Scientific Research Publishing

Open Journal of Applied Sciences, 2022, 12, 1243-1253
https://www.scirp.org/journal/ojapps
ISSN Online: 2165-3925
ISSN Print: 2165-3917

Implementation of a Semi-Classical Theory for Superconductors

Elie W'ishe Sorongane

Physics Department, University of Kinshasa, Kinshasa, Democratic Republic of the Congo
Email: wisheselie@gmail.com

How to cite this paper: Sorongane, E.W. (2022) Implementation of a Semi-Classical Theory for Superconductors. *Open Journal of Applied Sciences*, **12**, 1243-1253.
https://doi.org/10.4236/ojapps.2022.127084

Received: June 25, 2022
Accepted: July 17, 2022
Published: July 20, 2022

Abstract

When the temperature of certain materials is lowered to exceed a certain value called the critical temperature, a state transition occurs: the system passes from the normal state to the superconducting state. A superconductor has two fundamental physical properties: a zero electrical resistance to direct current and a Meissner effect (the material repels any external magnetic flux). Lacking a suitable theory, physicists have attempted to explain the existence of this exotic low-temperature state using phenomenological approaches. In this work, we introduce a semi-classical (non-phenomenological) theory of superconductors. We demonstrate then that only the behavior of the gas of free electrons following the variation of the temperature in the metal explains not only the physical properties of the superconductors but also the existence of superconductors at high critical temperature. The critical temperature then plays the same role as the liquefaction temperature in a gaseous state-liquid state transition and the same role as the Curie temperature in a paramagnetic state-ferromagnetic state transition.

Keywords

Superconducting State, Normal State, Critical Temperature, Free Electron, Electron Gas, Electron Density

1. Introduction

When the temperature of certain materials is lowered to exceed a certain value T_c called the critical temperature; there is a state transition: the system passes from the normal state to the superconducting state. The latter is characterized by two main physical phenomena: zero resistance to direct current and a Meissner effect (the material repels any magnetic field coming from outside). Until now, only two phenomenological theories have tried to explain these surprising characteristics of metals at low temperatures, but without real success, I quote the Ginzburg-Landau theory, which attempts to describe the superconducting state at the macroscopic scale and the Bardeen-Cooper-Schrieffer (BCS) theory which attempts to describe it on a microscopic scale [1].

Indeed, these two theories are based on a rather abject assumption: the existence of the Cooper pairs. In the superconducting state, it is assumed that the free electrons move in pairs, thus forming a system composed of particles of integer spin, each consisting of two electrons. The Cooper pairs thus formed are no longer subject to the Pauli exclusion principle and then form a single, coherent state of lower energy than that of the normal metal (unpaired free electrons).

However, we all know, first, that Coulomb repulsion does not allow such particles to exist in a stable state. We demonstrated this so well in our previous article entitled "Electromagnetic Interaction: A New Theoretical Approach" that we published in the same journal [2]. In this article, a new theoretical approach in which electromagnetic repulsion is described as a consequence of attraction has been introduced. We have illustrated this approach as follows: two little girls each stand at the ends of a rope. One like the other pulls to her side to try to attract the other toward her. If all of a sudden, the rope gave way and was cut in two, the two girls will be thrown, each on their side and we will have the impression that our two little girls have pushed each other away. Let us now replace our two little girls with two charged particles, the cord by the electromagnetic interaction and we have our model which we have named: the binding cord approach. Starting from the Heisenberg uncertainty relation on energy and time, that is: $\Delta E \cdot \Delta t \geq \hbar$ (ΔE is the energy of the interaction *i.e.*, of the electromagnetic field, Δt is the lifetime of the system and $\hbar = \frac{h}{2\pi}$, with *h*, the Planck constant), we have shown that the lifetime of the system is given by:

$$\Delta t = \frac{\hbar}{\int_V \mathrm{d}^3 r \left(\frac{\varepsilon_0}{2} \left| \boldsymbol{E}(\boldsymbol{r},t) \right|^2 + \frac{1}{2\mu_0} \left| \boldsymbol{B}(\boldsymbol{r},t) \right|^2 \right)} \quad (1)$$

NB:

- The electric field $\boldsymbol{E}$ is defined by the total charge q of the system. We have:

$$\left| \boldsymbol{E} \right| = \frac{1}{4\pi\varepsilon_0} \cdot \frac{q}{r^2}.$$

- The magnetic field $\boldsymbol{B}$ has two components [3]:

  1) A component $\boldsymbol{B}_c$ due to the charged particle when it is not at rest.

  2) A component $\boldsymbol{B}_s$ due to the spin of the particle. So we will have:

$\boldsymbol{B} = \boldsymbol{B}_c + \boldsymbol{B}_s$

- The integral in the denominator is always greater than or equal to zero. It is equal to zero if only if $\boldsymbol{E} = \boldsymbol{0}$ and $\boldsymbol{B} = \boldsymbol{0}$, it is greater than zero otherwise. This means that the lifetime of any system will always be greater than zero, which makes physical sense.

Thus, for a system composed of two charged particles like the Cooper pair, we will always have $\boldsymbol{E} \neq \mathbf{0}$; which implies that $\Delta t < \infty$ (the lifetime of the particle is finite). The system is unstable; the two electrons repel each other. It is for the same reason that the isotope 2 of helium (${}_{2}^{2}\text{He}$) has never been observed.

Second, Cooper explained this coupling or pairing between two electrons by imagining an interaction between the electrons and the crystal lattice formed by positive ions. These attract each other with the electrons and move slightly (high inertia). Physicists have given the name phonons to these natural atomic vibrations. This interaction between electrons and phonons is at the origin of the existence of Cooper pairs. Attracted by the very rapid passage of an electron (10^6 m/s), the ions move and create a local electrically positive zone. Given the inertia, this zone persists while the electron has passed and can attract another electron which is thus, via a phonon, paired with the previous one. However, the superconducting state is a low-temperature state. Who says low temperature says slowing of the movement of electrons. Considering electrons moving at a speed of the order of 10^6 m/s necessarily requires that an external electric field be applied to the superconductor. Whereas the superconducting state of a material is independent of the applied external field. A superconductor remains superconducting below T_c even in zero fields. Moreover, we will see later that in reality, the crystal is not formed of positive ions and electrons but rather of neutral atoms bathed in a gas of electrons.

Thirdly, the formula of the critical temperature given by the BCS theory indicates that it cannot exceed 25 - 30 K. 30 K seemed to be a limit value since until 1986, no temperature exceeded 24 K. In April 1986, the discovery of a 34 K superconductor called it into question. Today, the discovery of high critical temperature superconductors up to 164 K clearly contradicts the BCS theory.

We will therefore have to turn to a new theory that better describes the physical behavior of materials in the superconducting state and above all which takes into account the existence of superconductors at high critical temperatures. In addition, the semi-classical theory introduced in this work explains the isotopic effect of superconducting elements and the superconductivity of fullerides.

2. The Semi-Classical Theory

2.1. Description

The electrical and thermal conductivities of metals are justified by the existence of free electrons (also called conduction electrons) in these materials. To explain the origin of these free electrons, specialists in solid-state physics claim that these are the valence electrons of atoms. They go on to say that in metals, the overlapping of orbitals of peripheral electrons is so strong that certain valence electrons no longer belong to a specific atom but are distributed throughout the crystal. It is then considered that the metal is formed of positive ions bathed in a gas of electrons [4]. This gas moves freely and binds ions together because the attraction of electrons to ions outweighs the repulsion of ions to each other and electrons to each other. However, note here that if this is the case, the metal cannot retain its conductive characteristic indefinitely. Indeed, Coulomb attraction requires that there be a recombination of charges. The ions will attract the electrons towards them and after a certain time, all the atoms will become neutral again with the total disappearance of the free electrons. This is exactly what happens in a plasma which is also a system made up of positive ions and electrons. Let us also add that if it was indeed the valence electrons that formed the conduction electrons in the metal, then the metals having four valence electrons such as lead or tin should have the highest electrical conductivities of all metals. But this is not the case; these are rather metals with a single valence electron that have the highest electrical conductivities of all metals (silver, gold and copper).

We then introduce here a new hypothesis that explains much better the existence of free electrons in metals. In fact, the various metallic elements that we find in nature in a stable state have been produced by radioactive decays of the heavier elements, notably the decay β^-. The latter is a transformation of a neutron into a proton with the emission of an electron and an antineutrino according to the reaction [5]:

$$n \rightarrow p + e + \overline{\nu}$$

These emitted electrons are then trapped in the material and cannot escape. They are the ones that constitute the gas of (free) electrons and are therefore responsible for electrical and thermal conduction in metals. This hypothesis is confirmed by observations because most of the unstable metals found in nature or created in the laboratory de-excite by decay β^-, producing stable metals [6]. Examples include niobium-94, which produces molybdenum, copper-64 which produces zinc, cobalt-60 which produces nickel, manganese-56 which produces iron, iridium-192 which produces platinum, iron-59 which produces cobalt, palladium-107 which produces silver, nickel-63 which produces copper.

The metal is therefore made up of neutral atoms bathed in a gas of free electrons. This gas of charged particles behaves like any gas of neutral atoms. Indeed, when the temperature of inert gas is lowered below the liquefaction (or vaporization) temperature, a change of state occurs: the system passes from the gaseous state to the liquid state. This transition corresponds to an increase in the density of the system (decrease in volume) and therefore, a decrease in the interatomic distance (the distance between two neighboring atoms). Consider then two distinct gases A and B at a given temperature T. If at this temperature, the interatomic distance in gas A is greater than that in gas B, then the liquefaction temperature of A will be lower than the liquefaction temperature of B. We can cite by way of example helium and nitrogen. At 288 K, helium has a density of 0.1785×10^{-3} g/cm^3 while that of nitrogen is 0.1848×10^{-3} g/cm^3. The interatomic distance in helium gas is therefore greater than that in nitrogen gas. Hence the liquefaction temperature of helium (4.2 K) is lower than that of nitrogen (77 K).

Similarly, when the temperature of a material is reduced to exceed the critical temperature, a state transition occurs: the system passes from the normal state to the superconducting state. This transition corresponds to an increase in the density of the electron gas (decrease in volume) and therefore a decrease in the interelectronic distance (the distance between two neighboring electrons). Let us then consider two distinct materials A and B at a given temperature T. If at this temperature, the interelectronic distance in material A is greater than that in material B, then superconductor A will have a critical temperature T_c lower than that of material B. The critical temperature in the normal-superconducting state transition then plays exactly the same role as the liquefaction temperature in a gaseous-liquid state transition.

We also know that when the temperature of a ferromagnetic material is increased until it exceeds a certain value T_{cu} called the Curie temperature, a state transition occurs. The material changes from an ordered ferromagnetic state to a disordered paramagnetic state [7]. The ferromagnetic state is an ordered state because the spin magnetic fields of the atoms are aligned, while in the paramagnetic state they are not (see **Figure 1**).

In all superconductors, entropy decreases when cooling in zero field below T_c. This decrease in entropy from the normal state to the superconducting state indicates that the superconducting state is more ordered than the normal state. We therefore thought that the critical temperature in the superconducting state-normal state transition would play exactly the same role as the Curie temperature in the ferromagnetic state-paramagnetic state transition. The superconducting state is then an ordered state because the spin magnetic fields of the free electrons are aligned while in the normal state they are not.

Let us now show that this theory explains not only the physical properties of superconducting materials but also the existence of superconductors at high critical temperatures.

2.2. The Meissner Effect

When the material is in its normal state, that is to say, at a temperature T such that $T_c < T < T_{cu}$, the spin magnetic fields of the atoms are aligned while those

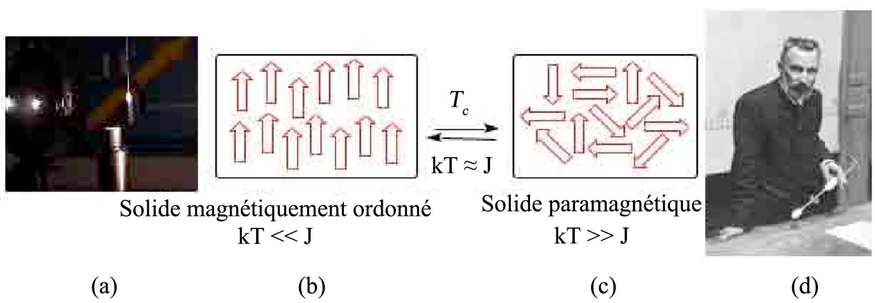

Figure 1. Curie temperature T_c: (a) "nail" experiment; in the center, modeling of the transition from a disordered magnetic solid (c) to a magnetically ordered solid (b) when the interaction between magnetic moments becomes of the same order of magnitude as the thermal agitation; (d) Pierre Curie carrying out experiments in the amphitheater of Physics, 12 rue Cuvier, in 1900 (photo origin: Curie museum, Paris).

of the free electrons are not aligned following the thermal agitation. When the material is subjected to an external magnetic field, the total spin magnetic field of the atoms interacts with the external field. One can use the binding cord approach to describe this interaction.

Note the external magnetic field $\boldsymbol{B}_m$ and $\boldsymbol{B}_a$, the resultant of spin magnetic fields of the atoms. The total magnetic field $\boldsymbol{B}$ of the system is then given by: $\boldsymbol{B} = \boldsymbol{B}_m + \boldsymbol{B}_a$. The system is composed of neutral atoms, the electric field $\boldsymbol{E} = \boldsymbol{0}$. Thus, the lifetime Δt of the system is given by:

$$\Delta t = \frac{\hbar}{\int_V \mathrm{d}^3 r \frac{1}{2\mu_0} \left|\boldsymbol{B}_m + \boldsymbol{B}_a\right|^2} \tag{2}$$

Two cases can then be distinguished:

- If $\boldsymbol{B}_m = -\boldsymbol{B}_a$ then $\Delta t = \infty$. The system is stable (no repulsion). The material is ferromagnetic and the spin magnetic fields of the atoms are parallel.
- If $\boldsymbol{B}_m \neq -\boldsymbol{B}_a$ then $\Delta t < \infty$. The system is unstable (the external magnetic field is repelled by the material). The material is diamagnetic and the spin magnetic fields of the atoms are antiparallel.

When the material becomes superconducting at a temperature T such that $T < T_c$, the spin magnetic fields of the electrons are aligned. When the superconductor is placed in an external magnetic field, the spin magnetic field resulting from the electrons interacts with the external field. Let's again use the binding cord approach to describe this interaction. Note $\boldsymbol{B}_m$, the external magnetic field and $\boldsymbol{B}_e$, the resultant of spin magnetic fields of the electrons. The total magnetic field $\boldsymbol{B}$ is given by: $\boldsymbol{B} = \boldsymbol{B}_m + \boldsymbol{B}_e$. The system is composed of charged particles, the electric field $\boldsymbol{E} \neq \boldsymbol{0}$. Hence the lifetime Δt of the system is given by:

$$\Delta t = \frac{\hbar}{\int_V \mathrm{d}^3 r \left(\frac{\varepsilon_0}{2}\left|\boldsymbol{E}(\boldsymbol{r},t)\right|^2 + \frac{1}{2\mu_0}\left|\boldsymbol{B}(\boldsymbol{r},t)\right|^2\right)} < \infty \tag{3}$$

The system is unstable. The external magnetic field is repelled by the superconducting material: Meissner effect.

NB: There are certain materials in nature for which a partial Meissner effect is observed (for weak fields) above the critical temperature: this is the reflection of light. Indeed, although the spin magnetic fields of electrons are not aligned in the normal state, it can happen that the magnetic fields due to the movement of electrons (charged particles) are aligned. A partial Meissner effect then occurs: the light, which is an electromagnetic field, is repelled by the material. We say that the light is reflected by the material. Note therefore that the reflectance of metal can be associated with its electrical conductivity. This is the reason why the four metallic elements with the highest electrical conductivities in nature (silver, gold, copper and aluminum) also have the highest reflectivity: 100% for silver, 85% - 90% for aluminum, 72% - 85% for gold and 64% for copper.

2.3. Zero Electrical Resistance

When the temperature of a superconducting material is reduced until it exceeds the critical temperature, the material has zero resistance to the passage of a direct electric current (infinite conductivity). To explain this phenomenon, let us consider in a superconductor, a free electron of charge q_e bathed in a magnetic field $\boldsymbol{B}$ created by all the other free electrons of the electron gas. This electron is then subjected to a Laplace force $\boldsymbol{F}_l$ given by:

$$\begin{aligned} \boldsymbol{F}_l &= \boldsymbol{j} \times \boldsymbol{B} \ (\boldsymbol{j} \text{ is the current density}) \\ &= q_e \boldsymbol{V}_e \times \boldsymbol{B} \ (\boldsymbol{V}_e \text{ is the speed of the electron}) \end{aligned} \tag{4}$$

In the superconducting state, that is to say, at low temperature, we have $\boldsymbol{V}_e \cong \boldsymbol{0}$. From where $\boldsymbol{F}_l \cong \boldsymbol{0}$. When the superconducting material is subjected to an external electric field $\boldsymbol{E}$, the electron is subjected to an electrostatic force $\boldsymbol{F}_e$ given by:

$$\boldsymbol{F}_e = q_e \boldsymbol{E} \tag{5}$$

The electron is therefore not subject to any force which opposes the electrostatic force to be slowed down in its course. Hence the zero resistance of superconductors to a direct current. In fact, the Laplace force $\boldsymbol{F}_l$ is a braking force that opposes the electrostatic force $\boldsymbol{F}_e$ when the material is subjected to an external electric field in the normal state. Hence the non-zero resistance of the material. Notice then that, in the normal state, when the temperature increases, that is to say when $\boldsymbol{V}_e$ increases, the electric resistance also increases, which agrees with the observations.

2.4. Isotope Effect

Measurements of critical temperatures show that these depend on the isotopic mass. In a given series of isotopes, the results can be put in the form:

$$M^{\alpha} T_c = Cst \tag{6}$$

with $\alpha \approx 0.5$.

This relation can be deduced from the semi-classical theory of superconductors. In fact, the different isotopes of a given metallic element are produced by successive radioactive decays of heavy elements, notably the decays β^-. Thus, if M_1 and M_2 are the respective isotopic masses of isotopes 1 and 2 of a given metal with $M_1 > M_2$, then it took more successive disintegrations β^- to produce 2 than to produce 1. However, each disintegration β^- increases the number of free electrons in the material. This increases the density of the electron gas and therefore decreases the interelectronic distance. Hence the critical temperature T_{c2} of isotope 2 will be greater than the critical temperature T_{c1} of isotope 1. We then arrive at the relationship:

$$M_1^{\alpha} T_{c1} = M_2^{\alpha} T_{c2} = M^{\alpha} T_c = Cst \tag{7}$$

with $\alpha \approx 0.5$.

2.5. Low Critical Temperature Superconductors

For the electrical resistance to be zero, the average speed of the electrons in the material must be close to zero; and for the Meissner effect to occur, there must be the coupling of the magnetic fields of the electrons, which requires a minimum interelectronic distance. These two conditions are met when the temperature becomes lower than the critical temperature.

Low critical temperature superconductors are usually type I [1]. The Meissner effect is total down to a weak field H_c, where the superconductivity disappears completely [8]. In this first type, only the spin magnetic fields of the electrons are aligned in the superconducting state. This type of behavior is observed in some pure metals where the electronic mean free path in the normal phase is high, as we can see in **Table 1**. This is quite plausible. Indeed, in the first approximation, the interelectronic distance is equal to the electronic mean free path in the material [9]. Thus, if the mean free path of the electrons is high then the interelectronic distance is too. Hence the low critical temperatures of type I superconductors. Note here that we will now be able to estimate the electronic mean free path in a material knowing its critical temperature and likewise, we will be able to estimate the critical temperature of the superconducting metal knowing the free electronic mean path in the material.

2.6. High Critical Temperature Superconductors

High critical temperature superconductors are type II [1]. The Meissner effect is total up to a weak critical field H_{c1}, then above H_{c1}, there is a mixed superconductor-normal metal phase with a partial Meissner effect, up to the critical field H_{c2}, where all the material becomes normal. In this second type, the critical temperature being high, some neutral atoms present spin magnetic fields aligned below T_c. Hence the partial Meissner effect in the mixed phase.

High critical temperature superconductors were discovered in 1986 by J.G. BEDNORZ and K.A. MÜLLER, who won the Nobel Prize. As you can see in **Table 2**, these are all copper-based alloys, which is completely logical. Indeed, the very high electrical conductivity of copper (the third highest of all metals after those of silver and gold) and its relatively high density (8.96 g/cm^3) at room temperature implies necessarily a high density of the electron gas, *i.e.*, a relatively small interelectron distance. It is therefore the copper atoms that give the materials in **Table 2** their high critical temperatures. And besides, it seems established that the superconductivity of these alloys takes place essentially in the CuO_2 planes.

2.7. Fullerides

They are made up of compounds centered around "fullerenes" [1]. The name "fullerene" comes from designer author BUCKMINSTER FULLER. It was he who invented the geodesic dome (structure in the shape of a football). Fullerenes exist at a molecular level when 60 carbon atoms join together to form a sphere.

Table 1. Type I superconducting single elements at normal atmospheric pressure.

Elements	Critical temperature (K)
Carbon (C)	15
Lead (Pb)	7.2
Lanthanum (The)	4.9
Tantalum (Ta)	4.47
Mercury (Hg)	4.15
Tin (Sn)	3.72
Indium (In)	3.40
Thallium (Tl)	1.70
Rhenium (Re)	1.697
Protactinium (Pa)	1.40
Thorium (Th)	1.38
Aluminum (Al)	1.175
Gallium (Ga)	1.10
Gadolinium (Gd)	1.083
Molybdenum (Mo)	0.915
Zinc (Zn)	0.85
Osmium (Bone)	0.66
Zirconium (Zr)	0.61
Americium (Am)	0.60
Cadmium (Cd)	0.517
Ruthenium (Ru)	0.49
Titanium (Ti)	0.40
Uranium (U)	0.20
Hafnium (Hf)	0.128
Iridium (Ir)	0.1125
Lutetium (Lu)	0.100
Beryllium (Be)	0.026
Tungsten (W)	0.0154
Platinum (Pt)	0.0019
Rhodium (Rh)	0.000325

Table 2. Critical temperatures of some materials at high critical temperature.

Material	Critical temperature (K)
$La_{2-x}Sr_xCuO_4$	38

Continued

$Eu_2Ba_2Cu_3O_{10-x}$	43
(La, Sr, Ca)$_3Cu_2O_6$	58
$Pb_2Sr_2YCu_3O_8$	70
$YBa_2Cu_4O_8$	80
$YBa_2Cu_3O_{6+x}$	92
$Bi_2Sr_2Ca_2Cu_3O_{10}$	110
$Tl_2Ba_2Ca_2Cu_3O_{10}$	125
$HgBa_2Ca_2Cu_3O_{8+x}$	135

When a fullerene is doped with one or more alkali metals, it becomes a "fulleride" and often also a superconductor. Superconducting fullerides have a critical temperature between 8 K for $Na_2Rb_{0.5}Cs_{0.5}C_{60}$ and which can go up to 40 K for Cs_3C_{60}. Other even higher critical temperatures have been reached for C_{60}. A critical temperature of 117 K was recently found. The high critical temperatures of fullerides are easily justified. Of all the elements in **Table 1**, carbon has the smallest interelectron distance, *i.e.*, a relatively high electron gas density. Thus, by associating a large number of carbon atoms in a molecule, one can form a compound having an even higher density of free electrons, that is to say, an even smaller interelectronic distance. Hence the high critical temperatures of fullerides.

3. Conclusions

In this work, we have introduced a new semi-classical theory to describe the superconducting state. We showed that only the behavior of the electron gas could explain not only the physical properties of superconductors but also the existence of superconductors at high critical temperature. Thus, zero electrical resistance is due to the slowing of the movement of electrons to a speed close to zero; and the Meissner effect is caused by the interaction between the external magnetic field and the magnetic field due to the coupling of the aligned spin magnetic moments of the electrons. The normal state-superconducting state transition when the temperature is lowered simply corresponds to a decrease in the density of the electron gas until a minimum interelectronic distance is reached. This minimum distance is reached much faster in materials with high free electron densities. This explains the high critical temperatures of copper-based alloys. The minimum interelectron distance is reached at much lower temperatures in materials with relatively low free electron densities. This explains the low critical temperatures of pure metals in which the electronic mean free path in the normal phase is high.

Today, the objective is to reach a critical temperature of around 300 K (ambient temperature). To achieve this, we must turn to alloys based on metals with very high densities of free electrons. Alloys containing gold and/or silver are serious leads that will allow us to make this dream come true.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

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