High-Temperature Superconductivity

Edited by V. L. Ginzburg and D. A. Kirzhnits

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PROBLEMA VYSOKOTEMPERATURNOI SVERKHPROVODIMOSTI
V. L. Ginzburg and D. A. Kirzhnits
ПРОБЛЕМА ВЫСОКОТЕМПЕРАТУРНОЙ СВЕРХПРОВОДИМОСТИ

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English Editor's Foreword

I first learned of the existence of this book on high-temperature superconductivity when I received a copy in the office of one of the co-editors, Prof. V. L. Ginzburg, shortly after publication. I had known of the work on problems and prospects of achieving high-temperature superconductors by the members of the I. E. Tamm Department of Theoretical Physics of the P. N. Lebedev Physical Institute. I was naturally anxious to read and study this volume, which integrates the work of more than a decade.

Lest one think that the contributions contained here are of the nature of a reflective looking backward, two important considerations should be kept in mind. First, achievement of high-T_c superconductivity is very much a current and future goal. Elsewhere, one of the authors has described it in these words: "Yes, high-temperature superconductivity is a dream, but a sufficiently realistic one." Second, the current physics literature contains reports of new and astounding findings–perhaps some of these will later be recognized as precursors to achieving the "dream." As I write this, the latest *Physical Review Letters* (11 August 1980) carries a report suggesting that the well-known insulator CdS, which has been investigated for decades for photoluminescence, photoconductivity, and Raman and Brillouin light scattering, may be a high-temperature superconductor or at least a "superdiamagnet!"

Many basic scientific problems remain before we reach a firm understanding of the *sina qua non* for high-T_c superconductors, or of the diamagnetic anomalies in CdS and similar anomalies reported a few years ago for CuCl. I commend this book warmly to the English-speaking and -reading audience interested in these problems.

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Preface to the English Edition

The Russian edition of this book reflected the state of the problem of high-temperature superconductivity at the beginning of 1977. It is natural, therefore, that in preparing the book for translation we should endeavor to make additions and changes that reflect the results published over the last few years. The greatest progress during this time has occurred in the understanding of the problems connected with the electron-phonon interaction in metals and with lattice stability. Therefore, the contents of Chapters 3 and 4 of the book required the greatest changes and additions.

However, the schedule requirements and limitations imposed upon the process of publishing a translated work precluded a fundamental revision of the text, and we had to limit ourselves to relatively short additions to the text and to the expansion of the references.

We hope, nevertheless, that the translation of the book will be of benefit to readers and will help stimulate efforts in the solution of the important and interesting problem of high-temperature superconductivity.

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Preface

The problem of high-temperature superconductivity is one of the most interesting physical problems, and one of the problems that is potentially important from the point of view of technical applications. Although research in this field has been going on for about 10 years now, it has been growing relatively slowly and has not yet led to any spectacular results; there nevertheless has been progress and the volume of published work is increasing all the time. It is quite probable that this trend will continue in the next few years, even if there are no major successes, such as the production of superconductors with a critical temperature tens of degrees higher than the presently known highest critical temperature.

In such a situation, it is hardly necessary to justify the publication of this book, which attempts to present the current state of the problem. The authors form the nucleus of a group engaged in research on the theory of superconductivity at the I. E. Tamm Department of Theoretical Physics of the P. N. Lebedev Physical Institute, Academy of Sciences of the USSR. Although we do not limit ourselves to the investigation of the problem of the critical temperature of superconductors and the means of raising it, this theme is the focus of our attention. Therefore, writing this book was for us an organic part of our work in progress.

The problem of high-temperature superconductivity is now beginning to interest an ever-increasing number of people, not all of whom are highly qualified physicists. Therefore, Chapter 1 (written by V. L. Ginzburg) is devoted to the formulation of the problem and an elementary introduction to it. This chapter also present the general characteristics of the problem in light of the results obtained (the results are described in greater detail in the other chapters).

Chapter 2 (by D. A. Kirzhnits) is devoted to the exposition of the general theory of superconductivity in the form widely used by us (the dielectric formalism). It is only when such a formalism is used that the critical temperature turns out to be especially clearly connected with the parameters of the metal.

In Chapter 3 (by E. G. Maksimov and D. I. Khomskii) the problem of describing the electron–phonon system in metals and the question of crystal-lattice stability are discussed.

Then Chapter 4 (by E. G. Maksimov and D. I. Khomskii) gives the present state of the problem of the computation of the critical temperature, T_c, for three-dimensional quasiisotropic metals as a function of the parameters characterizing the metal in the normal state.

The problem of lattice stability is also touched upon in Chapter 5 (by Yu. V. Kopaev), where the primary topics of discussion are the electronic phase transitions and their connection with the critical temperature. Chapter 6 (by L. N. Bulaevskii) is devoted to quasi-two-dimensional and layered compounds; Chapter 7 (by L. N. Bulaevskii), to one-dimensional and quasi-one-dimensional systems; Chapter 8 (by G. F. Zharkov), to dielectric-metal-dielectric "sandwiches." The problems touched upon in Chapters 6 and 8 are especially closely connected with each other. In Chapter 9 (by Yu. V. Kopaev) nonequilibrium superconductivity, which can set in, for example, during laser irradiation, is considered.

Considerable assistance was rendered in the writing of Chapters 5 and 8 by A. I. Rusinov and Yu. A. Uspenskii, respectively.

The general editing of the text was by V. L. Ginzburg and D. A. Kirzhnits, but all the authors participated in it. A good deal of work was done by L. N. Bulaevskii in preparing the manuscript for publication.

Thus, the book is indeed an integrated work, although it undoubtedly does retain in many respects the characteristics of a collection of papers by different authors. To the extent that these characteristics do not hinder understanding the book, we did not try to eliminate them, and, in particular, we had no misgivings about the presence of repetitions that facilitate the reading.

Let us emphasize that the above-noted structure of the book is to a large extent a reflection of the state of the problem of high-temperature superconductivity itself. The range of superconducting structures in question is unusually broad, and it is still impossible to single out any one of the known directions of search for high-temperature superconductors with any degree of confidence.

The authors are aware of a number of shortcomings of the book and the possibility that it may quickly become obsolete. But we are convinced of the importance of the problem of high-temperature superconductivity and of the appropriateness of the presentation of the investigations in this field. Therefore, we hope that our efforts have not been in vain and that the publication of the book is justified.

In conclusion, the authors take this opportunity to thank all those (and especially the reviewer of the book, I. O. Kulik) who by their comments contributed to the improvement of the manuscript.

September 1976 *The Authors*

Notation

T_c	Critical temperature†
T_p	Structural transition temperature
v_F	Fermi velocity
p_F	Fermi momentum
q_F, k_F	Fermi wave number
Δ	Energy gap
E_F	Fermi energy
$\varepsilon(\omega, q)$	Permittivity (or dielectric function, or permeability)
Θ_D	Debye temperature
ω, Ω	Frequency
$N(0)$	Density of states
V	Electron interaction
Π	Polarization operator
$\varkappa$	Inverse Debye screening radius
G	Electron Green function
D	Phonon Green function
Σ	Electron self-energy
λ	Dimensionless electron-phonon interaction constant
$f(E)$	Electron distribution function
$N(\omega)$	Phonon distribution function
E	Energy
N	Electron density
F	Free energy
σ	Conductivity

†In some chapters it is assumed that $\hbar = 1$ and $k_B = 1$, i.e., that the temperature varies in energy units; k_B is the Boltzmann constant.

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The Problem of High-Temperature Superconductivity (General Review)[†]

1. Introduction

Superconductivity was discovered in 1911, and the history of the study of this phenomenon can be divided (arbitrarily) into three periods. The first period (from 1911 through 1945) is characterized by a modest scale of investigations and the absence of practical applications. The study of superconductivity was difficult, especially because of the necessity of working with liquid helium. Before World War II, liquid helium could be produced in only about 10 laboratories in the world (there were two such laboratories in the USSR). Further, the parameters of superconductors—the critical temperature T_c, the critical magnetic field H_c, and the critical current j_c—for the then known materials did not allow the construction of powerful magnets or other practical devices. Finally, superconductivity remained a puzzling phenomenon since no consistent macroscopic, let alone, microscopic, theory of superconductivity has as yet been developed.

The situation completely changed in the second period, which began after World War II and ended about 10 years ago. The production of liquid helium and, hence, the feasibility of the study and use of superconductors ceased to be a problem, except for the cost and scarcity of helium. The nature of superconductivity was understood, and the corresponding theory was developed in a number of directions even better than was the case for many other fields of solid state physics. Superconducting alloys having critical temperatures T_c as high as 18 K, and remaining superconducting in fields H_c up to 100–200 kG (and in even stronger fields) and for quite high critical currents j_c were discovered. As a

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[†] In this chapter the author used in part the text of his earlier review [1].

TABLE 1.1

Material	T_c, K	Year of discovery of superconductivity
Hg	4.1	1911
Pb	7.2	1913
Nb	9.2	1930
Nb_3Sn	18.1	1954
$Nb_3(Al_{0.75}Ge_{0.25})$	20–21	1966
Nb_3Ga	20.3	1971
Nb_3Ge	23.2	1973

result, superconducting magnets for fields as high as 100 kG, as well as a number of other superconducting instruments and devices have been constructed.

The third period in the study of superconductivity, which began about 10 years ago is characterized, first, by the production of materials with still higher T_c values [of the presently known materials the highest T_c ($\approx$ 23 K) is possessed by Nb_3Ge] and critical fields $H_c \gtrsim 600$ kG [2]. The second, and especially important characteristic, is that problems pertaining equally well to physics and materials science have now become the major and decisive problems. We are referring to the feasibility of controlling and varying the superconducting parameters and the possibility of understanding the factors governing them. The problem of the critical temperature T_c is an especially acute one.

The point is that the values of H_c and j_c for superconducting materials have, over the history of the investigations of superconductivity, increased hundreds of times. For example, for the first superconductor discovered–mercury–even at absolute zero, $H_c \approx 400$ G. Now, however, many alloys are known for which the values of $H_c \approx$ 100-200 kG, and, thus, the "magnetic-current barrier," which prevented the wide application of superconductors, has been overcome. At the same time, the known T_c values have increased over the past 60-65 years by only a factor of 5 to 6 (Table 1.1) and, above all, the use of superconductors still requires cooling by liquid helium. More precisely (as can be seen from Tables 1.1 and 1.2), in principle, liquid hydrogen can also be used now for the cooling, but this is still impracticable, with the exception, perhaps, of the case when we are working with the Nb_3Ge alloy. The point here is that liquid hydrogen can be used only under pumping (the boiling point, T_b, of liquid hydrogen at atmospheric pressure is equal to 20.3 K, while the melting point T_m = 14 K). Moreover, it is not advantageous to work with superconductors in the region of

TABLE 1.2

Substance:	He	H_2	Ne	N_2	O_2	H_2O
T_b, K:	4.2	20.3	27	77.4	90	373.46

temperatures close to T_c, and sometimes it is even impossible because of the lowering of the values of H_c and j_c (let us recall that as $T \longrightarrow T_c$ the parameters $H_c \longrightarrow 0$ and $j_c \longrightarrow 0$).

At present the main obstacle standing in the way of a still wider use of superconductivity is the existence of the "temperature barrier"–the fact that for the known materials $T_c \lesssim 23$ K. It is natural, therefore, that the elucidation of the causes impeding the production of materials with $T_c > 20$-23 K and the attempts to overcome the corresponding difficulties are at the focus of attention. Here, of course, the problem is on the whole a broader one and consists of the general development of the "materials science of superconductors." Below, however, we shall consider, at least explicitly, only the problem of the critical temperature.†

Here we can distinguish two problems. First, we can try to achieve temperatures $T_c \approx 25$ K (perhaps even 30 K) with the aid of the traditional methods of production and adaptation of new alloys. If we are indeed able to produce such superconductors and utilize them fairly successfully in technology, then there will arise simultaneously the possibility of the wide use of liquid hydrogen for their cooling. The stage of "hydrogen" or "medium-temperature" superconductivity will thereby be opened. The object of this stage will consist, in particular, in the construction of liquid-hydrogen-cooled superconducting magnets for the production of fields in the hundred-kilogauss range. Such success could be of decisive importance, say, for the construction of magnetic systems in facilities for controlled thermonuclear fusion.

Second, it is necessary to investigate the possibility of radically raising the T_c with new types of materials or systems. Specifically, we have in mind the possibility of producing "high-temperature" superconductors with $T_c \gtrsim 90$ K, which can be cooled by liquid air (nitrogen) or even superconductors with critical temperatures of the order of room temperature, i.e., with $T_c \approx 300$ K.

The "dream" of high-temperature superconductivity probably arose long ago, but the first extensive, realistic discussion of it occurred, as far as we know, in 1964. We have in mind the suggestion to investigate the the superconductivity of long organic molecules [3] or superconductivity in the vicinity of metal-dielectric interfaces [4] using, above all, the electronic (exciton) mechanism instead of the conventional phonon mechanism, the dominant mechanism in superconductors, to provide attraction between the conduction electrons near the Fermi surface. (For greater details about this, see [5] and below.)

The advances made in the study of the problem during the ten years follow-

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†Both the theoretical and empirical data indicate that the critical field, $H_{c,\max}$, for the disappearance of superconductivity at $T = 0$ generally speaking increases with increasing T_c (in the simplest approximation, for example, we can use the formula $H_{c,\max} = 1.76\sqrt{2}k_BT_c/g\mu_B \approx 18500\, T_c$ kG, where T_c is measured in K). In this connection, there is no special reason to fear that the production of superconductors with high T_c values will be accompanied by a decrease in the parameters H_c and j_c.

ing the appearance of [3] cannot be described as impressive. True, we have gained a significantly better insight into a number of theoretical questions, but in the crucial area—in the experimental field—we have gained only limited experience and have taken only the first steps. In our opinion, this situation is not at all discouraging, for considering the difficulty of the problem, we cannot but admit that only very insignificant efforts have been made to solve it. Besides, as follows from a number of examples, the solution of major problems under conditions when success cannot be guaranteed usually takes many years. In any case, the problem of high-temperature superconductivity unquestionably exists, and it is one of the most important and interesting problems of both contemporary physics and of materials science.

The present chapter is devoted to a general introduction to the problem of high-temperature superconductivity and to a discussion of the general features of its present state in light of the material that will be dealt with in the following chapters. In this chapter the material is introduced with brief remarks of an elementary nature dealing with the nature of and the mechanisms underlying superconductivity. Undoubtedly, these remarks are totally inadequate for a real familiarization with the theory of superconductivity. Besides, they are often insufficiently exact and all embracing. Nevertheless, we are convinced that this mode of exposition, which is intended for a great many readers, is justified. Those readers who are sufficiently well conversant with the theory of superconductivity can, without difficulty, choose, in the present chapter as well as in the subsequent ones, the material that is of interest to them.

2. The Nature and Mechanisms of Superconductivity. High-Temperature Superconductivity (Formulation of the Problem)

As a result of the success of the electron-gas model in its application to metals in the normal (not superconducting) state, the phenomenon of superconductivity for a long time seemed especially puzzling. In fact, the applicability of the electron-gas model to the electrons in a metal, despite the fact that the kinetic energy of the electrons in a metal is of the order of their interaction potential (Coulomb) energy, on account of which they form a liquid rather than a gas, was only slightly less surprising.

The theory of a Fermi liquid and the concept of pseudopotentials and investigations related to them have made it possible for us to understand the behavior of metals in the normal state. In particular, it has been ascertained that the presence of repulsion between the electrons does not impair the applicability of the gas model in the qualitative respect. On the other hand, if the conduction electrons in the vicinity of the Fermi surface attract each other, then the Fermi particle (quasiparticle) distribution that is characteristic of the normal state turns out to be unstable.

The point is that in the presence of attraction it is more advantageous for the quasiparticles in the vicinity of the Fermi surface to form pairs. These pairs have integral spin and undergo something like a Bose-Einstein condensation, although because of the large size of the pairs compared to the distance between pairs, the connection with the Bose-Einstein condensation should not be taken literally. As a result of the formation of the pairs and their "condensation," there arises in the energy spectrum of the system a gap whose width is temperature dependent and is greatest at $T = 0$ K (here and below we do not discuss the so-called gapless superconductors). To break up a pair into two quasiparticles, it is necessary to expend an amount of energy not less than $2\Delta(T)$, where $\Delta(T)$ is the minimum energy of one quasiparticle. The critical temperature T_c is determined from the condition $\Delta(T_c) = 0$ and is, in the cases under discussion, proportional to the maximum gap width $\Delta(0)$.

Thus, the occurrence of superconductivity in metals is the result of attraction between the electrons in the vicinity of the Fermi level. In the simplest case such an attraction (interaction) is characterized by some dimensionless "interaction function," $U(\xi, \xi')$, which in a number of cases can be assumed to depend on the difference $\xi - \xi'$ [clearly, under such conditions $U = U(\xi - \xi')$]. The arguments ξ and ξ' are the energies of the interacting electrons, as measured from the Fermi surface, which is assumed here to be spherical (the isotropic case). As is well known, $\xi = v_F(p - p_F)$, where v_F and $p_F = \hbar q_F = mv_F$ are the velocity and momentum at the Fermi level E_F (it is assumed that $\xi << E_F = p_F^2/2m$).

If the interelectron interaction energy does not vanish at the Fermi level in the first-order perturbation theory, then attraction corresponds to the condition $U(\omega) < 0$ (we have set $\hbar\omega = \xi - \xi'$). The theoretical problem in its simplest variant under discussion consists of the determination, given the function $U(\omega)$, of the gap $\Delta(T)$ and, thus, the critical temperature, T_c, at which $\Delta(T_c) = 0$.

Another aspect of the problem consists of the determination of the mechanism underlying superconductivity, or, formally, in the computation or estima-

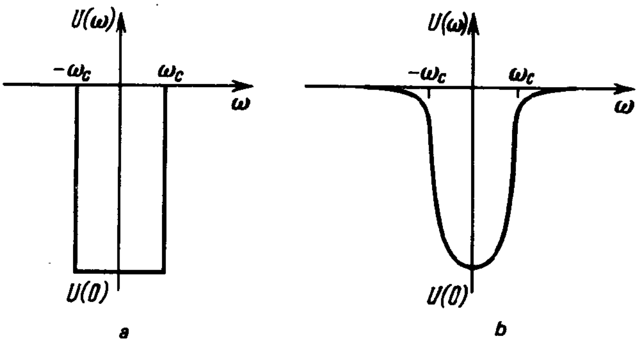

Figure 1.1. (a) Interaction energies in the form of a square well (as assumed in the BCS theory). (b) A smoothed out well for the interaction energy.

tion of the function $U(\omega)$ itself that gives rise to superconductivity. Below we shall briefly discuss both of these questions, but this and the following sections of this chapter can in no way be a substitute for the reviews of the microscopic theory of superconductivity (see Chapter 2 and, for example, [6–8]).

In the first successful microscopic theory of superconductivity, constructed in 1957 by Bardeen, Cooper, and Schrieffer (BCS), it was assumed that the function $U(\omega)$ has the form of a square well [see also Fig. 1.1a and the slight refinement made below in going from formula (1.22) to (1.23)]:

$$\begin{aligned} U(\omega) &= -N(0)V = \text{const}, \qquad |\omega| < \omega_c, \\ U(\omega) &= 0, \qquad\qquad\qquad\qquad\ \ |\omega| > \omega_c. \end{aligned} \tag{1.1}$$

In this case when $N(0)V \ll 1$ [the merit in setting $U(0) = -N(0)V$ will become apparent below

$$\begin{aligned} T_c = \left(\frac{\gamma}{\pi k_B}\right)\Delta(0) = \left(\frac{2\gamma}{\pi}\right)\left(\frac{\hbar\omega_c}{k_B}\right)\exp\left(-\frac{1}{N(0)V}\right) = \\ = 1.14\frac{\hbar\omega_c}{k_B}\exp\left(-\frac{1}{N(0)V}\right), \end{aligned} \tag{1.2}$$

where $\gamma = e^C = 1.781\ldots$ ($C = 0.577\ldots$ is the Euler constant) and $k_B = 1.38 \times 10^{-16}$ erg/deg is the Boltzmann constant.

The approximation of the function $U(\omega)$ by a square well can have some physical meaning only if a similar result is obtainable for a well with smooth edges (Fig. 1.1b), which, in fact, is what happens. For a well of the type shown in Fig. 1.1b, we obtain the BCS formula in the form

$$T_c = \Theta e^{-1/g}, \tag{1.3}$$

where

$$g \ll 1, \tag{1.4}$$

i.e., the weak-coupling approximation is used here. In the formula (1.3) the parameter Θ characterizes the width of the well–the region of attraction for the particles located in the vicinity of the Fermi level; the parameter g is a measure of the attraction and corresponds to the well depth. As is evident from (1.2) and (1.3), in the model (1.1), $\theta = 1.14(\hbar\omega_c/k_B)$ and $g = N(0)V$.

Attraction between the conduction electrons in a metal can arise only when their interaction with the ions (the lattice) and the other electrons (i.e., generally speaking, the electrons at lower energy levels) is taken into account. In some approximation the effect of all the other particles (electrons, ions) on the inter-