu_o H_c^2(T)$ , namely

$$c_n - c_s = -T \frac{d^2}{dT^2} \left( \frac{1}{2} \mu_o H_c^2(T) \right)$$

(and  $S_n - S_s = -\mu_o H_c \frac{\partial H_c}{\partial T} \rightarrow$  transition 1<sup>st</sup> order in finite  $H$ ) Although in this relation  $c_n$  and  $c_s$  should strictly speaking be evaluated at  $H = H_c(T)$ , it is usually adequate to insert the  $H = 0$  values. In particular as  $T \rightarrow T_c$  ( $H_c \rightarrow 0$ ) we have

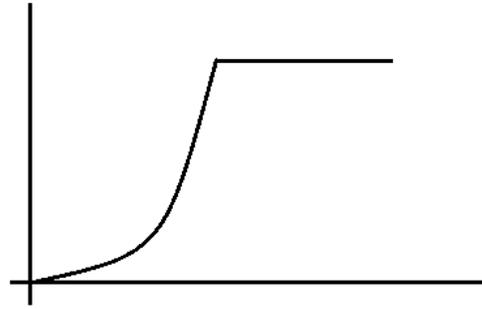
$$c_n(T_c) - c_s(T) = -T \mu_o \left( \frac{\partial H_c}{\partial T} \right)_{T_c}^2$$

<sup>†</sup> Note the fact that  $c_s \sim c_n$  indicates only electrons with  $\epsilon \sim k_B T_c$  (much) affected by the onset of superconductivity.

This can be checked experimentally, and is often used to determine  $c_s$  more accurately. Note that since  $c_s \rightarrow 0$  as  $T \rightarrow 0$  while  $c_n \propto T$ , the form of  $H_c^2$  (hence also of  $H_c$ ) in this limit is  $H_c(T) \cong H_c(0)(1-(T/T^*)^2)$  where  $T^* \sim T_c$ .

(b) Pauli susceptibility  $\chi$  (Type – I)

This can often be measured from the Knight shift. We find  $\chi$  drops off sharply for  $T < T_c$  and as  $T \rightarrow 0$  tends exponentially to zero, like  $c_v$ .



(c) Ultrasound attenuation ( $\alpha$ )

The longitudinal attenuation remains proportional to  $\omega$  as in the normal phase, but the coefficient drops off sharply. (roughly as  $(T/T_c)^4$ ) The transverse ultrasonic attenuation has a discontinuous drop at  $T_c$  (consequence of Meissner effect), thereafter drops similarly.

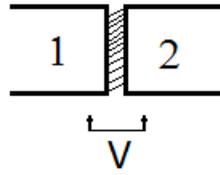
(d) Thermal conductivity ( $\kappa$ )

The thermal conductivity in the  $N$  phase for  $T \sim T_c$  is usually dominated by electrons rather than phonons. Generally speaking it has no discontinuity in the superconducting phase, but drops similarly to the ultrasonic attenuation and  $\rightarrow 0$  for  $T \rightarrow 0$ . (For low enough  $T$ , phonons may again dominate).

(e) Nuclear relaxation rate  $T_1^{-1}$

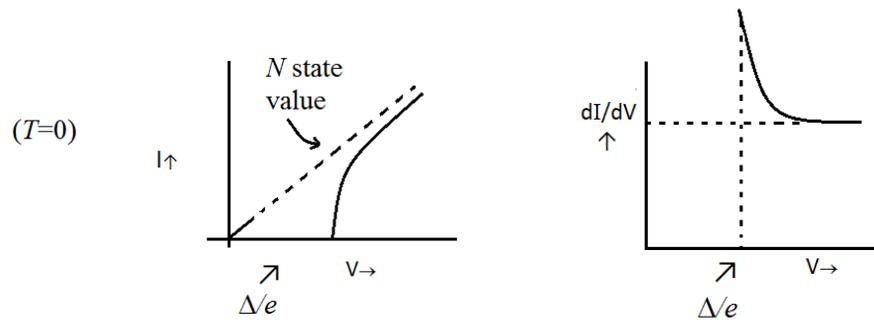
In the  $N$  state  $\Gamma \equiv T_1^{-1}$  is roughly  $\propto T$ . (Korringa law). As  $T$  falls below  $T_c$ ,  $\Gamma$  first rises (the famous Hebel-Slichter peak) then falls, roughly similar to  $\chi$ , and  $\rightarrow 0$  as  $T \rightarrow 0$ .

EM absorption (as seen e.g. in reflectivity): lower than in  $N$  state at low  $\omega$ , rises sharply at  $\omega \sim 2\Delta$ , when  $\Delta$  is “gap” observed in  $c_v$ .



(f) Tunneling.

The tunneling current between two  $N$  metals, whether the same or different, is usually proportional to the voltage applied across the barrier, so  $dI/dV = \text{const}$ . When one metal is a  $S$  and the other a  $N$  metal, no current flows for either polarity until  $e|V| = \Delta$ , where  $\Delta$  is the same quantity as appears in the low-temperature specific heat. If we plot  $dI/dV$  rather than  $I(V)$



At finite  $T < T_c$ :

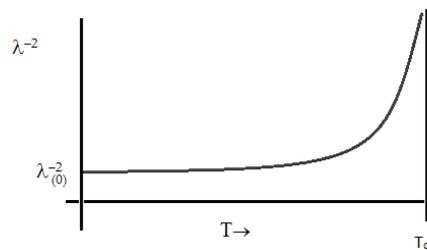


If both metals are  $S$ , we get qualitatively similar behavior, with however  $\Delta$  replaced by the sum  $\Delta_1 + \Delta_2$ .

[Also: Josephson tunneling]

(g) Penetration depth.  $\lambda$ 

This is one quantity which is not defined in the  $N$  phase: it is the depth to which, in the Meissner phase, an  $EM$  field penetrates into the surface of the superconductor. It turns out to be more convenient to plot  $\lambda^{-2}(T)$ , which as we shall see has a direct physical interpretation:



$\lambda$  tends exponentially to its  $T=0$  limit as  $T \rightarrow 0$ , again with an exponent  $\sim \Delta/kT$ , and diverges in the limit  $T \rightarrow T_c$ , as  $(1 - T/T_c)^{-1/2}$ .