There is a characteristic sharp drop in resistivity at a critical temperature, $T_{\rm C}$. This effect has been observed in a wide range of elements and compounds.

SUPERCONDUCTIVITY I Lecture 30

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11 Superconductivity

- **11.1 Basic experimental observations**
- **11.1.1 Disappearance of resistance**

The phenomenon of superconductivity was first observed in mercury by Kammerlingh Onnes in 1911.



	Be 0.03 Superconducting elements Superconducting under pressure													 	-		
												Al 1.2	Si 7	P 5			T
			Ti 0.39	V 5.3							Zn 0.86	Ga 1.1	Ge 5	As 0.5	Se 7		
			Zr 0.53	Nb 9.2	Mo 0.92	T e 7.9	Ru 0.49				Cd 0.52	In 3.4	Sn 3.7	Sb 3.5	Te 4		
Cs 1.5	Ba 5	La 4.9	Hf 0.17	Ta 4.5	W 0.01	Re 1.7	Os 0.66	Ir 0.14			H g 4.2	TI 2.4	РЬ 7.2	Bi 8			T
				Ce 2						[
			-	Th	Pa 1 4	U		<u>l</u>								l	10.

New elements keep being added to the list – in 2002 lithium was shown to superconduct under pressures of 23 to 36 GPa with critical temperatures of 9 to 15 K^1 .

¹V.V. Struzhkin et al, 2002, Science **298** 1213.

Element	$\rho(77K) \mathrm{m}\Omega$	m T _C	r	$\overline{T_{\mathrm{C}}(\mathbf{K})}$
Al	3	1.2	Nb ₃ Sn	18
Tl	37	2.4	Nb_3Ge	23
Sn	21	3.7	V_3Si	17
Pb	47	7.2	$La_{1.8}Sr_{0.2}CuO_4$	35
Sb	80	3.5	$Y_{0.6}Ba_{0.4}CuO_4$	90
Bi	350	8	$Tl_2Ba_2Ca_2Cu_2O_{10}$	125
Nb	30	9.2	Bi _{1-x} K _x BiO _{3-v}	27
For elem	ents in the s	ame group, higher normal resistivity seems to	MgB_2	40

go with higher transition temperature.

For some compounds, much higher transition temperatures are found:



High-temperature superconductivity found in an *insulator* by Bednorz and Müller in 1986. Note that the transition is not very sharp.

There is also an *isotope effect*: for different isotopes of the same element in many cases

$$T_{\rm C}M^{1/2} = \text{constant.}$$

This is also found in some compounds:



In ${\rm MgB}_2$ only the B isotope affects T_C – Mg does not.

11.1.2 Specific Heat

The specific heats of normal and superconducting phases are different:

Aluminium

¥



11.1.3 Effect of magnetic field

An external magnetic field shifts $T_{\rm C}$ to lower temperatures:



From the specific heats, we can infer a variation of entropy with temperature²:



This shows that the superconducting state is a more *ordered* state.

11.1.4 Perfect diamagnetism

A superconductor expels magnetic flux (we will return to qualify this later) when it is cooled below its critical temperature.



If the flux is sero, it follows from

$$\mathcal{B} = \mu_0(\mathcal{H} + \mathcal{M})$$

that

$$\mathcal{M} = -\mathcal{H},$$

that is,

 $\chi = -1;$

we call this *perfect diamagnetism*. Note that there is a difference here between the behavior of a superconductor and a perfect conductor: from Maxwell's equations we know

$$abla imes \mathcal{E} = -rac{\partial \mathcal{B}}{\partial t}.$$

But a perfect conductor can support no electric field (even with finite current density \mathcal{J} , if the resistivity is zero $\mathcal{E} = \rho \mathcal{J}$ is zero. If \mathcal{E} is zero, so is $\nabla \times \mathcal{E}$ – in other words, for a perfect conductor the flux density \mathcal{B} cannot change with time – any flux present when the material becomes perfectly conducting will be locked in.

The magnetisation behaves in two different ways: Type I reverts suddenly to a normal material at a critical field \mathcal{H}_c : Type II begins to revert at \mathcal{H}_{c1} and the change is complete by \mathcal{H}_{c2} .



N.B think of rod, not sphere – field distortion effects (demagnetisation).

11.2 Basic thermodynamics

Consider the Gibbs free energy $G(\mathcal{B}, T)$. As we know that

$$\mathrm{d}G = -S\mathrm{d}T - \mathcal{M}.\mathrm{d}\mathcal{B},$$

the perfect diamagnetism in a field \mathcal{B} increases the free energy by

$$\frac{\mathcal{B}^2}{2\mu_0}.$$

In the normal state the magnetic field has negligible effect (because the field energy with a susceptibility $\chi \approx \pm 10^{-6}$ is tiny compared with that of the perfect diamagnet with $\chi = -1$:

$$G_{\mathrm{N}}(\mathcal{B},T) = G_{\mathrm{N}}(0,T).$$

Thus

$$G_{\rm S}(\mathcal{B},T) = G_{\rm S}(0,T) + \frac{\mathcal{B}^2}{2\mu_0}.$$

Now at the critical field, \mathcal{B}_C , the free energies of the superconducting and normal states are equal:

$$\begin{split} G_{\mathrm{S}}(\mathcal{B}_{\mathrm{C}},T) &= G_{\mathrm{S}}(0,T) + \frac{\mathcal{B}_{\mathrm{C}}^2}{2\mu_0} \\ &= G_{\mathrm{N}}(\mathcal{B}_{\mathrm{C}},T) \\ &= G_{\mathrm{N}}(0,T), \end{split}$$

SO

$$G_{\mathrm{S}}(0,T) = G_{\mathrm{N}}(0,T) - \frac{\mathcal{B}_{\mathrm{C}}^2}{2\mu_0},$$

so that the critical field is a measure of the stability of the superconducting state. In an applied field $B < B_C$,

$$G_{\rm S}(\mathcal{B},T) = G_{\rm N}(0,T) - \frac{\mathcal{B}_{\rm C}^2 - \mathcal{B}^2}{2\mu_0}.$$
(1)

At constant p and \mathcal{B} the entropy is given by

$$S = -\frac{\partial G}{\partial T},$$

so, using equation 1,

$$S_{\rm S} - S_{\rm N} = \frac{\mathrm{d}}{\mathrm{d}T} \left(\frac{\mathcal{B}_{\rm C}^2 - \mathcal{B}^2}{2\mu_0} \right)$$
$$= \frac{\mathcal{B}_{\rm C}}{\mu_0} \frac{\mathrm{d}\mathcal{B}_{\rm C}}{\mathrm{d}T}.$$

As the specific heat is

$$C = T \frac{\mathrm{d} \mathcal{B}}{\mathrm{d} T},$$

$$C_{\mathrm{S}} - C_{\mathrm{N}} = T \frac{\mathrm{d}}{\mathrm{d} T} \frac{\mathcal{B}_{\mathrm{C}}}{\mu_0} \frac{\mathrm{d} \mathcal{B}_{\mathrm{C}}}{\mathrm{d} T}$$

$$= \frac{T}{\mu_0} \left[\left(\frac{\mathrm{d} \mathcal{B}_{\mathrm{C}}}{\mathrm{d} T} \right)^2 + \mathcal{B}_{\mathrm{C}} \frac{\mathrm{d}^2 \mathcal{B}_{\mathrm{C}}}{\mathrm{d} T^2} \right].$$

dC

But when $T = T_{\rm C}$, the critical field $\mathcal{B}_{\rm C}$ is zero, so

$$C_{\rm S}(T_{\rm C}) - C_{\rm N}(T_{\rm C}) = \frac{T}{\mu_0} \left(\frac{\mathrm{d}\mathcal{B}_{\rm C}}{\mathrm{d}T}\right)^2$$

This gives an explanation of the observed specific heat discontinuity. Note that in an order-disorder transition such as this there is no latent heat at the critical temperature.

11.2.2 The shielding currents

The mechanism for excluding flux from the superconductor involves inducing currents in the surface. Of course, if the exclusion were perfect and occurred exactly at the surface this would imply infinite current density at the surface – which is unphysical. So we need to look rather more closely at the electromagnetism. Suppose that n charge carriers per volume, each with charge q and mass m, are continuously accelerated by a field:

$$\frac{\mathrm{d}\mathbf{v}}{\mathrm{d}t} = \frac{q\mathcal{E}}{m},$$

but the current is

SO

$$\mathcal{J}=nq\mathbf{v},$$

$$\mathcal{E} = \frac{m}{nq^2} \, \frac{\mathrm{d}\mathcal{J}}{\mathrm{d}t}.$$

Now

or

SO

$$\mathcal{E} = \frac{m}{n\mu_0 q^2} \, \nabla \times \frac{\mathrm{d}\mathcal{B}}{\mathrm{d}t}.$$

 $\nabla \times \mathcal{H} = \mathcal{J},$

 $\nabla \times \mathcal{B} = \mu_0 \mathcal{J},$

Now take the curl of both sides,

$$abla imes \mathcal{E} = \frac{m}{n\mu_0 q^2} \ \nabla \times \nabla \times \frac{\mathrm{d}\mathcal{B}}{\mathrm{d}t}$$

and recall the identity

$$\nabla \times \nabla \times = \nabla (\nabla .) - \nabla^2,$$

the Maxwell equation

$$\nabla \times \mathcal{E} = -\frac{\partial \mathcal{B}}{\partial t},$$

and

 $\nabla . \mathcal{B} = 0,$

so that

$$\frac{\mathrm{d}\mathcal{B}}{\mathrm{d}t} = \frac{m}{n\mu_0 q^2} \ \nabla^2 \frac{\mathrm{d}\mathcal{B}}{\mathrm{d}t}.$$

We can write this as

 $\frac{\mathrm{d}\mathcal{B}}{\mathrm{d}t} = \lambda^2 \ \nabla^2 \frac{\mathrm{d}\mathcal{B}}{\mathrm{d}t},$

(2)

with

$$\lambda = \sqrt{\frac{m}{nq^2\mu_0}}.$$

As one solution of equation 2 is

$$\frac{\mathrm{d}\mathcal{B}}{\mathrm{d}t} = Ae^{-x/\lambda},$$

we can see that there is an exponential decay of the magnetic field within the surface of the perfect conductor. We call λ the *penetration depth*, and find that it is typically about 10^{-8} m.