THEORY OF SUPERCONDUCTIVITY

M. Crisan

THEORY OF SUPERCONDUCTIVITY

M. Crisan
Institute of Physics and Technology of Materials, Bucharest
and
Department of Physics, University of Cluj, Romania

World Scientific
Singapore • New Jersey • London • Hong Kong

Published by

World Scientific Publishing Co. Pte. Ltd.,
P O Box 128, Farrer Road, Singapore 9128
USA office: 687 Hartwell Street, Teaneck, NJ 07666
UK office: 73 Lynton Mead, Totteridge, London N20 8DH

Library of Congress Cataloging-in-Publication Data

Crisan, M. (Mircea)
Theory of superconductivity/M. Crisan.
p. cm.
ISBN 997150569X
ISBN 9971509970 (pbk)
1. Superconductivity. I. Title.
QC611.92.C75 1989
537.6'23--dc20 89-16480
CIP

Printed in Singapore by Utopia Press.

PREFACE

Superconductivity was discovered in 1911 by Kamerling Onnes and at that time, it was difficult to realise the importance of this phenomenon. In 1934, Gorter and Casimir proposed the first model — the two-fluid model — for the superconducting state and in 1935, F. London and H. London developed the electrodynamics of superconductors.

Ginzburg and Landau used in 1950 the Landau theory of phase transitions to treat the transition from the normal to the superconducting state. The method was successfully applied by Abrikosov in 1958 to predict the vortex structure in superconductors.

The first microscopic model was developed by Bardeen, Cooper and Schrieffer between 1956 and 1958 and had as its main point the occurrence of electron pairs due to the attractive electron-electron interaction mediated by virtual phonons. In 1958, Gor'kov showed that the model proposed by Bardeen, Cooper and Schrieffer can be treated within the framework of the Green function method. In the same period, the important contributions to the theory of superconductivity were made by Bogoliubov and Anderson. The role of the electron-phonon interaction in the occurrence of the superconducting state was elucidated by Eliashberg in 1960 and Scalapino, Wilkins and Schrieffer in 1961. In 1962, Josephson predicted additional tunnelling current when both sides of a junction are superconductors.

Starting from 1960, Matthias traced the occurrence of superconductivity in a large number of alloys and compounds containing magnetic impurities. During that period the main problem was the discovery of materials as well as microscopic mechanisms for the coexistence of superconductivity with magnetic order. The phenomenological ideas were transformed between 1961 and 1966 in more and more sophisticated models, using the many-body methods of Abrikosov, Gor'kov, Fulde, de Gennes and Maki to develop the theory of superconducting alloys. The experimental results obtained since 1973 by Maple and Fischer demonstrate clearly the coexistence between superconductivity and magnetic order in some ternary compounds with a special crystalline structure. In another class of rare-earth compounds, the narrow band of the "f"-electrons present superconducting pairing called "heavy fermion superconductivity". The theory of coexistence between superconductivity and magnetic order was developed beginning in 1978 by Matsubara, Maekawa, Machida, Tachiki, Keller, Fulde, Levin *et al.*

In 1986, Bendorz and Müller showed the possibility of obtaining the superconducting state in all oxides and in 1987 many groups from the USA, the Soviet Union, Japan, W. Germany, England and France announced the discovery of high temperature superconductivity.

Even before this discovery there was great interest in possible practical applications of superconductivity, but in future, the technology will be drastically affected by this discovery. For the time being, the theoretical models are elaborated by reconsidering the electron-phonon interaction, but till now there is no decisive answer concerning the mechanism which is responsible for high temperature superconductivity.

All these problems will be treated in this small book in a unified way to assure an equilibrium between the physical ideas and the mathematical formalism which is necessary in the treatment of this difficult subject.

A prerequisite to reading this book is some familiarity with solid state physics, quantum and statistical mechanics and the theory of many-body systems. I have not tried to incorporate such special problems as the theory of superconducting slabs, or the theory of nonstationary behaviour of superconductors because there are many books on these subjects. The other class of problems which has not been treated is the unsolved problems as to the critical behaviour of superconductors.

Last but not least, I would like to thank Dr. Ulf Lindström for his help.

I hope that this book will help solid-state theorists to approach the existing treatments of superconductivity and solid-state experimentalists to become acquainted with theory of superconductivity.

M. Crisan

CONTENTS

I
PHENOMENOLOGICAL THEORY OF SUPERCONDUCTIVITY

1. Experimental Facts

Infinite conductivity: When any of a large class of crystalline or amorphous elements and compounds is cooled, the electrical resistivity disappears at a definite critical temperature T_c. In the first approximation, the transition is not accompanied by any change in structure or property of the crystal lattice and has been interpreted as an *electronic transition*.

If we assume the usual Ohm's law describing the superconducting state

$$\mathbf{j} = \sigma \mathbf{E}$$

and the Maxwell equation

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

for $\rho = 0, \mathbf{E} = 0$ and $\mathbf{B}$ remains constant for such a medium.

Meissner effect: The infinite conductivity is one of the most important characteristics of a new state. However, the true nature of the superconducting state appears more clearly in an external magnetic field.

Let us consider a normal metal in a uniform magnetic field: when the sample is cooled and becomes superconducting, experiments performed by

Meissner and Ochenfeld demonstrated that all the magnetic flux was expelled to the exterior. This indicates that $\mathbf{B}$ = constant, and it is in fact zero. In a multiply connected sample, as a ring, the holes trap the magnetic flux.

Critical field: The Meissner effect occurs only for sufficiently low magnetic fields. For simplicity, we consider a long cylinder of a pure superconductor in a parallel applied field H. If the sample is superconducting at temperature T in zero field, there is a unique critical field $H_c(T)$ above which the sample becomes normal. This field is temperature dependent and the empirical equation which describes well this dependence is

$$H_c(T) = H_{c0}\left[1 - \left(\frac{T}{T_c}\right)^2\right] .$$

Persistent currents and flux quantization: A different case of magnetic behaviour is connected to the flux trapping in a superconductor ring.

Suppose a normal metallic ring is placed in a magnetic field perpendicular on its plane. When the temperature is lowered, the metal becomes superconducting and the flux is expelled. If the external field is removed, no flux passes through the superconducting metal and the trapped flux must remain constant. This flux is maintained by the circulating supercurrent in the ring itself. The flux trapped in sufficiently thick rings is quantized in units of $\Phi_0 = \pi/e$.

Specific heat: The superconducting materials also have distinctive thermal properties. In the superconducting state, the specific heat C_s initially exceeds the specific heat of the normal state C_n and

$$C_s(T) \propto \exp\left(-\frac{\Delta}{T}\right) .$$

This dependence indicates the existence of a gap in the energy spectrum separating the excited states from the ground states by the energy Δ.

Isotopic effect: The transition temperature varies with the ionic mass M,

$$T_c \propto M^{-\frac{1}{2}}$$

and that demonstrates the importance of the ionic lattice in superconductivity.

Normal tunnelling: The conduction electrons in a superconductor and a normal metal can be brought into thermal equilibrium with one another by placing the metals into such close contact that they are separated by a thin insulating layer, which the electrons can cross by quantum tunnelling. When both metals are in the normal state, application of a potential difference raises the chemical potential of one metal with respect to the other and further electrons tunnel through the insulating layer. However, when one of the metals becomes superconducting then no current is observed to flow until the potential V reaches the value $eV = \Delta$. The size of Δ is in good agreement with the value inferred from low-temperature specific heat measurements.

Frequency dependent electromagnetic behaviour: The response of a metal to electromagnetic field is determined by the frequency dependent conductivity, which depends on the available mechanisms for energy absorption by the conduction electrons at the given frequency. Because the electronic excitation spectrum in the superconducting state is characterized by an energy gap Δ, one would expect the AC conductivity to differ substantially from its normal state form at small frequencies compared with Δ, and to be the same in the superconducting and normal states at large frequencies compared with Δ. Except that near the critical temperature, Δ is in the range between microwave and infrared frequencies. In the superconducting state, the AC behaviour does not differ from that in the normal state at optical frequencies.

2. Gorter-Casimir Two-Fluid Model

The first attempts to apply thermodynamics to the superconducting phase have been made by Rutgers and Ehrenferst in 1933.

The discovery of the Meissner effect finally enabled Gorter and Casimir (1934) to develop a thermodynamic treatment of the transition from the normal to the superconducting state using the standard theory of the phase transition with two supplementary assumptions:

a) The system exhibiting superconductivity possesses an ordered or condensed state, the total energy of which is characterized by an order parameter. This order parameter is generally taken to vary from zero at $T = T_c$ to unity at $T = 0$ K, and thus it can be taken to indicate that fraction of the total system which finds itself in the superconducting state.

b) The entropy of the system is due to the disorder of noncondensed individual excited particles which behave as the particles in the normal state.

In particular, the two-fluid models make the conceptual assumption that in the superconducting state a fraction n_s of the conduction electrons are "superconducting" electrons condensed in an ordered phase, while the other fraction $n_n = n - n_s$ remains "normal". The free energy of the superconductor is given by

$$F_S = \frac{n'}{n} F_n + \frac{n_s}{n} F_s \tag{2.1}$$

where $n = n_n + n_s$, $n' = (n_n n)^{\frac{1}{2}}$, F_n is the free energy of the normal electrons and F_s is the free energy of the superconducting electrons.
Using the new variables

$$x = \frac{n_n}{n} \qquad 1 - x = \frac{n_s}{n} . \tag{2.2}$$

Equation (2.1) becomes

$$F_S = x^{\frac{1}{2}} F_n + (1 - x) F_s . \tag{2.3}$$

The equilibrium state at a fixed temperature can be obtained from the condition

$$\left(\frac{\partial F_S}{\partial x}\right)_T = 0 \tag{2.4}$$

which gives

$$x = \frac{1}{4}\left(\frac{F_n}{F_s}\right)^2 \tag{2.5}$$

and the free energy (2.3) can be written as

$$F_S = F_s + \frac{1}{4}\frac{F_n^2}{F_s} . \tag{2.6}$$

In an external magnetic field H, the relation between F_n and F_s is

$$F_n - F_s = \frac{H_c^2}{2\mu_0} \tag{2.7}$$

and if $x = 1$, $F_S = F_n$, then all the electrons are in the normal state. At low temperatures

$$F_n = \frac{1}{2}\gamma T^2 \tag{2.8}$$

where γ is the Sommerfeld constant.

At $T = 0$, the electrons are in the superconducting state $H_c = H_{c0}$ and from (2.8), we get $F_n(T = 0) = 0$. The free energy of the superconducting electrons is

$$F_s(T = 0) = -\frac{H_{c0}^2}{2\mu_0} . \tag{2.9}$$

Using (2.6) and (2.9), the fraction x defined by (2.5) becomes

$$x = \frac{\mu_0^2 \gamma^2}{4H_{c0}^4} T^4 \tag{2.10}$$

and for $T = T_c$

$$x = \left(\frac{T}{T_c}\right)^4 , \qquad \gamma = \frac{2H_{c0}^2}{\mu_0 T_0^2} . \tag{2.11}$$

The free energies for the metal in the normal and superconducting states are

$$F_n = -\frac{H_{c0}^2}{\mu_0}\left(\frac{T}{T_c}\right)^2 , \qquad F_s = -\frac{H_{c0}^2}{2\mu_0}\left(1 + \frac{T^4}{T_c^4}\right) \tag{2.12}$$

and from Eq. (2.7), the critical field H_c can be calculated as

$$H_c(T) = H_{c0}\left(1 - \frac{T^2}{T_c^2}\right) . \tag{2.13}$$

With these results, we can calculate the difference between the electronic specific heats in the superconducting and normal states and we obtain

$$\Delta C_e = C_{es} - C_{en} = \gamma T_c \left[3\left(\frac{T}{T_c}\right)^3 - \left(\frac{T}{T_c}\right)\right] . \tag{2.14}$$

If ΔC_e is finite, the temperature dependence of C_{es} can be approximated as

$$C_{es} \cong \gamma T^3 . \tag{2.15}$$

The two-fluid model has a restricted applicability because the exponential was not obtained. The behaviour in the magnetic field as the Meissner effect cannot be explained in the framework of this model. Finally, the contribution at the normal phase of the $x^{\frac{1}{2}}$ fraction of electrons cannot be explained.

3. Electrodynamics of Superconductors

Perfect diamagnetism

Even in the absence of a microscopic explanation of the phenomenon of superconductivity, it is useful and reasonable to assume that the vanishing of the magnetic induction in a superconductor is due to induced surface currents. In an external magnetic field, the distribution of these currents is just to create an opposing interior field cancelling the applied one.

We can then give an image of the macroscopic superconductor in an external field:

a) in interior: $\mathbf{B} = \mathbf{H} = \mathbf{M} = 0$
b) at the surface: $\mathbf{j}_a \neq 0$ ($\mathbf{j}_a$ is the surface current density)
c) outside: $\mathbf{B} = \mathbf{H} + \mathbf{H}_a$ ($\mathbf{H}_a$ is the field due to the surface current).
Let us consider the surface of the superconductor. From the equation

$$\nabla \times \mathbf{B} = 4\pi \mathbf{j}_a ,$$

we get $\nabla \cdot \mathbf{B} = 0$ because in the bulk superconductor $\mathbf{j}_a = 0$. Taking the path 1-2-3-4 (Fig. 1) now we consider

$$\oint \mathbf{B} \cdot d\mathbf{l} = 4\pi I .$$

Using now

$$\oint \mathbf{B} \cdot d\mathbf{l} = \int_1^2 Bdl + \int_2^3 Bdl + \int_3^4 Bdl + \int_4^1 Bdl = Bl_{12} ,$$

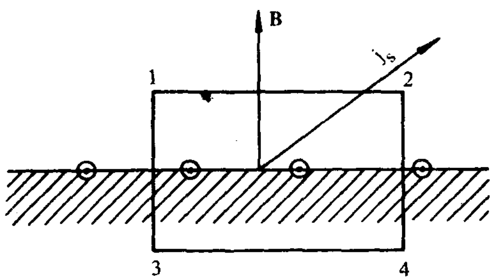
we get

$$Hl_{12} = 4\pi j_a l_{12} ,$$

an equation which can be generalized as

$$\mathbf{j}_a = \frac{1}{4\pi} \mathbf{n} \times \mathbf{H}$$

where $\mathbf{n}$ is the unit vector normal to the surface.



'ig. 1. The magnetic field **B** and the current $\mathbf{j}_s$ at the surface of a superconductor.

The intermediate state

The influence of the magnetic field on the superconductor is very sensitive to the geometry of the sample. If one considers an ellipsoidal superconducting sample in an applied magnetic field **H** (**H** is considered to have the direction of the major axis of the sample), the internal field $\mathbf{H}_i$ is

$$\mathbf{H}_i = \mathbf{H} - D\mathbf{M} \tag{3.1}$$

where D is the demagnetization factor and **M** the magnetization of the superconductor.

The magnetic induction is

$$\mathbf{B} = \mathbf{H}_i + 4\pi\mathbf{M}$$

which gives, for the magnetization,

$$\mathbf{M} = -\frac{1}{4\pi}\mathbf{H}_i \,. \tag{3.2}$$

From (3.1) and (3.2), we get

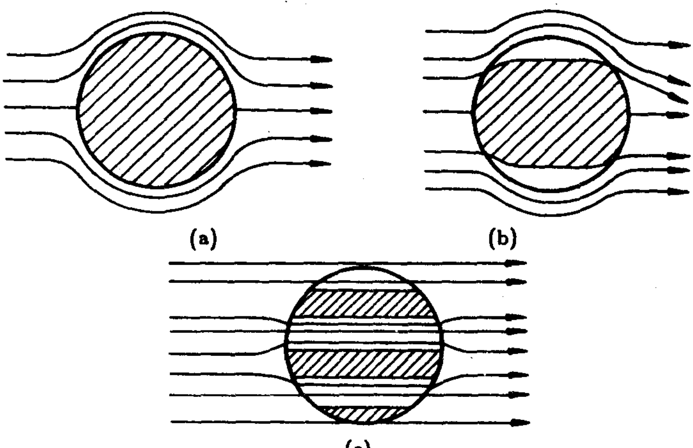
$$\mathbf{H}_i = \frac{4\pi}{4\pi - D}\mathbf{H} \tag{3.3}$$

which shows that $\mathbf{H}_i$ is dependent on the geometrical form of the superconducting sample and in the direction of the external field. The magnetic field in the exterior of the ellipsoidal sample $\mathbf{H}_e$ is different from the applied field, the field lines being deformed due to the magnetic properties and to the shape of the sample. Because $\nabla \cdot \mathbf{B} = 0$ and in the interior of the sample $\mathbf{B} = 0$, at the surface of the sample, the tangential components of the magnetic field must be continuous $H_i^t = H_e^t$ so that, projecting (3.3) on the tangent plane to the surface, we get

$$H_e^t = \frac{4\pi}{4\pi - D} H \sin\theta$$

where θ is the angle between **H** and the normal to the surface. For a spherical sample $D = 4\pi/3$ and $H_e^t = \frac{3}{2} H \sin\theta$, so that at the equator $(\theta = \pi/2)$, the effective field acting on the superconducting sphere has its maximum value $3/2\ H$ and its minimum one $H_e^t = 0$ is reached at the poles $(\theta = 0)$, see Fig. 2a.

If $H = H_c$ at the equator, the effective field overcomes H_c and penetrates the interior of the superconducting sphere to a certain depth on



Figs. 2. The penetration of the magnetic field in a spherical sample.

which the sample becomes normal. The remaining superconducting region may be equivalent to an ellipsoid for which D is smaller and the effective field becomes smaller than the critical field. This leads to the dividing of the sample into normal and superconducting regions like in Fig. 2c. Using thermodynamics, one can show that this state, called *intermediate state*, is more favourable energetically than the one presented in Fig. 2b.

London equations

We consider a simple model in which the total number of electrons is: $n = n_s + n_n$, n_s being the number of superconducting electrons, n_n the number of normal electrons and $n_s(T_c) = 0$. The current due to the superconducting electrons can be easily calculated. Indeed, from the motion equation we have

$$n_s m \frac{d\mathbf{v}_s}{dt} = n_s e\,\mathbf{E}$$

where m is the electron mass, $\mathbf{v}_s$ the velocity associated with superconducting electrons. If we define

$$\mathbf{j}_s = e n_s \mathbf{v}_s \ ,$$

the electric field is

$$\mathbf{E} = \frac{d}{dt}(\Lambda \mathbf{j}_s)$$

with

$$\Lambda = \frac{m}{n_s e^2} \ .$$

If $\partial \mathbf{j}_s/\partial t = 0$, $\mathbf{E} = 0$. If we change the chemical potential of the super conducting electrons, $\mathbf{j}_s \neq 0$. This can be done by the superconducting electron slab.

Let us consider that in a superconductor in each point $\mathbf{r}$, we have, the magnetic field $\mathbf{H}(\mathbf{r})$. The density of the energy is:

$$W_c = n_s \frac{mv_s^2}{2} = \frac{mj_s^2}{2n_s e^2} .$$

Using now the equation

$$\nabla \times \mathbf{H} = 4\pi \mathbf{j}_s , \tag{3.4}$$

we get

$$W_c = \frac{\lambda^2}{8\pi}(\nabla \times H)^2$$

where

$$\lambda^2 = \frac{m}{4\pi n_s e^2} .$$

The total energy will be:

$$F_{sH} = F_{s0} + \frac{1}{8\pi}\int dV[H^2 + \lambda^2(\nabla \times H)^2]$$

and we look for the minimum value $\delta F_{sH} = 0$. We have,

$$\delta F_{sH} = \frac{1}{8\pi}\int dV[2\mathbf{H}\cdot\delta\mathbf{H} + 2\lambda^2(\nabla \times \delta\mathbf{H})\cdot(\nabla \times \mathbf{H})] .$$

Using

$$\mathbf{a}\cdot(\nabla \times \mathbf{b}) = \mathbf{b}\cdot(\nabla \times \mathbf{a}) - \nabla\cdot(\mathbf{a}\times\mathbf{b}) ,$$

we get

$$\int dV[H^2 + \lambda^2(\nabla \times (\nabla \times \mathbf{H}))]\cdot\delta\mathbf{H} - \int dV[\nabla\cdot((\nabla \times \mathbf{H})\times\delta\mathbf{H})] = 0 .$$

The second integral can be calculated using the Gauss theorem as

$$\int dV[\nabla\cdot((\nabla \times \mathbf{H})\times\delta\mathbf{H})] \to \oint d\mathbf{s}\cdot((\nabla \times \mathbf{H})\times\delta\mathbf{H})$$

and we get the general equation

$$\mathbf{H} + \lambda^2\nabla \times (\nabla \times \mathbf{H}) = 0 . \tag{3.5}$$