THEORY OF SUPERCONDUCTIVITY

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EDITOR'S FOREWORD

The problem of communicating in a coherent fashion the recent developments in the most exciting and active fields of physics seems particularly pressing today. The enormous growth in the number of physicists has tended to make the familiar channels of communication considerably less effective. It has become increasingly difficult for experts in a given field to keep up with the current literature; the novice can only be confused. What is needed is both a consistent account of a field and the presentation of a definite "point of view" concerning it. Formal monographs cannot meet such a need in a rapidly developing field, and, perhaps more important, the review article seems to have fallen into disfavor. Indeed, it would seem that the people most actively engaged in developing a given field are the people least likely to write at length about it.

"Frontiers in Physics" has been conceived in an effort to improve the situation in several ways. First, to take advantage of the fact that the leading physicists today frequently give a series of lectures, a graduate seminar, or a graduate course in their special fields of interest. Such lectures serve to summarize the present status of a rapidly developing field and may well constitute the only coherent account available at the time. Often, notes on lectures exist (prepared by the lecturer himself, by graduate students, or by postdoctoral fellows) and have been distributed in mimeographed form on a limited basis. One of the principal purposes of the "Frontiers in Physics" series is to make such notes available to a wider audience of physicists.

It should be emphasized that lecture notes are necessarily rough and informal, both in style and content, and those in the series will prove no exception. This is as it should be. The point of the series is to offer new, rapid, more informal, and, it is hoped, more effective ways for physicists to teach one another. The point is lost if only elegant notes qualify.

A second way to improve communication in very active fields of physics is by the publication of collections of reprints of recent articles. Such collections are themselves useful to people working in the field. The value of the reprints would, however, seem much enhanced if the collection would be accompanied by an introduction of moderate length, which would serve to tie the collection together and, necessarily, constitute a brief survey of the present status of the field. Again, it is appropriate that such an introduction be informal, in keeping with the active character of the field.

A third possibility for the series might be called an informal monograph, to connote the fact that it represents an intermediate step between lecture notes and formal monographs. It would offer the author an opportunity to present his views of a field that has developed to the point at which a summation might prove extraordinarily fruitful, but for which a formal monograph might not be feasible or desirable.

Fourth, there are the contemporary classics—papers or lectures which constitute a particularly valuable approach to the teaching and learning of physics today. Here one thinks of fields that lie at the heart of much of present-day research, but whose essentials are by now well understood, such as quantum electrodynamics or magnetic resonance. In such fields some of the best pedagogical material is not readily available, either because it consists of papers long out of print or lectures that have never been published.

"Frontiers in Physics" is designed to be flexible in editorial format. Authors are encouraged to use as many of the foregoing approaches as seem desirable for the project at hand. The publishing format for the series is in keeping with its intentions. Photo-offset printing is used throughout, and the books generally are paperbound, in order to speed publication and reduce costs. It is hoped that the books will thereby be within the financial reach of graduate students in this country and abroad.

Finally, because the series represents something of an experiment on the part of the editor and the publisher, suggestions from interested readers as to format, contributors, and contributions will be most welcome.

David Pines

Urbana, Illinois
August 1961

PREFACE

The material presented here is an outgrowth of a series of lectures I gave at the University of Pennsylvania during the fall of 1962. I have stressed the fundamentals of the microscopic theory of superconductivity rather than attempting to give a broad survey of the field as a whole. As a result, a number of highly interesting and important areas are not discussed here; an example is the application of the microscopic theory to type II (or "hard") superconductors. The material presented here is primarily intended to serve as a background for reading the literature in which detailed applications of the microscopic theory are made to specific problems.

A variety of formal techniques have been used in the literature to describe the pairing correlations basic to superconductivity. For this reason I have developed a number of these techniques in the text and it is hoped that the inelegance of this approach will be justified by the usefulness of the material.

A brief review of the simple experimental facts and several phenomenological theories of superconductivity is given in the first chapter. This is followed in Chapter 2 by an account of the original pairing theory advanced by Bardeen, Cooper, and the author. A number of applications of this theory are worked out in Chapter 3. This first portion of the book uses only the techniques of quantum mechanics which are covered in a standard graduate course on quantum theory. While the notation of second quantization is used as a convenient shorthand, this formalism is reviewed in the appendix.

In Chapters 4 and 5 the many-body aspects of the coupled electron–ion system are developed with a view to treating in a more realistic manner the effective interaction between electrons which brings about superconductivity. In addition, the basis for treating strong quasi-particle damping effects important in strong coupling superconductors is developed. In Chapter 6 a discussion of elementary excitations in normal metals is given, which lays the ground work for the field-theoretic treatment of the superconducting state given in Chapter 7. There, the noninstantaneous nature of the interaction bringing about superconductivity is treated as well as the breakdown of the quasi-particle approximation and the resolution of this difficulty. In the final chapter the electromagnetic properties of superconductors are treated, as well as the collective excitations of the system.

I should like to thank Drs. P. W. Anderson, J. Bardeen, L. P. Kadanoff, D. J. Scalapino, Y. Wada, and J. W. Wilkins for many helpful discussions during the preparation of this manuscript. I am also indebted to Drs. F. Bassani and J. E. Robinson, who prepared a set of notes covering a lecture series I gave at Argonne National Laboratory during the spring of 1961. Much of the material in Chapters 4 and 5 and in the appendix is related to their notes. In addition, I would like to express my sincere appreciation to Mrs. Dorothea Hofford for the speed and accuracy with which she typed the manuscript. Finally, I should like to thank my wife for her considerable help in preparing this book.

J. R. SCHRIEFFER

Philadelphia, Pennsylvania
July 1964

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CHAPTER 1

INTRODUCTION

The phenomenon of superconductivity is a remarkable example of quantum effects operating on a truly macroscopic scale.[1] In a superconducting material, a finite fraction of the electrons are in a real sense condensed into a "macromolecule" (or "superfluid") which extends over the entire volume of the system and is capable of motion as a whole. At zero temperature the condensation is complete and all the electrons participate in forming this superfluid, although only those electrons near the Fermi surface have their motion appreciably affected by the condensation. As the temperature is increased, a fraction of the electrons evaporate from the condensate and form a weakly interacting gas of excitations (or "normal fluid"), which also extends throughout the entire volume of the system, interpenetrating the superfluid.[2] As the temperature approaches a critical value T_c, the fraction of electrons remaining in the superfluid tends to zero and the system undergoes a second-order phase transition from the superconducting to the normal state. This two-fluid picture of a superconductor is formally analogous to that which characterizes superfluid He^4, although there are important differences between these systems.[1, 3]

The amazing properties of superconductors (e.g., perfect diamagnetism, zero d-c electrical resistance, etc.[4]) are related to the peculiar excitation spectrum of the superfluid. As we shall see, the superfluid can carry out potential (or irrotational) flow with little change of its "internal energy" (i.e., energy associated with forces binding the superfluid together). On the other hand, the superfluid *cannot* support rotational flow. In analogy with superfluid He^4, if one tries to force the superfluid into motion having vorticity (i.e., a nonvanishing curl of its linear momentum), a fraction of the superfluid is necessarily converted into normal fluid. Since the normal fluid does not take advantage of the forces binding the superfluid together, there is in general a large increase in energy associated with creating this vorticity. It is reasonable, therefore, that the superfluid possesses a rigidity or stiffness with respect to perturbations which, like the magnetic field, tends to impart vorticity (i.e., angular momentum) to the system. On the basis of this assumed rigidity, London[1, 5] was able to account theoretically for the perfect diamagnetism of bulk superconductors in weak magnetic fields (the Meissner effect[6]) and for the apparent lack of d-c electrical resistance, as first observed by Kamerlingh Onnes in 1911.[7]

As we shall see, the microscopic theory of superconductivity proposed by Bardeen, Cooper, and the author[8] can be thought of in terms of this sort of two-fluid picture.[9] In the lowest approximation the superfluid is formed from pairs of electrons which are bound together by lattice polarization forces. The pairs *greatly overlap* with each other in space, and it is the strong *pair–pair correlations* in addition to correlations between mates of a pair which are ultimately responsible for the rigidity of the superfluid wave function discussed above. More generally, these correlations are responsible for an energy gap in the elementary excitation spectrum of a superconductor from which many properties of the superconductor (in addition to its electromagnetic behavior) follow as a consequence. In the theory, the normal fluid is composed of the gas of elementary excitations of the system.

It is perhaps not surprising that the microscopic theory of superconductivity followed Onnes' remarkable discovery of this phenomenon by almost fifty years, considering the physical and mathematical complications of the problem. It was not until 1950 that the basic forces responsible for the condensation were recognized, through the insight of Fröhlich.[10] He suggested that an effective interaction between electrons arising from their interaction with crystal lattice vibrations (phonons) was of primary importance in bringing about the condensation. At this time, independent experiments on the isotope effect in superconductors were being carried out by Reynolds *et al.*[11] and by Maxwell[12] which gave experimental support to Fröhlich's point of view. Early theories of Fröhlich[10] and Bardeen[13] based on a perturbation treatment of the electron–phonon interaction ran into mathematical difficulties. The significance of these difficulties was emphasized by Schafroth's[14] proof that the Meissner effect *cannot* be obtained in any *finite* order of perturbation theory, beginning with the uncoupled system. Later, Migdal[15] showed that there is no energy gap in the electronic excitation spectrum within the perturbation theory. In the BCS theory, the electron–phonon coupling constant g enters in the nonanalytic fashion e^{-1/g^2}, in agreement with Schafroth's and Migdal's results.

The microscopic theory explains essentially all of the general features of superconductivity. In addition to this qualitative explanation, it is in remarkably good quantitative agreement with experiment considering the crudeness of the approximations necessitated by our uncertainties regarding electronic and phononic band structure, electron–phonon matrix elements, etc., in real metals.

In this book we shall attempt to give an account of the underlying physical ideas of the theory. While some of the discussion is couched in the language of the many-body problem, much of this formalism is developed in the text. In general, we shall not give a detailed discussion of the relation between theory and experiment and the reader is referred to a number of books and review articles[9, 16] covering this area. We list below a few of the most important simple experimental facts about superconductors. One conventionally distinguishes between the behavior of type I (or soft) superconductors and type II (or hard) superconductors.

I-1 SIMPLE EXPERIMENTAL FACTS

Electromagnetic Properties

The d-c electrical resistivity of materials in the soft superconducting state is zero. This fact is established to better than one part in 10^{15} of the resistance of the normal state at the corresponding temperature.[16f] At $T = 0$ the resistivity of a superconductor ideally remains zero up to a critical frequency $\hbar\omega_g \sim 3.5k_BT_c$ (presumably the threshold for creating excitations out of the condensate). In practice, the edge of the gap is smeared and a precursor electromagnetic absorption is observed below the edge of the gap in certain cases. At finite temperatures, there is a finite a-c resistivity for all $\omega > 0$ (presumably because of absorption by the thermally excited normal fluid if $\omega < \omega_g$). For $\omega \gg \omega_g$, the resistivities of the normal and superconducting states are essentially equal, independent of temperature.

In 1933, Meissner and Oschenfeld[6] discovered that a bulk superconductor is a perfect diamagnet. Thus the magnetic field **B** penetrates only to a depth $\lambda \simeq 500$ Å and is excluded from the main body of the material. If one (incorrectly) argues that the vanishing *zero-frequency* electrical resistance implies that there can be no electric field (of any frequency) in a superconductor, Maxwell's equation

$$\nabla \times \mathbf{E} = -\frac{1}{c}\frac{\partial \mathbf{B}}{\partial t} \tag{1-1}$$

shows that the magnetic field present in the normal metal will be "frozen in" when the metal becomes superconducting. This is contrary to the Meissner effect, which states that the field is expelled in the superconducting phase. The point is that the superfluid gives rise to a purely inductive impedance which vanishes only at zero frequency.[9] It is this nonzero impedance which permits the expulsion of **B**. This point is discussed further below.

The perfect exclusion of the magnetic flux in bulk soft superconductors increases the free energy per unit volume of the superconductor by $H^2/8\pi$,[5] if H is the externally applied field. Since there is only a finite amount of energy reduction due to the condensation into the superconducting phase, there must be a critical field $H_c(T)$ at which the total free energy of the superconducting and normal states are equal. The critical field is a maximum H_0 at $T = 0$ and falls to zero at $T = T_c$ as shown in Figure 1-1. For typical "soft" superconductors like Al, Sn, In, Pb, etc., H_0 is of order a few hundred gauss. In "hard" superconductors like Nb_3Sn, superconductivity can persist to an "upper" critical field H_{c2} of order 10^5 gauss presumably due to the magnetic flux penetrating into the bulk of the material for H larger than a "lower" critical field H_{c1}.[17, 18] Thus, as opposed to a soft superconductor, a perfect Meissner effect does not exist above H_{c1} in a hard superconductor.

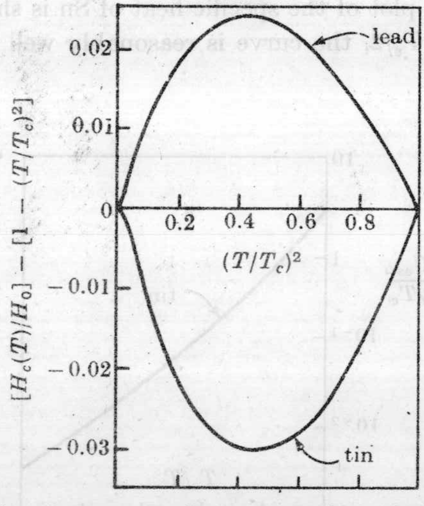

FIGURE 1-1 The deviations of the critical field from Tuyn's law $H_c(T) = H_0[1 - (T/T_c)^2]$, i.e., the prediction of the Gorter–Casimir model.

If one has a multiply connected superconductor, e.g., a hollow cylinder, the flux passing through the hole cannot have an arbitrary value, but is quantized to multiples of $hc/2e \simeq 4 \times 10^{-7}$ gauss cm^2. Quantization of flux in units twice this size was predicted by London[1] while the experimental observation of the effect and the establishment of the correct unit of flux was carried out independently by Deaver and Fairbank[20a] and by Doll and Näbauer.[20b]

Thermodynamic Properties

In zero magnetic field, there is a second-order phase transition at T_c.[21] The jump in specific heat is generally about three times the electronic specific heat γT_c in the normal state just above the transition. In well-annealed pure specimens the width of the transition can be as small as 10^{-4} °K although this is not believed to be the intrinsic width of the transition.[22] As $T/T_c \to 0$, the electronic specific heat generally falls as $ae^{-b/T}$, presumably due to the energy gap for creating elementary excitations. The ratio of the energy gap $2\Delta(0)$ at $T = 0$ to $k_B T_c$ is usually of order 3.5, the ratio being larger for stronger coupling superconductors like Pb and Hg. A plot of the specific heat of Sn is shown in Figure 1-2. For $T \geqslant T_c/2$, the curve is reasonably well fitted by αT^3

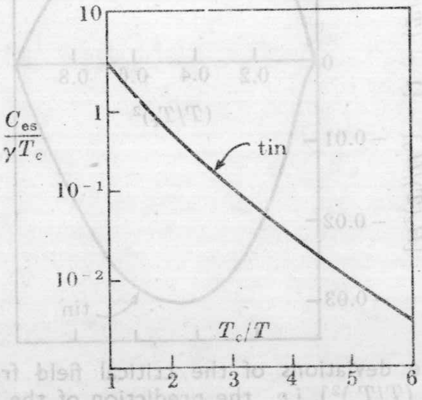

FIGURE 1-2 The electronic specific heat of Sn.