

This content has been downloaded from IOPscience. Please scroll down to see the full text.

Download details:

IP Address: 3.139.104.214

This content was downloaded on 28/04/2024 at 16:46

Please note that [terms and conditions apply](#).

You may also like:

[Focus on Superconductors with Exotic Symmetries](#)

T Maurice Rice, Manfred Sigrist and Yoshiteru Maeno

[Phonon softening in nanostructured phonon-mediated superconductors \(review\)](#)

S L Prischepa and V N Kushnir

[Potentials of iron-based superconductors for practical future materials](#)

Jun-ichi Shimoyama

[A dedication to Professor Jan Evetts](#)

Harald Weber, David Dew-Hughes, Archie Campbell, Zoe Barber, Rob Somekh and Bartek Glowacki

# Chapter 1

## Introduction to superconductivity, superconducting materials and their usefulness

### 1.1 Brief introduction to the phenomenon of superconductivity

Ohm's law governs the flow of electrical current,  $I$ , through a conductor in units of amperes. It states that the current  $I$ , passing through a conductor between any two points in it is directly proportional to the voltage applied across these two points,  $V$  in units of volts, i.e.

$$I \propto V$$

the constant of proportionality in this relation is  $1/R$ , where  $R$  is the electrical resistance of the conductor between the above two points, in units of Ohms, which when used gives the Ohm's law,

$$I = V/R$$

The Ohm's law used in materials science and electromagnetics is given as

$$J = \sigma E$$

where  $J$  denotes the current density at a point in a conductor,  $E$  the electric field at that point and  $\sigma$  (called sigma) denotes the conductivity, a parameter which is characteristic of a given conducting material, and is related to

$$\sigma = ne\mu_e$$

where  $n$  is the density of electrons (charge carriers),  $e$  is the fundamental unit of electric charge, and  $\mu_e$  is the mobility of the charge carriers, the electrons in this case. Electrical resistivity,  $\rho$ , is the inverse of electrical conductivity, and is defined as electrical resistance of a conductor of unit cross-sectional area and unit length. Electrical resistivity is a characteristic property of each material. SI units of electrical conductivity,  $\sigma$ , are Siemens per meter, and of  $\rho$  are Ohm meter.

Generally, atoms enter a crystal lattice as ions, with one or more electrons removed, resulting in positive ions forming a rigid lattice with the electrons stripped from ions generally free to move around, which determine the electrical conductivity of the material. Depending on how freely the electrons move, i.e. the mobility of charge carriers in that material, the conductivity of materials varies from high for metals, to medium for semiconductors and low for insulators.

At absolute zero temperature (0 K), one presumes that ions in a crystal lattice are static, though there is still what is known as a zero point motion, as per quantum mechanics. At finite temperatures (say, at room temperature of  $\sim 300$  K), the thermal energy makes them (i.e. the ions or atoms) vibrate around their equilibrium positions. Since these ions are part of a typical crystal structure, their vibrations are collective, with a large number of them being involved in any typical mode of vibration, which is characteristic of a given material. The vibration energy of any mode is quantized in multiples of  $h\omega$  (where  $\omega$  is vibration frequency and  $h$  is Planck's constant), the quantum of this energy, which is called a phonon. Phonons can be thought of as quanta of sound waves, just as photons are quanta of light waves.

At finite temperatures ( $>0$  K), thermal vibrations of the ionic lattice, i.e. the phonons, disturb the periodicity of a given lattice and cause resistance in the path of free conduction electrons which would have, otherwise, travelled without getting scattered at all in a perfectly periodic structure, of a metal, for instance.

Further, even at temperature  $T = 0$  K, when thermal vibration of the ionic lattice dies down, conduction electrons can still be scattered by defects, because all real crystals can have a variety of defects, some of which are, in fact, introduced deliberately in order to alter the useful properties of a given material in a controlled manner, towards different applications. The defects can be point defects, which can be a missing atom (vacancy) in a crystal lattice, or an additional atoms placed irregularly (called interstitial), or even impurity atoms inserted deliberately in the crystal. Among other defects which can exist in a crystal lattice are: (a) dislocations, which are linear in nature, arising from irregular placement of a group of atoms; and, (b) grain boundaries, which arise at an interface of two regions of a lattice when both of the regions are ordered individually as crystals but placed irregularly w.r.t. to each other, at the interface.

The above discussion points to the production of electrical resistance due to scattering of conduction electrons on two counts, by the lattice phonons, and by the defects in the lattice. The scattering by phonons gives rise to a component of the electrical resistivity of a metal which is proportional to its temperature,  $\rho \propto T$ , at ambient and higher temperatures. This should imply that the electrical resistivity should, in principle, fall to zero at a temperature of absolute zero ( $T = 0$  K), but that does not happen due to the scattering of conduction electrons by the defects in the lattice, as mentioned above, giving rise to what is called the residual resistivity, a component of resistivity which remains largely unchanged with rise in temperature. This component, while resisting the flow of electrical current causes dissipation of some energy as heat.

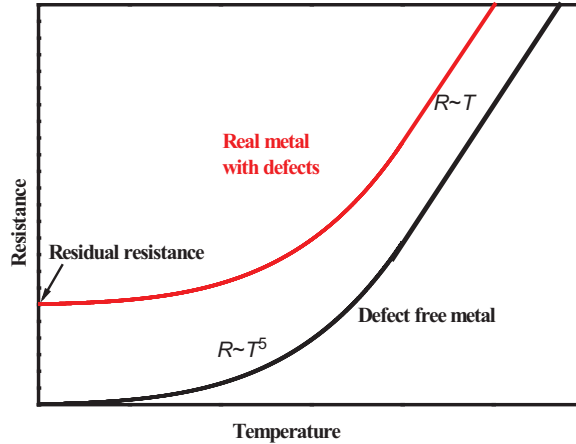
The effective resistivity of a pure conducting crystalline material, say a metal, is described by Matthiessen's rule as:

$$\rho = \rho_T + \rho_R$$

where  $\rho_T$  describes the contribution from phonon scattering, essentially due to thermal effects, and,  $\rho_R$  arising from scattering by defects in the lattice.  $\rho_R$  arises from two components,  $\rho_I$ , a contribution arising from scattering of conduction electrons by the impurities present in it, even if on a very minor scale, and,  $\rho_D$  arising from scattering by defects in the lattice,  $\rho_R (= \rho_I + \rho_D)$ . Therefore, one can write the total resistivity to be arising from three components, viz.

$$\rho = \rho_T + \rho_I + \rho_D$$

Above about 100 K, the electrical resistivity of a pure metal, such as copper, which invariably has some defects, shows a linear relationship with temperature,  $\rho \propto T$ , which continues almost up to its melting temperature, 1358 K, and is similar to the behavior of an ideal defect-free pure metal (figure 1.1). Before the availability of liquid helium to cool a metal sample to temperatures below 10 K, it was understood from the electrical resistivity measurements that at temperatures below about 100 K the resistivity of a pure metal falls steeply on cooling and varies as  $\rho \propto T^5$  [1]. In fact, on a log-log scale (not shown in figure 1.1), the  $\rho$  versus  $T$  plot for a pure metal like copper, can be fitted to two separate behaviors, viz.  $\rho \propto T$  above  $\sim 100$  K, and  $\rho \propto T^5$  for the low-temperature region  $< 100$  K. The contribution from defects for a real metal, and consequently the residual resistivity term  $\rho_R$ , becomes significant only at low temperatures. To summarize:



**Figure 1.1.** Electrical resistance as a function of temperature for an ideal defect-free pure metal compared with a real high conductivity metal, such as copper which invariably has some defects even in its pure form. Above about 100 K the resistance, rather the electrical resistivity, has a linear relationship with temperature,  $\rho \propto T$ . Below  $\sim 100$  K, however, the resistivity for the ideal defect free metal varies as  $\rho \propto T^5$ . For a real metal (the red-color plot), the residual resistivity component  $\rho_R$ , a constant term arising from scattering by the defects, becomes significant at low temperatures, and below  $\sim 10$  K, it overwhelms the  $T^5$  behaviour. Figure courtesy of Dr S K Gupta.

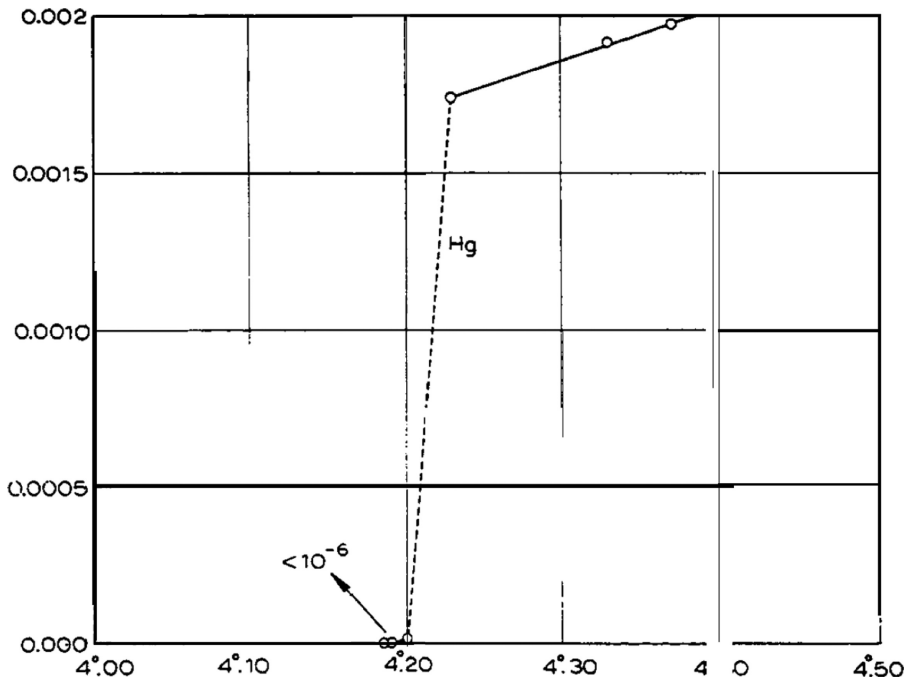
- (a) The residual resistivity,  $\rho_R$ , remains nearly constant, showing very little temperature dependence, and, in fact, overwhelms the  $T^5$  behavior below  $\sim 10$  K, as shown in figure 1.1.
- (b) At high temperatures, the variation of  $\rho_T$  is nearly linear with temperature, and becomes the main contributing factor to resistivity for pure, non-magnetic crystalline metals [2].

For instance, a sample of pure copper, which is highly conducting and has a very low resistivity of about  $2 \mu\Omega \text{ cm}$  at room temperature, shows a steep fall in its resistivity when cooled to 4.2 K, by immersing it in liquid helium, owing to a sharp reduction in the extent of the vibrations of the Cu-ion lattice. The resistivity falls to just  $2 \times 10^{-5} \mu\Omega \text{ cm}$  at 4.2 K, a contribution arising mainly from scattering by defects, i.e.  $\rho_R$ , its residual resistivity.

Lord Rayleigh had proposed a theory that every metal should end up being an insulator at very low temperatures because the conduction electrons should return to the parent atom, and stay bound to it. The Dutch physicist Heike Kamerlingh Onnes was the first person to liquefy helium gas at its boiling temperature of 4.2 K at 1 atm pressure, in 1908 [3]. Using it as a coolant, he wanted to verify Lord Rayleigh's theory, OR alternately, check if the resistance of a very pure metal will fall to zero when it is cooled to very low temperatures. He chose the metal mercury (Hg) for his experiment, because being a liquid at room temperature, it could be made 'ultra-pure' by taking it through a series of distillation processes. To his surprise, he observed in 1911 a sudden (abrupt) drop of electrical resistance to zero below a critical temperature ( $T_c$ ) of 4.2 K [4]. From 1/500, the resistance of mercury drops to a millionth part at 4.2 K (figure 1.2), signaling its entry into a new,  $R = 0$  state, which was called the state of superconductivity, a new phenomenon observed for the first time [5].

A material in its superconducting state ( $R = 0$  below its  $T_c$ ), would obviate Joule heating, enabling the passage of a large current to flow in the material, which should make feasible the production of strong magnetic fields using coils without iron, but using the coils wound by superconducting wire, instead. H K Onnes was indeed successful in sending a current of 0.8 A, i.e. of  $56 \text{ A mm}^{-2}$ , through such a coil [6].

When a material transforms to a superconducting state, all resistance to the flow of current disappears below a characteristic temperature ( $T_c$ ). Thus, a superconductor in the form of a closed loop should sustain current flow forever. This could not be explained by any of the known models of the dependence of resistance of a metal at low temperatures at the time of the discovery of superconductivity. And these models included the one proposed by Mathiessen under his Rule [7], or by Kelvin [8], who had proposed that resistance would achieve a minimum at a low temperature and then rise, as for semiconductors, when cooled further, or by Dewar [9], who had proposed that electrical resistance of a metal would continue to decrease, becoming zero at absolute zero Kelvin, when scattering of charge carriers would cease. None of these models could be of help to explain the phenomenon of



**Figure 1.2.** Resistance of Hg versus temperature. Figure 17 reproduced from the Nobel lecture delivered by H K Onnes, December 11, 1913 [6]. Reproduced with permission of [nobelprize.org](http://nobelprize.org). Copyright The Nobel Foundation.

superconductivity, which required quantum mechanics and a formal theory based on it, as discussed later in this book.

H K Onnes was awarded the Nobel Prize in Physics in 1913, ‘*for his investigations on the properties of matter at low temperatures which led, inter alia to the production of liquid helium*’, as the citation read. It took a few more decades before a formal theory emerged which explained the phenomenon of superconductivity in Hg or for three more elements of the periodic table, viz. lead ( $T_c = 7.2$  K), niobium ( $T_c = 9.2$  K), and thallium ( $T_c = 2.4$  K) for which, too, superconductivity was discovered in another few years [10]. Subsequently, superconductivity was discovered in many other metals (e.g. Sn at  $T_c = 3.2$  K), alloys (e.g. Nb–Ti, Nb–Ge, Nb–Sn), chalcogenides (e.g.  $\text{PbMo}_6\text{S}_8$ ), oxides e.g. Ba–Pb–Bi–O, and even organic compounds such as  $(\text{TMTSF})_2\text{ClO}_4$  (trimethyl-tetraselenafulvalene perchlorate). Until 1986, the highest recorded superconducting ( $T_c$ ) was 23 K ( $-250^\circ\text{C}$ ) for  $\text{Nb}_3\text{Ge}$ .

## 1.2 Does the resistance in the superconducting state really become zero?

If the resistance of a pure metal, such as copper is very small at low temperatures, then how does it compare with that of a superconductor? To settle that let us take an electromagnet, a coil with diameter, say 20 cm, wound with 10 000 turns of fine 0.3 mm pure Cu wire. This coil has a resistance of  $\sim 1$  k $\Omega$  at room temperature (300 K),

which upon cooling to 4.2 K falls to a value of about  $0.01\ \Omega$ . For certain applications as electro-magnets one requires the flow of large currents through such coils. Let us now pass a current through this coil, say 20 A, upon which it dissipates a power of about 0.4 MW at room temperature, due to its large  $1\ \text{k}\Omega$  resistance. But upon cooling this coil to 4.2 K, the amount of power dissipated falls sharply to just about 4 W, due to the low resistance of the whole coil ( $0.01\ \Omega$  at 4.2 K). But, even a heat of 4 W would be sufficient enough to boil the whole liquid helium coolant off in no time, bringing our experiment to nought! To highlight this, one can point out that the closed-cycle He refrigerators used in scientific experiments often have a cooling capacity of just about 0.5 W.

The lesson learnt from the above experiment is that even a low resistance of  $0.01\ \Omega$  is too high at 4.2 K for some applications. Conventional high-field magnets wound with copper coils may need electrical power of tens of MW, compared to almost nil when superconducting winding is used. Can we then put an upper limit to the value of the resistivity of a superconductor in its superconducting state? Or, is it really zero? One measure of that would be to test how long a superconducting current can persist in a loop made from a superconductor, say Nb. Let us cool this Nb ring to a temperature below its  $T_c$  value in a uniform magnetic field of flux density  $B_A$ . If we now change the flux density, a current will start flowing, as per Lenz's law, to oppose this change. Since the superconducting loop has 'zero' resistance, a 'persistent' current is set up in the loop, even when we suddenly remove the applied magnetic field. The current generates a magnetic field, and the magnitude of this field can be measured as a function of time, which allows the measurement of the decay constant of the effective  $R$ - $L$  circuit of this superconductor loop. Using this approach, it has been observed that no discernible change (fall) in current occurred for over two years, the period for which it was monitored. The current in the loop went on and on in a persistent mode, and the resistivity in the superconducting state was estimated to be  $\rho_{sc} \leq 10^{-24}\ \mu\Omega\ \text{cm}$ !

The 'induced' current in a copper cylinder quickly decays in about a millisecond (about  $1/1000\ \text{s}$ ) to zero after the source of the electrical potential has been removed. In contrast, the 'induced' current in the superconducting niobium loop does not decay more than 0.1% of its value over a year! Which means that the electrical resistance offered by a niobium cylinder is smaller than copper by  $(1000\ \text{years}/0.001\ \text{s})$ , i.e. at least 1 trillion times!

By recording NMR (nuclear magnetic resonance) spectra of a material in the magnetic field due to a persistent current in a superconducting solenoid, it has been predicted that no measurable variation in it would occur for even  $10^5$  years.

Zero electrical resistivity in a superconducting state occurs, characteristically, only up to a certain maximum value of current passing through it, called critical current, as well as up to a certain maximum value of applied magnetic field under which this superconductor is. Besides, the superconducting behavior of a material can also be influenced by the flux flow of the vortices, all of which is discussed later in this chapter.

A point to be noted here is that we have been discussing all along only the DC current, whereas the resistance of a superconducting sample is not strictly zero for an

alternating current (AC) in the presence of external magnetic field above a critical value, as discussed later in section 1.11.

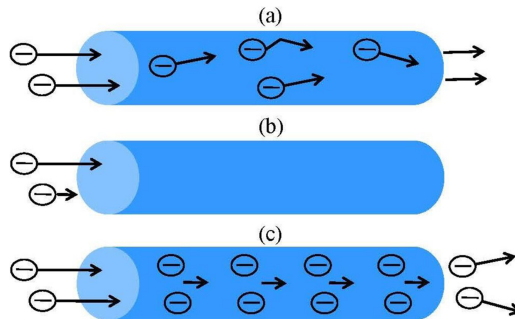
### 1.3 Flow of charge carriers in a metal, an insulator and a superconductor

If we make a simple comparison of the conductivities of wires made from a metal, an insulator, and a superconductor (figure 1.3) then we observe that electrons flow easily in a metallic wire (like that of Cu), just as water flows through a garden hose. As the electrons travel they suffer collisions, with the material resulting in dissipation of energy (heat). However, electrons (the charge carriers) in an insulator are tightly bound, hence no current flows in an insulating wire as if the hose is plugged with cement.

Zero electrical resistance observed for a material in its superconducting state, as observed first by K Onnes, defied a theoretical explanation, and was explained nearly 50 years later, by the BCS mechanism [11], to be discussed later, in section 1.9, the essence of which was the formation of bound electron pairs mediated by the exchange of phonons, below  $T_c$ . These bound electron pairs in the superconducting state, called Cooper pairs, cannot get scattered (figure 1.3(c)), because of a strange quantum phenomenon called ‘macroscopic quantum coherence’ and, hence, a superconducting wire offers no resistance, and there is absolutely no dissipation of energy (heat) as the current flows. Strictly speaking, a superconducting wire offers an infinite conductivity, which is why it is called a ‘super’conductor. The pair-forming has its origin in the ionic system—the lattice, and leads to a macroscopic coherence and perfect diamagnetism.

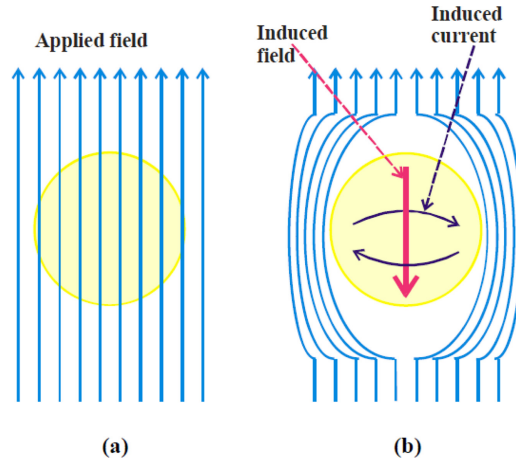
### 1.4 Meissner effect

Apart from zero resistance, a second important attribute of superconductors is diamagnetism. It was discovered in 1933 by Meissner and Ochsenfeld [12], when they observed that materials in a superconducting state act as perfect diamagnets,



**Figure 1.3.** Flow of charge carriers (electrons) in: (a) a metal, (b) an insulator, and (c) a material in its superconducting state. Figure courtesy of Dr V K Aswal.





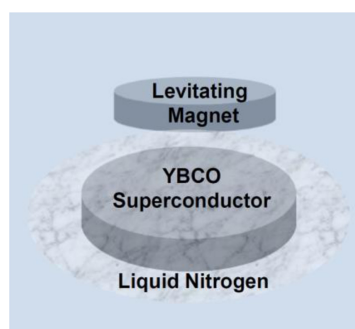
**Figure 1.4.** (a) A normal metal under an applied magnetic field; (b) Meissner effect, i.e. expulsion of magnetic lines of force (flux) by a material in its superconducting state. Figure courtesy of Dr S K Gupta.

i.e. they expel magnetic flux<sup>1</sup>. One can recall that for the case of ideal diamagnets, the magnetic susceptibility ( $\chi$ ), is  $\chi = -1$ , due to which they push out any magnetic flux, depicted as magnetic lines of force (figure 1.4), with constantly flowing resistance-less currents in them. This came to be known as Meißner–Ochsenfeld effect, or simply as Meissner effect.

The phenomenon of magnetic levitation, where a magnetic disc can float over a superconducting material cooled below its superconducting  $T_c$ , or vice versa, is based on the diamagnetic property of superconductors. The superconductor (figure 1.5) is magnetized in a direction opposite to the magnet, and therefore, it repels the latter.

It is worth noting that a material in its superconducting state attains its perfectly diamagnetic Meissner state (figure 1.4(b) above), irrespective of whether (a) it is first cooled below its  $T_c$  with no magnetic field applied, i.e. it is zero-field cooled (ZFC), and the field is switched ON, after it is cooled below  $T_c$ ; or (b) the sample is kept under an applied field and then cooled below its  $T_c$  (implying that it is in its field-cooled, FC, state). In other words, the Meissner state attained by a superconductor below its  $T_c$  is path-independent.

<sup>1</sup> Types of magnetism: when a magnetic material is placed in an applied magnetic field ( $H$ ), it is magnetized such that the field ( $B$ ) inside the material is increased or decreased. Magnetization of a material is denoted by  $M$  and field  $B$  may be written as  $B = H + 4\pi\chi M = \mu H$ , where  $\chi$  and  $\mu$  are called magnetic susceptibility and permeability, respectively. Most of the elements in the periodic table get magnetized in a direction opposite to that of the applied field and are called diamagnetic materials having  $\chi < 0$  and  $B < H$ . Examples of diamagnetic materials are copper, silicon, water, mercury etc, having typical susceptibility value of  $-10^{-6}$  to  $-10^{-5}$  in CGS units. Some other materials, however, get magnetized in the same direction as that of the applied field, so that  $\chi > 0$  and  $B > H$ . Examples of such paramagnetic materials are aluminum, platinum and sodium etc, having typical susceptibility values of  $\sim 10^{-6}$  CGS units. Then there are ferromagnetic materials (such as iron, cobalt and nickel) which get strongly magnetized in the direction of the applied field, with  $B \gg H$  and have typical values of  $\chi > 10^4$  CGS units. Superconductors are unique in their magnetic behavior in that the susceptibility is  $\chi = -1/4\pi$  and  $B = 0$ .



**Figure 1.5.** A permanent magnet disc levitating over a high- $T_c$  superconductor at 77 K. Figure courtesy of Dr V K Aswal.

Li	Be 0.026													B 1.14	C 1.14	N 1.14	O 1.14	F 1.14	Ne 1.14
Na	Mg													Al 1.14	Si 1.14	P 1.14	S 1.14	Cl 1.14	Ar 1.14
K	Ca	Sc	Ti 0.39	V 5.38	Cr	Mn	Fe	Co	Ni	Cu	Zn 0.87	Ga 1.09	Ge	As	Se	Br	Kr		
Rb	Sr	Y	Zr 0.54	Nb 9.5	Mo 0.92	Tc 7.7	Ru 0.51	Rh 0.03	Pd	Ag	Cd 0.56	In 3.40	Sn 3.72	Sb	Te	I	Xe		
Cs	Ba	La 6.0	Hf 0.12	Ta 4.48	W 0.01	Re 1.40	Os 0.65	Ir 0.14	Pt	Au	Hg 4.15	Tl 2.39	Pb 7.19	Bi	Po	At	Rn		

**Figure 1.6.** Elements of periodic table which can superconduct, shaded in yellow color. Values of  $T_c$ , the transition temperatures for each such element are provided in degrees kelvin. Figure courtesy of Dr S K Gupta.

## 1.5 Superconducting elements, alloys, intermetallics and compounds

As superconductivity was discovered in many metallic elements of the periodic table (figure 1.6), some thumb-rules emerged to rationalize their behavior, viz.

1. Metals with the highest conductivities (Cu, Pd, Ag, Pt and Au) are not superconductors.
2. The magnetic 3d elements, Cr, Mn, Fe and Co are not superconducting.
3. Transition temperatures ( $T_c$ ) and critical fields of metallic elements are generally low.

Subsequently, however it was discovered that several other elements of the periodic table can become superconducting under application of pressure. Among them were (with the value of  $T_c$ , transition temperature, given in brackets): iron (2 K under 20 GPa), Ca (15 K), Sr (4 K), Ba (5.1 K), Y (2.7 K), B (11 K), P (18 K), S (17 K), Ge (5.4 K), Si (8.5 K), Se (5.6 K), As (2.7 K), Sb (5.6 K), Te (7.4 K), Bi (8.7 K). Most lanthanides, except La, are magnetic/non-superconducting. A few other elements become superconducting at much lower temperatures (<2 K): such as Be, Pa, U, Am, and Lu (all at ambient pressure), and Sc, O, Br, I, Ce and Am (all under applied pressure) [13].

A superconductor combining ferromagnetic and semiconducting elements,  $\text{CoSi}_2$ , was first discovered in 1952 by Bernd Matthias [14], a pioneer who discovered

superconductivity in a large variety of metals, alloys and intermetallics. In fact, he gave his own rules—Matthias’ rules for looking for superconductivity in new materials, viz.

1. Transition metals are better than simple metals.
2. Peaks of density of states at Fermi level are good.
3. High symmetry is good: cubic is best.
4. Stay away from oxygen, magnetism, and insulating phases.

Among the popular categories of superconductors [13] are alloys and compounds, representatives of which are: alloys/intermetallics NbN ( $T_c = 16$  K), Nb–Ti ( $T_c = 9.2$  K), and Nb<sub>3</sub>Ge ( $T_c = 23$  K); a Chevrel phase compound PbMo<sub>6</sub>S<sub>8</sub> ( $T_c = 14.6$  K); and a heavy Fermion superconductor URu<sub>2</sub>Si<sub>2</sub> ( $T_c = 1$  K). We shall refer to these classes later in this book, at appropriate stages.

All the superconducting materials that we have mentioned thus far are what are known as low- $T_c$  compounds conforming mostly to the BCS theory, to differentiate them from the high- $T_c$  compounds such as bismuthate Ba<sub>0.63</sub>K<sub>0.37</sub>BiO<sub>3</sub> ( $T_c = 31$  K), the cuprate family of superconductors ( $T_c$  up to 138 K at ambient pressure and 164 K under high pressures), a typical example being YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub>, and MgB<sub>2</sub> ( $T_c = 39$  K), some of which do not behave as per BCS theory, as described later.

## 1.6 Critical field, $H_c$

It is important to note that the superconducting state of a material survives only up to a certain value of applied field,  $H_c$ , called the critical field, the value of which is temperature-dependent. Superconductivity is destroyed by increasing either the temperature above  $T_c$  or the field above  $H_c$ , as shown in the plot (figure 1.7) depicting a phase diagram of a superconductor in the  $H$ – $T$  plane.

The relationship between both these critical parameters is given by:

$$\frac{H_c(T)}{H_c(0)} = \left[ 1 - \left( \frac{T}{T_c} \right)^2 \right]$$

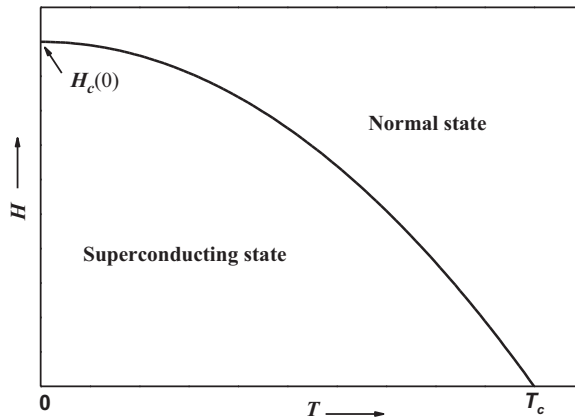


Figure 1.7.  $H$ – $T$  plane for a type I superconductor. Figure courtesy of Dr S K Gupta.

Dependence of induced field and magnetization on applied magnetic field for any sample is given as:  $B = H_0 + 4\pi M$ , where  $B$  is the magnetic induction, and  $M$  is the magnetic moment per unit volume.

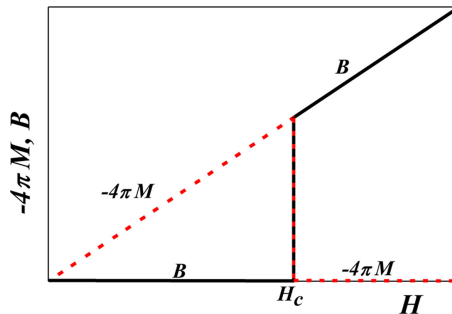
## 1.7 Type I and type II superconductors

It was observed soon after the discovery of superconductivity that superconducting metals like Hg and Pb could not sustain large currents since superconductivity disappeared under relatively weak magnetic fields, say 400–800 Oersted even at very low temperatures ( $T \rightarrow 0$ ), since they were, as we now call, type I superconductors, (figure 1.7), which remain diamagnetic only up to a rather low magnetic field, called the critical field,  $H_c$ , above which the magnetic flux associated with the current flow destroys the superconducting state.

For type I, typified by several elemental superconductors (figure 1.6), except Nb, which is type II, the induced magnetic flux,  $B$  suddenly becomes zero (expelled out of it) when the material enters a superconducting state, as shown in figure 1.8, because perfect diamagnetism survives only up to the critical field,  $H_c$ , the value of which is quite low for type I superconductors, with the result that the Meissner state suddenly disappears, and the material turns ‘normal’.

It was, however, found that a number of alloys and compounds, especially when suitably prepared, could sustain superconductivity even under very high fields and for fairly large currents passed through them, i.e. they belonged to the category of type II superconductors. A typical example of these type II superconductors is Nb–Ti, which made the technology of superconducting magnets a commercial reality since in type II materials, superconductivity can persist up to a much higher field, called  $H_{c2}$  (figure 1.9), and superconducting magnets made from them produce fields of 100 000 and even 200 000 Oe. This is made possible due to the existence of a ‘mixed state’ in a type-II superconductor (as shown in figure 1.9) which is discussed in section 1.8.

Up to the year 1960, the type II superconducting materials exhibiting the highest  $T_c$  were the alloys, such as Nb<sub>3</sub>Sn with  $T_c = 18.4$  K and critical field at 4.2 K around 20 T.



**Figure 1.8.** Critical field,  $H_c$ , for type I superconductors. Figure courtesy of Dr S K Gupta.

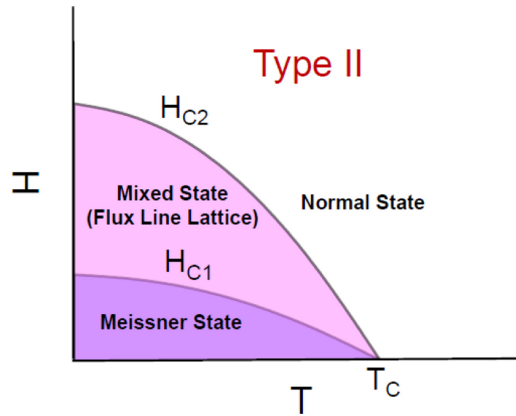


Figure 1.9.  $H$ - $T$  plane for a typical type II superconductor. Figure courtesy of Dr V K Aswal.

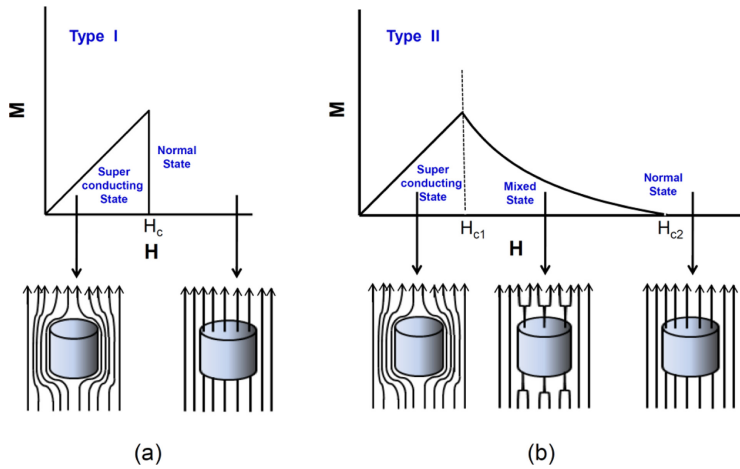
## 1.8 Abrikosov vortices, flux line lattice and the mixed state

The type II superconductors are those for which not only the value of the critical field is high, but which also exhibit two states. As the applied field is raised, it first approaches the Meissner state under applied field of magnitude less than the first critical field,  $H_{c1}$ , above which the magnetic flux starts penetrating the material but does so in a gradual manner, and complete flux-penetration and destruction of superconductivity occurs only at the second critical field  $H_{c2}$ , the value of which is quite high. The useful superconducting properties of the alloys are due to their type II character, a behavior predicted by Abrikosov [15] and outlined earlier by Shubnikov [16], before the experimental discovery of the type II superconductors.

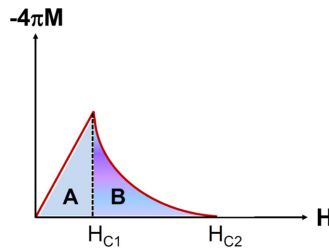
The type II superconductors are the most suited for applications as they have a distinct response to applied magnetic field, i.e. above a certain value,  $H_{c1}$ , the magnetic field penetrates the material in the form of flux lines, until a second (upper) critical field  $H_{c2}$  is reached. We should take note of the fact here that the magnetic flux that is penetrating into a type-II superconductor is quantized in unit of  $h/2e$  (where  $2e$  is the charge held by a pair of electrons, i.e. the Cooper pair, about which we shall discuss more, later, in section 1.9). The magnetic flux quantum,  $h/2e$ , has a constant value of  $2.067\ 833\ 848... \times 10^{-15}$  Wb.

As stated above, the magnetic flux penetrates a type I superconductor abruptly making it a normal conductor at a low value of  $H_c$ , (shown in figure 1.10(a)), the flux starts penetrating a type II superconductor only restrictively above  $H_{c1}$ , and the normal state occurs only at a much higher value of  $H_c$ , called  $H_{c2}$  (figure 1.10(b)). The properties of these superconductors can be described in the framework of the Ginzburg–Landau theory.

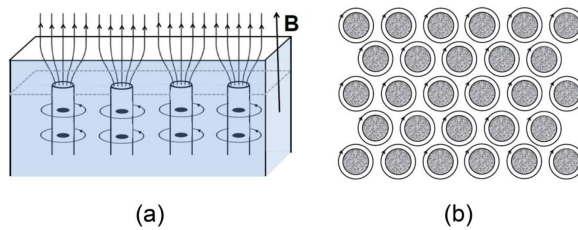
The ‘mixed state’ of a type II superconductor located between  $H_{c1}$  and  $H_{c2}$ , called Shubnikov phase (shown in figure 1.10(b), and also in figure 1.11), consists of a regular lattice of Abrikosov vortices (A A Abrikosov, Nobel Prize, 2003) (figure 1.12). In actual practice this renders the type II superconductors to be useful



**Figure 1.10.** (a) and (b)  $M$  versus  $H$  for type I and type II superconductors describing their magnetic field response. Figure courtesy of Dr V K Aswal.



**Figure 1.11.**  $M$  versus  $H$  behavior and the mixed state in a type II superconductor. The region marked 'A' denotes the Meissner state, and the region 'B' of the figure denotes the mixed state or the Shubnikov phase where Abrikosov vortices permeate, but the critical field persists with a long tail making the mixed state useful for applications of superconductors in magnets. Figure courtesy of Dr V K Aswal.



**Figure 1.12.** (a) Magnetic flux,  $B$ , enters a type II superconductor as vortices, separated by superconducting regions; (b) a planar depiction of vortices in the mixed state of a type II superconductor, forming an Abrikosov lattice. Figure courtesy of Dr V K Aswal.

for applications such as for making high-field magnets<sup>2</sup>, since they can sustain large enough fields in the superconducting state without entering a ‘normal’ state, sustaining the high currents by the windings of a magnetic coil since the resistive heating which is an attribute of a normal state does not set in below  $H_{c2}$ .

Under a magnetic field applied in the mixed state of a type-II superconductor, a vortex lattice is formed from flux-line bundles (figure 1.12). Each vortex has a tube-like shape and all these vortices are aligned along the direction of the applied field. Each of these so-called Abrikosov vortices has a normal-conducting core of a few nm radius. Each vortex is screened by a supercurrent circulating around it, generating a magnetic flux quantum. The circular currents make any two flux-lines repel each other, which results in an ordered hexagonal lattice, such that the normal phase cannot pervade the superconducting phase surrounding them, until the field exceeds  $H_{c2}$ .

Vortices in superconductors consist of a normal core with size  $\xi$  (coherence length) and supercurrents flowing over a distance  $\lambda$  (penetration depth). The value of the magnetic penetration depth  $\lambda$  characterizes the decay of an external magnetic field inside a given superconductor and is related to the coherence length  $\xi$  by the formula

$$\kappa(T) = \frac{\lambda(T)}{\xi(T)}.$$

where  $\kappa(T)$  is known as the Ginzburg–Landau (G–L) parameter, which also determines the type of superconductivity of a material. If the value of the G–L parameter  $\kappa$  is  $<1/\sqrt{2}$  then it is said to be a type-I superconductor, and if it is  $>1/\sqrt{2}$ , it is termed as type-II superconductor. Based on this relation, one can state that for a type-I superconductor the value of coherence length is greater than its penetration depth. So if two vortices are generated in a type-I superconductor the normal cores would overlap first, due to the larger value of  $\xi$  with respect to  $\lambda$ , thus leading to

<sup>2</sup> Basics of magnetism for superconducting magnets: we provided a summary on types of magnetism in footnote 1 of this chapter. Further on that, in the context of superconducting magnets, one generally talks about the strength of the magnetic field,  $H$ , which is a vector having direction as well as a magnitude (i.e. its strength). Another useful parameter is the flux density,  $B$ , which signifies the number of magnetic flux lines which pass through a unit area held perpendicular to the magnetic field.  $H$  and  $B$  are related by the equation  $B = \mu H$ , where  $\mu$  is the permeability of the medium, a measure of its magnetizability.  $H$  has units of Oersted, Oe or Ampere/meter,  $A\ m^{-1}$ , where  $1\ kA\ m^{-1} = 12.54\ Oe$ . Flux density  $B$  is measured in units of Gauss (G) or Tesla (T), where  $1\ G = 1\ Oe = 0.1\ mT = 0.079\ 77\ kA\ m^{-1}$ .

When the medium is air,  $\mu$  is mostly taken to be equal to 1, in which case  $1\ Gauss\ (G) = 1\ Oersted\ (Oe)$ . As per SI units, the magnetic field strength  $H$  is defined in units of  $Oe\ A\ m^{-1}$  (Oersted Ampere/meter). As per old convention, the flux density  $B$  is described in units of Gauss (G), or in Tesla (T), which includes the magnetizability,  $\mu$ . The magnetic parameters of a permanent magnet are described in terms of the residual magnetic flux density,  $B_r$ , and magnetic coercive force,  $H_c$ .  $H_c$  is described in units of Oe, and defines the strength of magnetic field required to cause the magnetic pole reversal. The unit of magnetic field is tesla. For an easy reference, the field of a fridge magnet is about 0.01 T. In the early 1960s, the discovery of niobium–titanium boosted the strength of superconducting magnets to 10 T, enabling their use in everything from MRI machines to particle accelerators. In the mid 1970s, scientists discovered that  $Nb_3Sn$  was an even better superconductor, leading to magnets of upto a strength of 24 T, now used for research at numerous labs and universities.

vortex–vortex attraction [17]. Two vortices in a type-II material, however, would have their supercurrents overlapping first, in view of  $\lambda > \xi$ , leading to vortex–vortex repulsion. An attractive vortex–vortex interaction results in the formation of macroscopic normal domains in the intermediate state [18], while vortex–vortex repulsion leads to the appearance of the Abrikosov lattice [19].

Density of vortex lines in a plane is given by their number/unit area, is:  $n = B/\phi_0$ . Magnetic flux enters a type II superconducting sample in its mixed state as an Abrikosov lattice of vortex lines (figure 1.12(a)), cores of which are separated by superconducting regions. More specifically, Meissner effect in the mixed state of type II superconductors is not complete, and magnetic flux lines enter them as vortices (figure 1.12(b)), with each flux line carrying a flux quantum of:  $\phi_0 = h/2e = 2.07 \times 10^{-7}$  gauss cm<sup>2</sup>.

The penetration of the magnetic field in the intermediate range  $H_{c1} < H < H_{c2}$  has been clearly evidenced and studied; and the dynamics of the vortices has been clarified. The vortices have been found to move very easily for temperatures not so far below  $T_c$  and they control the transport properties. Only below a so-called irreversibility temperature  $T_{irr} < T_c$  can the vortices be considered fixed (in a way depending from impurities and/or defects) and thus no dissipation occurs.

First quantitative description of the properties of the superconducting state was formulated by the London brothers in 1935 [20]. Seven years before the publication of the microscopic BCS theory, a phenomenological theory developed by Ginzburg and Landau [21], which was based on Landau's concept of an order parameter used to describe a thermodynamic phase transition, succeeded in explaining many of the observed properties of superconductors, in spite of the prevailing uncertainties on the pairing mechanism. Even the two characteristic length scales,  $\lambda$  and  $\xi$ , came out as solutions of the G–L equations.

## 1.9 BCS mechanism: flux quantization and energy gap

The BCS theory applies well to the conventional low- $T_c$  superconducting materials and explains the phenomenon of superconductivity in them. This microscopic theory was proposed in 1957 by Bardeen, Cooper, and Schrieffer, the BCS theory [11], almost 50 years after the experimental discovery of superconductivity. According to the BCS theory, the key microscopic factor behind this phenomenon is the attraction between electrons mediated by the exchange of phonons, such that below  $T_c$  within the electronic system there forms a macroscopic manifold of bound electron pairs (known as the Cooper pairs). Thus the attraction has its origin in the ionic system—the lattice, and the pairing of electrons leads to macroscopic coherence and perfect diamagnetism.

According to this theory, superconductivity arises because of the formation of bound pairs of electrons. For this to occur, a pre-requisite is a strong attractive interaction between pairs of electrons, strong enough to overcome the normal Coulomb repulsion between these pairs. A second condition to be fulfilled is that the superconducting state must exhibit a unique electrodynamic behavior under which all the bound pairs of electrons must exist in one and the same quantum mechanical state.



The BCS attractive mechanism of superconductivity owes itself to the conduction electrons deforming the crystal lattice, slightly. A simple model to describe the BCS mechanism of stabilizing the superconducting state by the electron–phonon interactions is as follows. The ionic lattice of a metal is a periodic crystalline array of positive ions immersed in the sea of conduction electrons. Consider a negatively charged conduction electron traveling through this array of positive ions. As it moves it pulls the much heavier positive ions towards it, though only slightly since the movement of the ion is restrained by neighboring ions of the ionic lattice, elastically. The maximum displacement of the ions occurs a bit after the fast moving electron has passed. That leaves a region of excess positive charge, behind the electron that passed. This positively charged region attracts (pulls in) a second passing electron towards it. This way, these two electrons get coupled via the ‘virtual quanta’ of phonons of the ionic lattice. It is pertinent to take note that superconductivity exists even at  $T = 0$ , where there are no thermal phonons, which are ‘real quanta’, which in fact degrade superconductivity! Effectively, this leads to the formation of mutually attracted pair of electrons, a stable bound Cooper pair, arising from the dynamic distortion of the lattice, called phonons, and hence the attractive interaction under the BCS theory is known as the phonon-induced electron–electron attraction. Since at any reasonably high temperature, the lattice of ions undergoes lattice vibrations due to thermal effects, the pair of electrons, the Cooper pair, owes its coupling (attraction) to phonons. The electrons are fermions, but the Cooper pairs are bosons, and the superconducting state is characterized by the Bose condensation of Cooper pairs.

A Cooper pair is formed by two electrons (spin singlets) having equal and opposite momentum and spin. Thus the angular momentum of a Cooper pair is 0 (it is in  $s$ -state), and the pair has a coherence length ( $\sim 100$  nm which is  $\gg$  atomic spacings). e–ph coupling occurs between two electrons with opposing spin directions and opposite momenta, viz. an electron with momentum  $\mathbf{k}$  and spin direction  $\uparrow$ , coupled via a phonon with another electron with momentum  $-\mathbf{k}$  and spin direction  $\downarrow$ . A theoretician would describe this attraction as due to exchange of ‘virtual phonons’.

The superconducting state involves the pairing of a sizeable part of about  $10^{22}$  electrons per cubic centimeter. The pairs at  $S = 0$  obey the Bose–Einstein statistics and all can set in a single quantum state, while single electrons are continuously scattered in different single-electron states. The BCS theory describes a variety of properties of the superconducting state resulting from the transition driven by pair condensation.

The energy price of breaking a Cooper pair is  $2\Delta_0$  where  $\Delta_0$  is the band-gap, known as superconducting gap. But to pick up a single Cooper pair to do so is not simple since this is a part of a Bose condensate which is a sea of such pairs at the Fermi level. The energy relation for the band-gap for a BCS superconductor is given as:  $2\Delta_0 = 3.52 k_B T_c$  and the value of  $\Delta_0$  drops gradually to zero as the temperature of this material rises to its  $T_c$  value.

The second condition for superconductivity, namely, that all the pairs should be in the same state, allows one to satisfy the conditions of coordinated motion. It is

thus energetically favorable for many pairs to be in the same state so that at low enough temperatures a condensate of paired electrons can result. As we raise the temperature we eventually come to the point where some of the pairs are thermally disrupted. The effect of these disrupted pairs is two-fold. Firstly, they reduce directly the number of bound pairs, and secondly, due to the now uncoordinated motion of the individual electrons, they interfere with and weaken the attractive interaction of the remaining pairs making it easier for the remaining pairs to be broken. As the temperature is raised further this break up becomes catastrophic, and above a well-defined transition temperature  $T_c$ , no bound pairs can exist. This transition reflects the transition from the superconducting to the normal state.

The factor 2 in the relation for a flux quantum ( $\phi_0 = h/2e = 2.07 \times 10^{-7}$  gauss cm<sup>2</sup>) is itself a proof of the charge carriers acting as Cooper pairs in the superconducting state. Flux quantization has been demonstrated in the superconducting state experimentally [22, 23]. Flux quantization has been observed in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>, too, which shows that electrons are paired in the case of this high- $T_c$  material, just like the low- $T_c$  superconductors which obey the BCS mechanism, although what holds a pair of electrons together in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-δ</sub> is debatable, because it is thought that the typical  $e-ph-e$  attraction is not valid in the case of cuprate superconductors.

As discussed above, there are two fundamental length scales of the superconducting state: (a) the penetration depth ( $\lambda$ )—the length over which magnetic flux can penetrate a superconductor; and (2) the Pippard coherence length ( $\xi$ )—the length over which the super-electron density  $n_s$  rises from zero at the boundary between normal and superconducting regions, to a maximum value over a distance  $\xi$  (order of which is  $10^{-4}$  cm).

Phonons (lattice waves) can propagate in any metal and usually cause some attraction between electrons near the Fermi surface. According to the BCS theory, electrons with opposite momenta pair up, and for the phonon mechanism of superconductivity  $T_c \leq 20\text{--}40$  K. The penetration depth  $\lambda$  and the coherence length  $\xi$  emerge as natural consequence of the BCS theory. The London equation is obtained for magnetic fields that vary slowly in space. Thus, the central phenomenon in superconductivity, the Meissner effect, is obtained in a natural way. Magnetic flux through a superconducting ring is quantized and the effective unit of charge is  $2e$  rather than  $e$ . And that gives evidence of pairing of electrons.

### 1.9.1 The isotope effect

The first hint of the underlying electron–phonon interaction being responsible for superconductivity came from the discovery of the isotope effect. It was observed that the critical temperature,  $T_c$ , of a superconductor varies with the isotope of that element, as per the relation:  $M^\alpha T_c = \text{constant}$ , where  $\alpha \sim 0.5$  [24–26], where  $M$  is the isotopic mass. For instance, for the superconductors Hg, Sn, Pb, Cd and Tl, the term  $\alpha$  was found to be in the range of  $\sim 0.50$ . This is called the isotope effect. The dependence of  $T_c$  on the isotopic mass  $M$ , points to the involvement of the lattice vibrations (phonons). The  $e-e$  interaction via the phonons ( $ph$ ), the  $e-ph-e$  interaction, orders the participating  $e$ 's in the  $k$ -space w.r.t. the Fermi gas of

electrons, a cornerstone of the origin of superconductivity in the BCS theory. In solid phase, the lattice vibrations are quantized and can be described by quasi-particles, called phonons. Under the quantum mechanical approach, it is assumed that the phonons represent a normal mode vibration such that all parts of the lattice vibrate with the same frequency. Thus the isotope effect can also be elaborated as:  $T_c \propto \theta_{\text{Debye}} \propto M^{-\alpha}$ , where  $\alpha = 1/2$ , and  $\theta$ , the Debye temperature, can be taken to be proportional to the frequency of the vibration of the lattice  $\nu$ , implying:  $\theta \propto \nu \propto M^{-1/2}$ .

### 1.9.2 The band gap and heat capacity

A model was developed by Peter Debye in 1912 for estimating the phonon contribution to the specific heat (heat capacity) of a solid. As against the Einstein model which treats a solid as many individual, non-interacting quantum harmonic oscillators, the Debye model treats the phonons (i.e. the atomic lattice vibrations or the thermal vibrations) as particles in a box, and predicts the low temperature dependence of the heat capacity to  $T^3$ —the Debye  $T^3$  law. The Debye model is to solid-state, what Planck's law is to black body radiation, where one treats electromagnetic radiation as a photon gas<sup>3</sup>.

At temperatures much below the Debye temperature and the Fermi temperature ( $T_F$ ), the heat capacity of metals is a sum of electron- and phonon contributions:  $C = \gamma T + AT^3$ , where  $\gamma$  is called the Sommerfeld parameter. The electronic term dominates at low temperatures.

A heat capacity jump, a second-order phase transition occurs for a superconductor at  $T_c$ . Below  $T_c$ , the total heat capacity (electronic + lattice contributions together) shows an exponential temperature dependence. The electronic part of the heat capacity contains an experimental factor,  $E_g/2$ , that may be used to determine the value of  $E_g$ , the energy gap.

In a normal metal, at  $T = 0$  K, all states below the Fermi energy are filled, and all states above it are empty. Superconductors exhibit energy gap between the ground state and the lowest excited state. BCS theory predicts that at  $T = 0$ ,  $E_g = 3.52 k_B T_c$ . Unlike the energy gap of insulators, which arises from electron–lattice interaction, the energy gap of superconductors is due to e–e interaction, which orders the electrons in  $k$ -space with respect to the Fermi gas of, electrons. Electrons in the excited state above the energy gap behave as normal electrons causing resistance. Representative values of the energy gap  $E_g$  are (in meV): Nb (3.05), Pb (2.73), La (1.9), Hg (1.65), and In (1.05). Therefore, the energy gap (energy needed to break apart a Cooper pair) in a superconductor is very small, of the order of  $k_B T_c$  ( $10^{-3}$  eV) at 0 K, as compared with the band gap in semiconductors ( $\sim 1$  eV).

<sup>3</sup> The beauty of the Debye model was that it could arrive at, just as the Einstein model did, the classical Dulong–Petit law (c. 1819) in thermodynamics, which states that for a solid at normal (room) temperatures, or higher, the heat capacity per mole is nearly constant and is equal, as was later established to,  $C = 3k_B N$  where  $N$  is total number of atoms in the sample. The Debye  $T^3$  model is followed well only at temperatures  $T \gg \theta_D$  where lattice heat capacity prevails,  $\theta_D$ , the Debye temperature being the approximate temperature limit below which quantum effects dominate.

The electronic part of heat capacity  $C_e$  in the superconducting state is given as:

$$C_{es}/\gamma T_c \propto a \exp(-bT_c/T)$$

proportional to  $-1/T$ , suggestive of excitation of electrons across an energy gap. In a superconductor, the energy gap  $E_g$  arises due to the electron–electron interaction via phonons, and the energy gap term,  $-E_g/2k_B T$ , is related to the exponential factor in the electron heat capacity of a superconductor, i.e.

$$C_{es} = \gamma T_c \exp(-1.76 T/T_c)$$

The weak  $e$ – $ph$  coupling superconductors have a typical value:  $E_g(0)/k_B T_c = 3.52$ , whereas the strong  $e$ – $ph$  coupling superconductors have  $E_g(0)/k_B T_c > 3.52$ .

## 1.10 Wires and cables from low $T_c$ superconductors NbTi and Nb<sub>3</sub>Sn

The workhorse for high field magnets used in superconducting accelerators is NbTi wires/cables. Stability criteria requires making of superconductors as fine filaments embedded in a matrix of copper. Magnetic fields induce persistent screening currents in a superconductor. Flux jumping occurs when screening currents go unstable and quench the magnet. To avoid this one uses fine filaments. Screening currents produce magnetization and the use of fine filaments leads to their getting coupled in changing fields. Increased magnetization can be tackled by twisting. Accelerator magnets need high currents, and coupling can be controlled by using oxide layers on wires or by using resistive core foils.

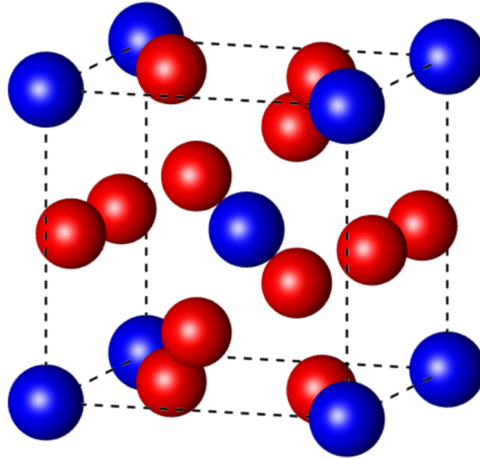
Performance of superconductors is described by the critical surface in  $B$ – $J$ – $T$  space. It is important to take note that the performance of superconducting magnets gets often degraded and shows ‘training’.

### 1.10.1 A<sub>3</sub>B superconductors

Perhaps the most widely used class of type-II superconducting compounds are the A<sub>3</sub>B family having the A-15 structure (beta-tungsten), where A are TM-atoms, such as V or Nb, and B denote non-transition metal atoms such as Sn, Al, Ga, Si, Ge (figure 1.13). Six A15 compounds have transition temperatures over 17 K, and high values of upper critical fields  $H_{c2}$  at 4.2 K [27]. Specifically, the values of  $T_c$  and  $H_{c2}$  (at 4.2 K) for different A-15 compounds, respectively, are: V<sub>3</sub>Ga (15.4 K, 23 T), V<sub>3</sub>Si (17.1 K, 23 T), Nb<sub>3</sub>Sn (18.3 K, 24 T), Nb<sub>3</sub>Al (18.9 K, 33 T), Nb<sub>3</sub>Ga (20.3 K, 34 T), and Nb<sub>3</sub>Ge (23.0 K, 38 T).

Nb<sub>3</sub>Ge thin films held the record for the highest known  $T_c$  of 23 K for a number of years up to 1986. *This was thought to be close to the limit imposed by BCS theory, within phonon exchange mechanism!* Nb<sub>3</sub>Sn, is the most widely used material while constructing very high field superconducting magnets for particle accelerators.

Fabrication of Nb<sub>3</sub>Sn cables is not an easy task because the phase diagram of Nb–Sn is complex, such that one can get Nb<sub>3</sub>Sn (A-15 structure) only after an annealing process above 930 °C. One method that is deployed is to take Sn strands surrounded by Nb strands and embed the Nb–Sn strands into a Cu-matrix, swage



**Figure 1.13.** The unit cell of A15 Nb<sub>3</sub>Sn, showing the Sn atoms in blue and the Nb atoms in red. This structure holds for other A<sub>3</sub>B compounds, too, where A stands for Nb or V, and B is a non-transition metal atom like Sn, Al, Ga, Si or Ge. Reproduced from [28]. Copyright IOP Publishing. Reproduced with permission. All rights reserved

them first before annealing at high temperatures to get multifilamentary Nb<sub>3</sub>Sn cables embedded in a Cu-matrix. Another choice to fabricate Nb<sub>3</sub>Sn films is to adopt liquid Sn diffusion method, under which one dips a Nb-substrate in a liquid Sn bath for about 15 min. Subsequent annealing above 1025 °C yields Nb<sub>3</sub>Sn films with characteristic  $T_c$  value of 17.7 K. One may recall that pure Nb superconducts below 9.3 K and pure Sn below 3.6 K.

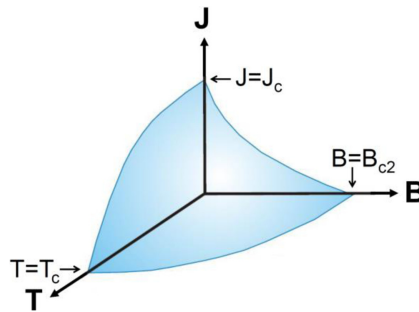
Current applications of high-field magnets fabricated from type-II superconductor wires are for magnetic resonance imaging (MRI), magnetically levitated trains, high-energy particle accelerators, and toroidal fusion reactors. Superconducting cables also find applications in magnetic energy power storage rings.

### 1.10.2 The triumvirate: $T_c$ , $B_{c2}$ and $J_c$

Both Nb<sub>3</sub>Sn and NbTi can provide upper critical magnetic fields  $H_{c2} \sim 10$  T. There are other superconducting materials giving much higher  $H_{c2}$  such as 41 T by Nb<sub>3</sub>Al<sub>0.7</sub>Ge<sub>0.3</sub> and >100 T by some high- $T_c$  cuprates (all values at 4.2 K), but to make wires/cables of these materials for commercial use is still difficult.

It is the successful pinning of flux lines which makes a superconducting material useful for high-field applications. It has to stay hard to remain useful against increase in the magnetic induction  $B$ . As shown by the triumvirate (figure 1.14) the superconducting state can be destroyed by raising either of the three parameters beyond their critical values, viz. the Critical temperature ( $T_c$ ), critical current density ( $J_c$ ) and critical induction ( $B_{c2}$ ).

In addition to the two parameters,  $T_c$  and  $B_{c2}$ , which are intrinsic characteristics of a superconductor, the superconducting state is also destroyed if the material carries a current density higher than a critical value,  $J_c$ , called the critical current



**Figure 1.14.** The triumvirate— $T_c$ ,  $B_{c2}$  and  $J_c$ . Figure courtesy of Dr V K Aswal.

density. Temperature, magnetic field and current density thus determine together whether a material would remain superconducting or not. The superconducting state thrives below and vanishes above a three-dimensional critical surface unique to each superconductor. In contrast to  $T_c$  and  $B_{c2}$ , the  $J_c$  of a superconductor can be controlled by metallurgical processing and by introducing defects in it.

A superconductor may have high  $T_c$  and  $B_{c2}$  values, but their  $J_c$  is very much dependent on the processing and fabrication conditions. Thus, the quality of a candidate superconductor material is assessed on the basis of: (i) how high the  $T_c$  is, the higher the better; (ii) how much current it can carry in the superconducting state; and (iii) how large a magnetic field (internal as well as externally applied) it can withstand without losing its superconductivity.

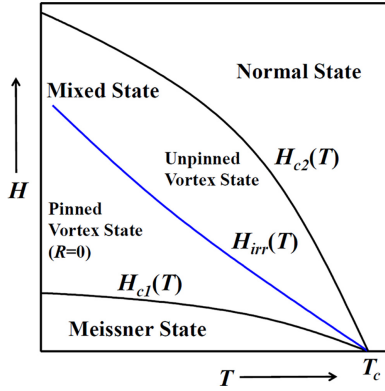
### 1.10.3 The irreversibility line

The potentially useful state of a type II superconductor is below the irreversibility line (shown in figure 1.15) below which the material is in a state where the flux lines are trapped (pinned) in the vortex lattice. Above the irreversibility line there is almost no pinning, fluxoids are not trapped, and magnetization is reversible, rendering the  $J_c$  to plunge to negligible levels.

The increase of the superconducting temperature, the critical fields and critical currents in the alloys is related to the reduction of the coherence length accompanying the decrease of the mean free path of the electrons. The alloying process transforms the metallic superconductors from type I to type II.

Pinning has technological importance in order to lock the vortices and avoid dissipation. For a current flowing perpendicular to the field  $H$ , the Lorentz force pushes the vortices along the  $j \times H$  direction.

In the early 1900s, we had elemental *sp* metals like Hg, Pb, Al, Sn, Ga, etc. In the middle of the 1900s we saw the discovery of transitional metals, alloys, and compounds with somewhat higher  $T_c$  values, like Nb, NbN (16 K), Nb<sub>3</sub>Al (17.5 K), Nb<sub>3</sub>Sn (18.5 K), Nb<sub>3</sub>Ge (23 K), K<sub>3</sub>C<sub>60</sub> (19.2 K), V<sub>3</sub>Ga (16.5 K), V<sub>3</sub>Si (17.1 K) La<sub>3</sub>In (16 K), etc. In the late 1900s, we saw the emergence of high- $T_c$  perovskite oxides YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> (90.0 K), Rb<sub>2</sub>CsC<sub>60</sub> (31.3 K). Whereas, the A-15 compounds A<sub>3</sub>B had  $T_c$  = 15–23 K, the highest  $T_c$  observed in the case of an oxide superconductor, under ambient pressures is 138 K for (Hg<sub>0.8</sub>Tl<sub>0.2</sub>)Ba<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>8.33</sub>.

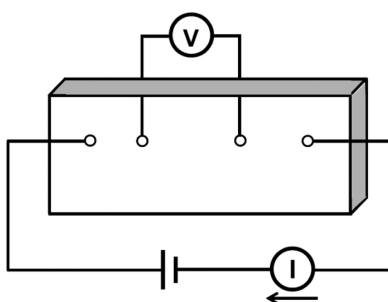


**Figure 1.15.** The irreversibility line,  $H_{irr}(T)$ , of a type II superconductor, shown in blue color, separates two distinct regions of the  $H$ - $T$  plane. Below  $H_{irr}(T)$ , we have a useful state, where the flux lines are trapped (pinned) in the vortex lattice, and above it, there is almost no pinning, and magnetization is reversible, rendering the  $J_c$  to plunge to negligible levels, making the latter useless for applications. Figure courtesy of Dr S K Gupta.

### 1.11 Techniques employed to evaluate the basic physical characteristics of superconducting materials

Crystal structure of new materials is established by employing various complementary diffraction techniques which use x-rays, neutrons, or electrons, and high resolution electron microscopy [29, 30]. However, when materials with known crystal structures are prepared, then one just goes for x-ray diffraction to match the fingerprints of diffraction peaks with a standard x-ray pattern from literature. The superconducting transition temperature  $T_c$  (and its sharpness),  $H_c$ , and current density  $J_c$  are evaluated using DC/AC magnetization techniques; electrical resistance of a sample is measured using the four-probe method, which is also used commonly to check the value of  $T_c$  and the transport current density. Heat capacity, particularly the electronic part is measured by using adiabatic calorimetry; valence state of relevant cations is checked using XPS (x-ray photoelectron spectroscopy); and band-gap details using ARPES (angle-resolved photoemission spectroscopy). Details of these experimental methods are explained in several textbooks, book chapters and review articles.

It is, nonetheless, relevant to describe the four-probe method (also called four-point probe method) [31] used to measure electrical resistance of a superconducting sample, as we cool it from its normal state through its superconducting transition, when its electrical resistance disappears. Quite often a doubt comes to the mind of beginners in this field as to how the very low value of resistance (say, less than micro-ohms and tending to zero), can be measured, when the resistance of lead-wires and the resistance of the contacts applied are themselves orders of magnitude higher, of the order of a few to hundreds of milliohms. Contact and lead resistances become irrelevant because voltmeters have very high internal resistance (typically  $10^6$ – $10^{12}$  ohm) and practically do not draw any current (figure 1.16). Thereby true sample



**Figure 1.16.** DC resistivity measurements are performed using a four probe technique to eliminate the influence of the contact and lead resistances. The contacts are made by pasting fine 25  $\mu\text{m}$  gold wires with a small amount of silver or carbon paint. Figure courtesy of Dr V K Aswal.

voltage between the inner two contacts is accurately measured without any drop on lead/contact resistances [32].

Zero resistance in superconducting materials implies absence of a voltage drop along the material when a current is passed through it, and thereby no dissipation of power. But this happens only for a DC current of constant value, but not when we pass an AC current. The JJ decoupling can play a significant role in the AC response obtained below critical temperature in granular YBCO, for instance. The AC loss due to frequent JJ decoupling is directly proportional to the applied AC frequency [33], and therefore, the AC resistance depends directly on the applied AC frequency and increases with an increase in frequencies.

## References

- [1] Kasap S O 2017 *Principles of Electronic Materials and Devices* 4th edn (Dubuque, IA: McGraw-Hill)
- [2] Kasap S, Kouhgia C and Ruda H E 2017 *Electrical Conduction in Metals and Semiconductors* (Springer Handbook of Electronic and Photonic Materials) ed S Kasap and P Capper (Berlin: Springer) ch 2
- [3] Onnes H K 1908 The liquefaction of helium *Proc. R. Acad. Amsterdam* 11 168
- [4] Onnes H K 1911 Further experiments with liquid helium. G. On the electrical resistance of pure metals, etc. VI. On the sudden change in the rate at which the resistance of mercury disappears *Communications from the Physical Laboratory of the University of Leiden* vol 124C (Dordrecht: Springer) pp 21–6
- [5] Onnes H K 1911 *Communications from the Physical Laboratory of the University of Leiden* vol 120b KAWA (*Proc. of the Koninklijke Akademie van Wetenschappen te Amsterdam*, 28 Apr 1911) pp 1479–81
- [6] The Nobel lecture delivered by Prof. Heike Kamerlingh Onnes, on Dec. 11, 1913: <https://nobelprize.org/uploads/2018/06/onnes-lecture.pdf>
- [7] Matthiessen A and Vogt C 1864 On the influence of temperature on the electric conducting-power of alloys *Philos. Trans. R. Soc.* **154** 167–200
- [8] Kelvin L 1902 XXIX. Aepinus atomized *Philos. Mag. Ser. 6* **3.15** 257–83
- [9] Dewar J 1904 On electric resistance thermometry at the temperature boiling hydrogen *Proc. R. Soc. Lond.* **73** 488–96



- [10] Onnes H K 1991 *Through Measurement to Knowledge—The Selected Papers of Heike Kamerlingh Onnes 1853-1926* 1 edn (Dordrecht: Springer)
- [11] Bardeen J, Cooper L N and Schrieffer J R 1957 Theory of superconductivity *Phys. Rev.* **108** 1175–204
- [12] Meissner W and Ochsenfeld R 1933 Ein neuer Effekt bei Eintritt der Supraleitfähigkeit *Naturwissenschaften* **21** 787–8
- [13] [https://en.wikipedia.org/wiki/List\\_of\\_superconductors](https://en.wikipedia.org/wiki/List_of_superconductors)
- [14] Matthias B T 1952 Superconductivity in the cobalt–silicon system *Phys. Rev.* **87** 380
- [15] Abrikosov A A 1952 *Dokl. Akad. Nauk SSSR* **86** 489
- [16] Shubnikov L V *et al* 1937 *Zh. Eksp. Teor. Fiz.* **7** 221
- [17] Brandt E H 1986 *Phys. Rev. B* **34** 6514
- [18] Huebener R P 1990 *Magnetic Flux Structures of Superconductors* (New York: Springer)
- [19] Abrikosov A A 1957 *Zh. Eksp. Teor. Fiz.* **32** 1442  
Abrikosov A A 1957 On the magnetic properties of superconductors of the second group *Sov. Phys. JETP* **5** 1174–82
- [20] London F and London H 1935 The electromagnetic equations of the supraconductor *Proc. R. Soc. A: Math. Phys. Eng. Sci.* **149** 71–88
- [21] Ginzburg V L and Landau L D 1950 On the theory of superconductivity *Zh. Eksp. Teor. Fiz.* **20** 1064–82
- [22] Doll R and Näbauer M 1961 Experimental proof of magnetic flux quantization in a superconducting ring *Phys. Rev. Lett.* **7** 51–2
- [23] Deaver B S Jr and Fairbank W M 1961 Experimental evidence for quantized flux in superconducting cylinders *Phys. Rev. Lett.* **7** 43–6
- [24] Lock J M, Pippard A B and Shoenberg D 1951 Superconductivity of tin isotopes *Proc. Camb. Phil. Soc.* **47** 811–9
- [25] Maxwell E 1952 Superconductivity of the isotopes of tin *Phys. Rev.* **86** 235–42
- [26] Serin B, Reynolds C A and Lohman C 1952 The isotope effect in superconductivity. II. Tin and lead *Phys. Rev.* **86** 162–4
- [27] Testardi L R 1975 Structural instability and superconductivity in A-15 compounds *Rev. Mod. Phys.* **47** 637–48
- [28] Posen S and Hall D L 2017 Nb<sub>3</sub>Sn superconducting radiofrequency cavities: fabrication, results, properties, and prospects *Supercond. Sci. Technol.* **30** 033004
- [29] Barrett C and Massalski T B 1987 Structure of metals *Crystallographic Methods, Principles, and Data* (International Series on Materials Science and Technology) vol 35 3rd rev edn (Oxford, New York: Pergamon)
- [30] Ashcroft N W and Mermin N D 1976 *Solid State Physics* (New York: Holt, Rinehart, and Winston)
- [31] Smits F M 1958 Measurement of sheet resistivities with the four-point probe *Bell Syst. Tech. J.* **34** 711–8
- [32] Samarappuli S, Schilling A, Chernikov M A, Ott H R and Wolf T 1992 Comparative study of AC susceptibility and resistivity of a superconducting YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> single crystal in a magnetic field *Physica C* **201** 159–65
- [33] Sarangi S, Chockalingam S P and Bhat S V 2005 Frequent Josephson junction decoupling is the main origin of ac losses in the superconducting state *J. Appl. Phys.* **98** 073906