REVIEWS OF TOPICAL PROBLEMS

PACS numbers: 74.20.-z, 74.25.-q, 74.72.-h, 74.90.+n

Superconductivity: the day before yesterday — yesterday — today — tomorrow¹

V L Ginzburg

DOI: 10.1070/PU2000v043n06ABEH000779

Contents

1. Introduction	573
2. The day before yesterday (1911 – 1941)	573
3. Yesterday (1942 – 1986)	576
4. Today (1987-?)	579
5. Tomorrow	580
6. Supplement	581
References	582

<u>Abstract.</u> This talk is devoted to the history of the study of superconductivity and the prospects for further research in this field.

1. Introduction

Actively working physicists usually take little interest in the past, and I myself am not an exception — I began studying the theory of superconductivity in 1943, but only in 1979 did I find time to look through the classical papers of Kamerlingh Onnes (1853–1926). And I found them fairly interesting

Briefly presenting the history of the study of superconductivity, I shall divide it, although rather conditionally, into three periods: the day before yesterday (1911–1941), yesterday (1942–1986), and today (1987–?).

2. The day before yesterday (1911-1941)

Helium was first liquefied in 1908 and, which is rather significant, up to 1923 liquid helium had been obtained and used only in Kamerlingh-Onnes's laboratory in Leiden, where superconductivity was discovered in 1911. This happened in the course of systematic measurements of low-temperature electric resistance of metals. This point was quite obscure at that time. True, Drude hypothesized in 1900 that metal contained an electron gas responsible for the electrical conductivity. Drude also proposed the well-known formula

VL Ginzburg P N Lebedev Physical Institute, Russian Academy of Sciences Leninskiĭ prosp. 53, 117924 Moscow, Russian Federation Tel. (7-095) 135-8570. Fax (7-095) 135-8533 E-mail: ginzburg@td.lpi.ac.ru

Received 5 April 2000 *Uspekhi Fizicheskikh Nauk* **170** (6) 619 – 630 (2000) Translated by M V Tsaplina; edited by S D Danilov

for electrical conductivity $\sigma = e^2 n/mv$, where n is the electron concentration and v is the frequency of electron collisions with the lattice. However, the temperature dependences n(T) and v(T) remained quite unknown, and the electron model itself was contradictory (in the classical theory the electron gas had to make a large contribution to the specific heat, which is not observed). Kamerlingh Onnes, and probably not he alone, at first believed that with decreasing temperature T the electrical conductivity σ should decrease, i.e. according to the modern terminology, metals were considered to be semiconductors. This hypothesis was not confirmed, and as T decreased, a fall of the resistance $R(T) = \rho l/S$, $\rho(T) = 1/\sigma(T)$, (*l* is the length of the wire and S its cross-section) was observed. Furthermore, Kamerlingh Onnes was inclined to think that for a pure metal (platinum) the resistance R = 0 at T > 0 ("... the conclusion seems quite grounded that the resistance of pure platinum within the experimental errors due to the achieved degree of purity is already equal to zero at helium temperatures" [1]). Exceedingly pure samples were to be examined to confirm this hypothesis. But for platinum and gold the purification from impurities was a very complicated task, especially at the beginning of the century. It was for this reason that Kamerlingh Onnes passed over to the examination of mercury which is comparatively easy to purify and distill. This was an especially lucky choice because, in addition, the helium boiling temperature at atmospheric pressure $T_{\rm b, He} = 4.2 \text{ K}$ appeared to be close to the critical superconducting transition temperature $T_c(Hg) = 4.15 \text{ K}$ for mercury. The latter fact (i.e. the closeness of $T_{b,He}$ and T_c) was a certain detail which facilitated the discovery of a superconducting jump [2]². The main thing is that mercury becomes superconducting at

² As is clear from Ref. [2], the superconducting jump and superconductivity in general in an explicit form was first observed by Gilles Holst who conducted measurements of mercury resistance. Holst was a highly qualified physicist (later, the first director of the Philips Research Laboratories and Professor of Leiden University). Kamerlingh Onnes, however, did not even mention his name in the corresponding publication. As mentioned in [2], Holst himself had not apparently thought of such a demeanor of Kamerlingh Onnes as unjust or unusual. The situation is not clear to me, and for our generation it is quite unnatural; perhaps 90 years ago morals and manners in the scientific community were totally different.

¹ This talk was delivered on March 29, 2000 at the scientific session of the Division of General Physics and Astronomy of the Russian Academy of Sciences and on April 1 at the MTSC 2000 Conference (Major Trends in Superconductivity in the New Millennium; March 31 – April 6, 2000, Klosters, Switzerland).

temperatures which were attainable in those times. If Kamerlingh Onnes had continued measurements on platinum, gold, silver or copper, he would obviously have never discovered superconductivity unless by chance he tried to measure the resistance of some superconductor. This circumstance might have put off the discovery of superconductivity for years. With mercury, success came with the first experiments [3] (since the original papers [1, 3-5] are hardly available, I shall refer to the fact that some of their results are presented in Ref. [6], where paper [4] is placed as an appendix). Here I shall only note that in works [3], the appearance of which became known in April and May of 1911, the resistance of mercury at T = 3 K was shown to be immeasurably small. But the crucial thing, i.e., the detection of a sharp superconducting transition (which may be considered as the discovery of superconductivity), was made in paper [4] reported on November 25, 1911.

Of course, the studies were continued, and in 1913 the discovery of superconductivity in white tin ($T_c = 3.69 \text{ K}$) and lead ($T_c = 7.26 \text{ K}$) was reported [5] and the disappearance of superconductivity upon the passage of a rather strong current was also stated. H Kamerlingh Onnes was awarded the 1913 Nobel prize for physics for 'his investigations into the properties of matter at low temperatures which led, inter alia, to production of liquid helium'. As we see, the prize was awarded not for the discovery of superconductivity, but this issue was also touched upon in Kamerlingh Onnes's Nobel lecture [7]. In particular, he noticed: 'Mercury has passed into a new state, which on account of its extraordinary electrical properties may be called the superconducting state. There is left little doubt, that, if gold and platinum could be obtained absolutely pure, they would also pass into the superconducting state at helium temperatures'. Thus, Kamerlingh Onnes still supported the wrong hypothesis that all metals were superconducting at helium temperatures. I am unaware of his arguments, but they undoubtedly could not have been serious because the theory of metals did not exist at that time. In this connection, the discovery of superconductivity was not obviously so amazing. Moreover, there was nobody to repeat the Leiden experiments, for as has already been mentioned, no other laboratory obtained liquid helium until 1923. And it so happened that the discovery of superconductivity, which was an event of paramount importance, had quite a moderate resonance, at least by today's measure³.

Let us mention some consequent Leiden works. The existence of a critical magnetic field $H_{\rm cm}(T)$ was revealed in 1914; for mercury $H_{\rm cm}(0)=411$ Oe, and for lead $H_{\rm cm}(0)=803$ Oe. The first magnet with a superconducting winding was constructed in 1914. Particularly noteworthy is the fact that as far back as 1922 an attempt was made [9] to observe the isotope effect, namely, the dependence of $T_{\rm c}$ on the isotope mass in a metallic lattice in lead samples with different isotopic compositions (common lead with atomic weight A=207.30 and uranium lead with A=206.06 were employed). Unfortunately, the isotope effect for such samples makes up only about 10^{-2} K, and it was not observed. As is

well known, the isotope effect in superconductors was discovered only in 1950 (see references, e.g., in Ref. [10]), and it played an outstanding role in showing the importance of the electron-phonon interaction for the appearance of superconductivity.

It is no less interesting that in 1924 Kamerlingh Onnes was also close [11] to the discovery of the Meissner-Ochsenfeld effect (this effect, which is most significant for the study of superconductivity, was discovered only in 1933 [12]). Namely, Kamerlingh Onnes was investigating the behavior of a lead ball in an external magnetic field and failed to register the field pushing out of the ball upon its transition to the superconducting state probably only because he used an empty ball to spare liquid helium which was scarce at that time. In the case of an empty ball, a closed superconducting ring analogous to a doubly connected torus may form. Under such conditions the Meissner effect is masked.

In spite of this failure, the contribution of the Leiden laboratory and certainly of Kamerlingh Onnes himself can hardly be overestimated. To what has been said above I shall add that not a single superconductor had been discovered outside Leiden before 1928. In addition, Kamerlingh Onnes began liquid helium studies that led to the discovery of its superfluidity in 1938. The first step in this direction was made in 1911, the year of the discovery of superconductivity. Namely, the curve of the temperature dependence of the helium density $\rho(T)$ was found [13] to exhibit a kink corresponding to the λ -point. After that, liquid helium studies were conducted over many years [14, 15], which in the 1930s resulted in the discovery (for the most part by W H Keesom, Kamerlingh Onnes's successor in the Leiden laboratory, and his colleagues) of clearly pronounced anomalies — the λ singularity in the specific heat and superthermal conductivity of He II [14, 15]. Finally, in 1938 these studies ended in the discovery of superfluidity of helium II by Kapitza [16] and Allen and Misener [17]. Undoubtedly, the long path (27 years!) to the discovery of superfluidity compared to the expeditious discovery of superconductivity (see above) is first of all explained by methodology: to measure electrical resistance is easy, while to observe helium flow through a narrow gap or a capillary is difficult and, besides, one must hit upon the idea of carrying out such experiments.

The discovery and further study [18] of superfluidity and, which is most important, the Landau theory of superfluidity [19] made it possible to consider superconductivity as the superfluidity of the electron liquid in metals. However, the understanding of this fact did not play any particular role at that time because the Landau theory [19] was phenomenological and referred to the Bose–Einstein liquid (it is another thing that at first Landau did not regard the connection with Bose–Einstein statistics to be crucial for superfluidity). And one should have understood superconductivity as a phenomenon in an electron gas (or liquid), i.e., involving particles that obey Fermi–Dirac statistics. No advances were then made in this direction.

Even before that, superconductivity had become the most enigmatic phenomenon in condensed-matter physics and, more concretely, in the physics of metals. Properly speaking, before the creation of quantum theory, the behavior of nonsuperconducting metals (or, more precisely, metals in the normal, non-superconducting state) had also been absolutely unclear. But the application of quantum mechanics to a degenerate Fermi-gas in works by Pauli, Sommerfeld, Bethe,

³ For instance, the bibliography placed at the end of monograph [8] devoted to superconductivity contains 450 references embracing the period of 1911–1944 (some other data are also presented in [6]). Of them, only 34 refer to the interval of 1911–1925, and the author or a coauthor of 19 of these references is Kamerlingh Onnes. For comparison we can say that within ten years after the discovery of high-temperature superconductivity in 1986–1987, nearly 50 000 publications were devoted to this subject.

Bloch, Landau and many others in the period from 1926 to 1930 changed the situation radically — everything seemed to become, in principle, clear in the theory of metals. Indeed, the advances (see, e.g., Refs [20], [21]) were impressive and as far as I remember and know, they were practically unconditionally accepted by a wide range of physicists. In actual fact, as Landau used to emphasize, 'nobody has abrogated the Coulomb law', and in this connection it remained unclear why the electron gas approximation was so successful when applied to metals. Indeed, in normal metals the kinetic (Fermi) energy $E_{\rm F}$ is by no means lower than the Coulomb electron – electron interaction energy (e.g., in Ag the electron concentration is $n = 5.9 \times 10^{22} \,\mathrm{cm}^{-3}$, the Fermi energy is $E_{\rm F} = 8.5 \times 10^{-12} \, {\rm erg}$, and the characteristic interaction energy is $e^2 n^{1/3} = 19.3 \times 10^{-12} \, {\rm erg}$). The situation became transparent only when Landau created the Fermi-liquid theory in 1956-1958 (see, e.g., Ref. [22]). But this is already another epoch.

In the 1930s and, in fact, up to the mid-1950s superconductivity, as has already been said, remained an enigma. So, in 1933 Bethe wrote: 'The success in the theory, in the explanation of normal phenomena in conductivity is great, whereas very little has yet been done in solving the problem of superconductivity. Only a number of hypotheses exist which until now have in no way been worked out and whose validity cannot therefore be verified' [20]. These hypotheses are listed in Refs [20, 23] and all of them turned out to be erroneous. In the well-known monograph "Quantum Theory of Metals" by A Wilson [21], published in England in 1936 (and in Russian in 1941), we find the words: "In spite of all the progress made by the theory of metals over the past years, the phenomenon of superconductivity remains as enigmatic as it was before, and as before it leaves unsuccessful all attempts to explain it". Interestingly, in the second edition of the book, which appeared in England in 1953, the chapter devoted to superconductivity was dropped completely [21]. There may have been good reason for this: the author had nothing new to say.

Thus, the first period in the study of superconductivity, entitled in the present paper 'The day before yesterday (1911–1941)', ended, in respect of the microtheory of superconductivity, with the understanding of the existence of a real problem and the recognition of obscurity on the way to its solution. Incidentally, this was not for lack of attention or intellectual efforts. Suffice it to say that the attempts of Einstein [24] and Bohr [23] to gain insight into the nature of superconductivity also failed. It was apparent that the interaction between conduction electrons should be taken into account in one or another way. But the key to an effective approach to this issue was only found in 1950, when the above-mentioned isotope effect was found and pointed to the role of the interaction between the conduction electrons and the crystal lattice.

At the same time, great success was achieved in the understanding of the macroscopic behavior of superconductors even at this early stage. After the discovery of the Meissner effect in 1933 [12] it became evident (see Ref. [25] and the literature cited there) that the superconducting state is a phase of matter in the thermodynamical sense of this notion. In the depth of a superconductor the magnetic field $\mathbf{H} = 0$ (here and below we do not distinguish between the field \mathbf{H} and the magnetic induction \mathbf{B}) and

$$F_{\rm n\,0} - F_{\rm s\,0} = \frac{H_{\rm c\,m}^2(T)}{8\pi} \,, \tag{1}$$

where F_{n0} and F_{s0} are the free energies of unit volume of a metal respectively in the normal (n) and superconducting (s) states (phases) and $H_{\rm cm}(T)$ is the critical magnetic field for massive samples. Differentiation of relation (1) with respect to T yields a number of thermodynamic relations. It would obviously be out of place to dwell longer on the thermodynamics of superconductors, on the influence of the field, current, etc. (see, e.g., Refs [8, 10, 26-29]). When we speak of the history, the above-mentioned paper by Gorter and Casimir [25] is worthy of note as is the so-called two-fluid model [30] which they introduced in 1934. According to this model, along with a superconducting current with density is, in a superconductor a normal current may flow with density \mathbf{j}_n which is due to the flow of 'normal electrons' present in the superconductor at T > 0. The total current density is of course $\mathbf{j} = \mathbf{j}_s + \mathbf{j}_n$, and it is this density that enters the ordinary electrodynamic equation rot $\mathbf{H} = (4\pi/c)\mathbf{j} + (1/c)(\partial \mathbf{E}/\partial t)$ where E is the electric field strength (the polarization of the medium is neglected). The normal current in a superconductor does not, in fact, differ from the current in a non-superconducting state, and in the local approximation in the absence of a temperature gradient (and generally in a homogeneous medium) we have

$$\mathbf{j}_{\mathbf{n}} = \sigma_{\mathbf{n}}(T)\mathbf{E}. \tag{2}$$

A significant step forward was the equation for is

$$rot (\Lambda \mathbf{j}_{s}) = -\frac{1}{c} \mathbf{H}, \qquad (3)$$

with Λ as a new constant. This equation was introduced by Londons [31] in 1935.

The meaning and, so-to-say, the origin of this equation becomes obvious if we consider the hydrodynamic equation for a conducting liquid (gas) consisting of particles with a charge e and a mass m and moving at a velocity $\mathbf{v}_{s}(\mathbf{r}, t)$:

$$\frac{\partial \mathbf{v}_{s}}{\partial t} = -(\mathbf{v}_{s}\nabla)\mathbf{v}_{s} + \frac{e}{m}\mathbf{E} + \frac{e}{mc}[\mathbf{v}_{s}\mathbf{H}]$$

$$\equiv \frac{e}{m}\mathbf{E} - \nabla\frac{v_{s}^{2}}{2} + \left[\mathbf{v}_{s}\left(\operatorname{rot}\mathbf{v}_{s} + \frac{e}{mc}\mathbf{H}\right)\right].$$
(4)

Such an equation corresponds to a medium with ideal conductivity [32] and does not prevent a constant magnetic field from being present in this medium. Imposing an additional condition, namely, the condition of the absence of vortices extended to the case of a charged liquid

$$\operatorname{rot} \mathbf{v}_{s} + \frac{e}{mc} \mathbf{H} = 0, \qquad (5)$$

we arrive at the Londons equation (3) if we take into account that $\mathbf{j}_s = e n_s \mathbf{v}_s$ (n_s is the concentration of 'superconducting' charges). Given this, obviously,

$$\Lambda = \frac{m}{e^2 n_c} \,. \tag{6}$$

Moreover, under condition (5), we obtain from (4) the second Londons equation

$$\frac{\partial (\Lambda \, \mathbf{j}_{\mathrm{s}})}{\partial t} = \mathbf{E} - \nabla \frac{\Lambda}{2en_{\mathrm{s}}} \, j_{\mathrm{s}}^{2} \,. \tag{7}$$

The last term on the right-hand side is rather small and is therefore typically omitted, although it has quite a real meaning (see, e.g., Ref. [33]).

Equation (3) together with the field equation rot $\mathbf{H} = (4\pi/c)\mathbf{j}_s$ in a homogeneous medium (i.e., for $\Lambda = \text{const}$) leads to the equations

$$\Delta \mathbf{H} - \frac{1}{\delta^2} \mathbf{H} = 0 , \quad \Delta \mathbf{j}_s - \frac{1}{\delta^2} \mathbf{j}_s = 0 , \quad \delta^2 = \frac{Ac^2}{4\pi} = \frac{mc^2}{4\pi e^2 n_s} . \tag{8}$$

This implies that the field and the current decrease with the penetration into the superconductor according to a law of the form $H = H_0 \exp(-z/\delta)$, which corresponds to the Meissner effect. At first, however, it was only a qualitative agreement between the theory and experiment, while quantitative measurements [10] remained contradictory for a long time and, in particular, did not confirm the conclusion of the theory concerning the dependence of the critical magnetic field on the thickness of superconducting films (see Refs [10, 34] and the literature cited therein). Furthermore, in the Londons theory, to provide stability of the boundary between the normal and superconducting phases, it was necessary to introduce the surface energy σ_{ns} at the interface. But the energy $\sigma_{n\,s}$ is rather high, and it remained quite unclear how it could be calculated [34, 35]. Here however we pass over to the next period in the study of superconductivity the period referred to as 'Yesterday (1941 – 1986)'.

True, the research of thermoelectric phenomena in superconductors which was started in 1927 should also be ascribed to 'The day before yesterday (1911 – 1941)'. The result of this research was as follows: 'Many experiments have shown that all thermoelectric effects disappear in the superconducting state' [10] (see p. 86). Indeed, at first glance this statement seems to reflect the situation correctly. But in reality, as I pointed out later, in 1944 [36] (see also [33, 37]), thermal effects exist in the superconducting state as well, but they are masked to a great extent because of the existence of two currents — \mathbf{j}_s and \mathbf{j}_n . Strange as it is, thermoelectric effects in the superconducting state have even now been investigated quite insufficiently. This problem however stands aside from the magisterial trends in the field of superconductivity, and is therefore beyond the scope of our further discussion (see Refs [37, 38]).

Finally, it is noteworthy that type II superconductors were in fact discovered in the late 1930s, although it took two decades to make things clear. Namely, in 1935–1936 L V Shubnikov and his co-authors revealed the behavior of some alloys in a magnetic field, typical of type II superconductors (for the explanation and references see Refs [8, 10]; above we meant, although implicitly, type I superconductors)⁴.

3. Yesterday (1942-1986)

It is of course somewhat conditional that the first period in the history of investigation of superconductivity ('The day before yesterday') is thought of as finished in 1941. One should not however forget that this boundary was determined, among other things, by the fact that the Second World War broke out in Western Europe in 1939, and in the USSR in 1941. Naturally, the investigations of superconductivity then were nearly stopped. In the bibliographical index [39], which

includes papers devoted to superconductivity over the period 1911–1970, only 36 out of the 6579 publications refer to 1942–1945 (in 1941, according to [39], only nine papers were published, some of them having been written earlier). What a contrast this is with the present-day situation, for which we can point out that within the period 1989–1991 nearly 15 000 papers appeared devoted to high-temperature superconductors, i.e., on the average about 15 papers a day were issued.

I was among those few physicists who took an interest in the theory of superconductivity in the war years and this happened under the influence of Landau's paper [19] published not long before. We were in evacuation in the town of Kazan' where we were pretty cold and hungry. But people sometimes indulge in research work under any circumstances. All my activities in the field of superconductivity and superfluidity, started in 1943, are described in detail in paper [35]. Here I shall dwell on only two directions of my own work which seem of importance in a rather broad context. One is the formulation of the quasi-phenomenological theory of superconductivity, which was then called the Ginzburg-Landau theory (I refer to it as the Ψ -theory of superconductivity). The other direction of this work, which was started in 1964, was the discussion of the possibility of creating high-temperature superconductors.

As has been mentioned above, the Londons theory correctly reflected the existence of the Meissner effect, but was inapplicable to 'strong' magnetic fields comparable with the critical field $H_{\rm c}$. In other words, it was only applicable under the condition

$$H \ll H_{\rm c}$$
 (9)

True, condition (9) was established with sufficient clarity only later, but the impossibility of deriving a correct expression for the critical field H_c on the basis of the Londons theory in the case of thin films became apparent as far back as 1939 (see Refs [40, 34]). The question of the surface energy σ_{ns} on the boundary of the superconducting and normal phases also remained absolutely uncertain [34]. All this stimulated the search for a generalization of the Londons theory; the Ψ -theory published in 1950 [41] may be thought of as such a generalization.

In the Ψ -theory, the scalar complex function $\Psi(\mathbf{r})$ is introduced as an order parameter to describe superconductivity. This function Ψ is sometimes termed the macroscopic or effective wave function, and is in fact associated with the electron density matrix in a superconductor [41, 35]. The free energy density of the superconductor and the field is written in the form

$$F_{sH} = F_{s0} + \frac{H^2}{8\pi} + \frac{1}{2m} \left| -i\hbar \nabla \Psi - \frac{e^*}{c} \mathbf{A} \Psi \right|^2,$$

$$F_{s0} = F_{n0} + \alpha |\Psi|^2 + \frac{\beta}{2} |\Psi|^4,$$
(10)

where **A** is the vector potential of the field rot $\mathbf{A} = \mathbf{H}$ and F_{n0} is the free energy density in the normal state.

Under the condition of thermodynamic equilibrium in the absence of a field, $\partial F_{s0}/\partial |\Psi|^2=0$ and $|\Psi|^2=0$ at $T>T_c$, while at $T< T_c$ we already have $|\Psi|^2>0$. This implies that $\alpha(T_c)\equiv\alpha_c=0, \beta(T_c)\equiv\beta_c>0$, and $\alpha(T)<0$ at $T< T_c$. The theory develops in the region near T_c and within the validity limits of the expansion (10) one can put $\alpha(T)=\alpha_c'(T-T_c)$, and $\alpha_c'\equiv(d\alpha/dT)_{T=T_c}, \beta(T_c)\equiv\beta_c$. From this, in equilibrium

⁴ I cannot but mention with bitterness that the outstanding physicist L V Shubnikov fell victim to terror: although completely innocent he was shot in 1937.

at $T < T_c$ we have

$$\begin{aligned} |\Psi|^2 &= |\Psi_{\infty}|^2 = \frac{\alpha_{\rm c}'(T_{\rm c} - T)}{\beta_{\rm c}} \,, \\ F_{\rm s\,0} &= F_{\rm n\,0} - \frac{\alpha^2}{2\beta} = F_{\rm n\,0} - \frac{(\alpha_{\rm c}')^2 (T_{\rm c} - T)^2}{2\beta_{\rm c}} = F_{\rm n\,0} - \frac{H_{\rm c\,m}^2}{8\pi} \,. \end{aligned} \tag{11}$$

In the presence of the field, the equation for Ψ is derived upon variation of the free energy $\int F_{sH} dV$ over Ψ^* and has the form

$$\frac{1}{2m} \left(-i\hbar \nabla - \frac{e^*}{c} \mathbf{A} \right)^2 \Psi + \alpha \Psi + \beta |\Psi|^2 \Psi = 0.$$
 (12)

Variation of the integral $\int F_{sH} dV$ over **A** (under the condition div **A** = 0) leads us to the equation

$$\Delta \mathbf{A} = -\frac{4\pi}{c} \,\mathbf{j}_{s} \,,$$

$$\mathbf{j}_{s} = -\frac{\mathrm{i}e^{*}\hbar}{2m} (\boldsymbol{\Psi}^{*}\nabla\boldsymbol{\Psi} - \boldsymbol{\Psi}\nabla\boldsymbol{\Psi}^{*}) - \frac{(e^{*})^{2}}{mc} |\boldsymbol{\Psi}|^{2} \mathbf{A} \,. \tag{13}$$

If we put $\Psi = \Psi_{\infty} = {\rm const}$, then ${\bf j}_{\rm s} = -[(e^*)^2/mc]\Psi_{\infty}^2\,{\bf A}$, which, as is readily seen, is equivalent to the Londons equation (3). In fields comparable with the critical field, the function Ψ is already not constant, which makes the Londons theory inapplicable (and thereby comes the criterion (9)). It should be noted that far from T_c , where the Ψ -theory is generally quantitatively inapplicable (at least without some changes), the Londons theory may appear to be inapplicable in the weak field as well. The point is that for type I superconductors far from T_c the coupling of the field with the current is nonlocal. This circumstance was pointed out by Pippard in 1953 [42]. The state of the theory of superconductivity (both macroscopic and microscopic) before the creation of the microtheory of superconductivity by Bardeen, Cooper, and Schrieffer in 1957 [43] was elucidated in the large review by Bardeen published in 1956 [44]. I refer the reader to this review, in particular, in respect of the allowance for nonlocality [42]. The current state of the theory of superconductivity is presented in books [26–29, 38] and elsewhere. But now, in the brief review of the crucial points in the history of the development of this field, we shall only make some more remarks concerning the Ψ -theory.

Of interest is the question of the charge e^* , entering the equations of the Ψ -theory [see (10), (12), (13)]. This charge is involved in the expression for a very important parameter of the theory

$$\varkappa = \frac{mc}{e^*\hbar} \sqrt{\frac{\beta_c}{2\pi}} = \frac{\sqrt{2}e^*}{\hbar c} H_{cm} \delta_0^2, \qquad (14)$$

where $H_{\rm cm}$ is a thermodynamic critical field [see (1) and (11)] and δ_0 is the penetration depth of the weak magnetic field, and

$$\delta_0^2 = \frac{mc^2 \beta_c}{4\pi (e^*)^2 |\alpha|} = \frac{mc^2}{4\pi (e^*)^2 \Psi_{\infty}^2} . \tag{15}$$

The quantities $H_{\rm cm}$ and δ_0 can of course be measured experimentally and, moreover, a number of measurable quantities (the surface energy $\sigma_{\rm ns}$ and fields for limiting supercooling and superheating) depend on \varkappa . Thus, using

the measurable quantities $H_{\rm cm}$, δ_0 , and \varkappa , one can determine e^* according to (14). In this way one can arrive at the conclusion [45] that $e^* \approx (2-3)e$, where e is the electron charge. This seemed strange because, as Landau noted, the effective charge e^* must not depend on coordinates (otherwise, the gradient invariance of the theory is violated) and must therefore be universal. Only after the creation of the BCS theory [43] Gorkov showed [46] that $e^* = 2e$ holds strictly. This result certainly means that we are dealing with Cooper pairs with charge 2e. Consequently, the charge $e^* = 2e$ is actually universal (in the sense that it does not depend on coordinates), but at the same time it is not equal to e. Interestingly, such a simple idea occurred to no one, in particular neither to me nor to Landau. For Landau it was not accidental — as mentioned above, in his theory of superfluidity [19] Landau did not see any relationship between superfluidity and the Bose-Einstein statistics of ⁴He atoms. Hence, the idea of electron 'pairing' with so-tosay transformation of fermions into bosons did not suggest itself. As for myself, I cannot find any excuse because I even pointed out that for a charged Bose-gas the Meissner effect must take place [47]. Furthermore, I might have known (I do not remember it now) that the idea of electron pairing with subsequent Bose – Einstein condensation and the appearance of superconductivity was suggested by Ogg as far back as 1946 [48], and then by Schafroth [49]. However, Bardeen did not mention Ogg in his extensive 1956 survey [44] and, although he knew the papers by Schafroth, he never even mentioned the possibility of pairing. It was only the paper by Cooper [50] that made the idea of pairing popular and led directly to the creation of the BCS theory [43]. But, which is interesting, in the BCS paper [43] there is not a single word about Bose-Einstein condensation and, obviously, they failed to recognize the direct relation between this condensation and pairing and its role in the explanation of superconductivity. This can be understood to a certain extent because pairs in the BCS theory have a large size $\xi_0 \sim 10^{-4}$ cm and the condensed (superconducting) state is very far from the boson condensate with atomic size $\xi_0 \sim 10^{-8}$ cm.

However I have got ahead of my story. The Ψ -theory proved to be very efficient and made it possible to consider a large number of questions and problems (the behavior of films and other superconducting samples in a magnetic field, supercooling and superheating, the calculation of the surface energy, etc.). The Ψ -theory turned out to be successful because it lies within the scope of the general phase transition theory and in this sense is more general than the BCS theory. At the same time, from the BCS theory near T_c one certainly obtains the Ψ -theory equations (12) and (13) with concrete values of the coefficients α and β (see Ref. [46]). It is of course very important that in conventional superconductors the coherence length $\xi = \delta_0/\varkappa$ (the penetration depth δ_0 is more frequently denoted by the letter λ) is large, and therefore the fluctuations are small (see Refs [51, 52, 37]). The Ψ -theory is readily extended to the anisotropic case [53] and also holds when more complicated (non-scalar) order parameters are used [54]. In the original work [41], consideration was only given to the case where $\underline{\varkappa} < 1/\sqrt{2}$. Then $\sigma_{ns} > 0$, and it was proved that for $\kappa = 1/\sqrt{2}$ we already have $\sigma_{ns} = 0$, and with further growth of \varkappa the energy becomes $\sigma_{n\,s} < 0$. In other words, only type I superconductors were dealt with in Ref. [41], where it was shown that for $\varkappa > 1/\sqrt{2}$ a certain instability occurs. Only after the work of Abrikosov [55] was it understood that for $\varkappa > 1/\sqrt{2}$ a vortex lattice is formed and

superconductors behave as had been established in the 1930s by Shubnikov and colleagues (this has already been mentioned above). In today's terminology, these are type II superconductors which now remain the object of intense investigations not only in cuprates.

The numerous applications of the Ψ -theory are elucidated in books [22, 27–29] and in many other publications. A huge number of papers are devoted to various applications and generalizations of the Ψ -theory (as an example I may refer the reader to Refs [38, 56–61]). This is a whole field of research (especially in what concerns vortices and vortex structures), and we cannot dwell on it here.

The creation of the BCS theory in 1957 [43], i.e., 46 years after the discovery of superconductivity, was of course a fairly significant event in the history of the study of superconductivity and, properly, for the whole physics of condensed media. The BCS work was followed by a series of investigations in which virtually the same results were obtained by other methods, some points were specified, etc. (Bogolyubov [62], Valatin [63], Gorkov [46] and others; see the review [64] and the collection of papers [65]).

The most typical result of the BCS theory is the expression for the critical temperature

$$T_{\rm c} = \theta \exp\left(-\frac{1}{\lambda_{\rm eff}}\right),$$
 (16)

where $k_{\rm B}\theta$ is the energy range near the Fermi energy $E_{\rm F}$ where the conduction electrons (more precisely, the corresponding quasi-particles) are attracted, which causes pairing and instability of the normal state; next, in the simplest case $\lambda_{\rm eff} = \lambda = N(0)V$, where N(0) is the level density near the Fermi surface in the normal state and V is a mean matrix element of the interaction energy corresponding to the attraction.

In the BCS theory, the coupling 'constant' λ is assumed to be small ('weak coupling'), that is,

$$\lambda \ll 1$$
. (17)

The theory implies a number of results that can be verified by experiment, for example,

$$\frac{2\Delta(0)}{k_{\rm B}T_{\rm c}} = 3.52\,, (18)$$

where $\Delta(0)$ is a superconducting gap (per one quasi-particle) at T=0; for many type I superconductors the BCS theory proved to be in full agreement with experiment.

Since it is impossible to dwell in more detail here on the development of either experiment or the theory, we shall only mention the Josephson effect [66] and the extension of the BCS theory to the case of strong coupling by Eliashberg [67].

The main landmarks of this stage in the study of superconductivity, which has been described as 'Yesterday (1942 – 1986)', are in my opinion the creation of the Ψ -theory (1950), the BCS theory (1957) and, finally, the search for high-temperature superconductors (1964–1986). More precisely, we are now mostly speaking of the theory. The experimental research is of course no less important, but it was largely determined by the theory and in any case there was no contradiction or contrast between them.

Undoubtedly, the question of why superconductivity is only observed at low temperatures arose long ago. However,

before the creation of the BCS theory no concrete answer to this question could be given, while within the BCS theory the answer is already clear when one applies formula (16). The point is that in the BCS work the electron—phonon interaction was regarded as the interaction responsible for the attraction between electrons and thus for their pairing. This is clear, for the role of this interaction becomes obvious from the isotope effect and, more concretely, from the validity in some cases of the relation

$$T_{\rm c} \propto M^{-1/2} \,, \tag{19}$$

where M is the ion mass in the lattice (see, for example, Ref. [29]).

In the case of electron-phonon interaction, in formula (16) for T_c we have

$$\theta \sim \theta_{\rm D}$$
, (20)

where θ_D is the Debye temperature of a corresponding metal. Estimate (20) is particularly clear in the language explaining the electron–phonon interaction as a result of the fact that two electrons exchange phonons. But the maximum phonon energy $\hbar\omega_{\rm ph}$ is precisely of the order of $k_{\rm B}\theta_{\rm D}$, and therefore $k_{\rm B}\theta_{\rm D}$, i.e., the energy range where interelectron attraction occurs, is considered in the BCS theory and thus in formula (16).

For the majority of metals $\theta_{\rm D} \lesssim 500$ K and $\lambda \lesssim 1/3$. Hence, according to (16), $T_{\rm c} \lesssim 500$ exp(-3) = 25 K. Such estimates suggest the following value for the phonon mechanism:

$$T_c \lesssim 30 - 40 \text{ K}$$
 (21)

True, for instance, for lead we have $\lambda \approx 1.5$, but in this case $\theta_{\rm D}=96$ K; formula (16) will not hold here, but the analysis based on the expressions for $T_{\rm c}$ also holding for strong coupling leads to the actual value $T_{\rm c,Pb}=7.2$ K (see, e.g., Ref. [68]). For hypothetical metallic hydrogen, where $\theta_{\rm D} \sim 3000$ K, one can however expect the values $T_{\rm c} \sim 200-300$ K, but it was not until 1986 that materials with $T_{\rm c} > 24$ K were created (for Nb₃Ge synthesized in 1973 the temperature was exactly $T_{\rm c} = 23.2-24$ K). That is why, the opinion was widely spread that estimate (21) was valid.

Getting somewhat ahead, I should note that for hightemperature cuprates the electron-phonon coupling is strong and the Debye temperature is high (e.g., $\lambda \approx 2$, $\theta_{\rm D} \approx 600$ K; see Refs [69–71]). It is generally clear that the electron-phonon mechanism can in principle account for HTSC, too, at least $T_c \lesssim 200$ K (for example, for $\lambda \approx 2$ and $\theta_{\rm D} \approx 1000$ K we already have $T_{\rm c} \approx 200$ K; see below). However, the temperature T_c is only one of the characteristics of a superconductor, and what has been said above does not of course guarantee that the phonon mechanism is the basic one responsible for superconductivity in the known HTSC cuprates. Moreover, in the framework of the phonon mechanism it is apparently not easy to explain the d-pairing and the high value of $2\Delta(0)/k_BT_c$. Historically, the search for HTSC by creating materials with simultaneously high θ_D and λ values was at one time unpopular obviously for fear that the lattice would be unstable upon strong coupling.

In any case, the search for HTSC went at first in a different direction (I shall not mention purely empirical attempts). Namely, as is already apparent from (16) and from the aforesaid, to increase $T_{\rm c}$ one can raise the temperature θ .

But this need not necessarily be the electron-phonon interaction, and any mechanism that provides electron pairing will do. Not phonons, but bound electrons which, of course, also interact with the conduction electrons, may in principle be responsible for superconductivity. As far as I know, W Little was the first to pay attention to such a possibility in 1964 [72]. Specifically, he considered a metallic (i.e., conducting) quasi- one-dimensional thread or 'spine' on the side of (or, more precisely, around) which there are 'polarizers', i.e., some molecules interacting with the conduction electrons in the quasi-one-dimensional thread. This interaction (which is obviously a Coulomb interaction by nature) is the one to provide pairing. In the same year 1964 D A Kirzhnits and I discussed the possibility of the existence of two-dimensional superconductors [73]. That is why it was natural that after the appearance of paper [72] I proposed [74] something analogous, but quasi-two-dimensional instead of quasi-one-dimensional, i.e., a metallic film with dielectric layers on both sides (a 'sandwich').

The proposed mechanism of superconductivity in general and under the conditions of Refs [72, 74] in particular can be called the exciton mechanism (more precisely the electron-exciton mechanism) meaning that phonons in this case are replaced by electronic excitons, i.e., excitations in a system of bound electrons. Briefly speaking, this is the electronic mechanism of superconductivity. The typical exciton energy $\hbar\omega_{\rm ex}=k_{\rm B}\theta_{\rm ex}$ of the order of 0.1–1 eV corresponds to the temperature $\theta_{\rm ex}\sim 10^3-10^4$ K. Hence, substituting in the BCS formula $\theta\sim\theta_{\rm ex}$ when $\lambda=1/3$, we obtain $T_{\rm c}\sim 50-500$ K. They say that 'paper will withstand anything', but how such possibilities could be realized was unclear and remains unclear to the present date. Nevertheless, many points had been clarified and discussed [68, 75] before the discovery of HTSC in 1986–1987 [76, 77] (the history of the early HTSC research is elucidated in Refs [35, 78]).

Of what became clear 'yesterday' I shall only linger on two things. First, in quasi-one-dimensional systems fluctuations are particularly large, which causes the lowering of $T_{\rm c}$ (in a strictly one-dimensional system generally $T_{\rm c}=0$). From this point of view, quasi-two-dimensional systems, i.e., 'sandwiches' and layered compounds are much more advantageous. This conclusion [74, 75, 79, 68] has been completely confirmed because all HTSC cuprates are layered compounds. Second, it was established [68] that the doubts as to the possibility of the existence of HTSC [80], aroused by the lattice instability, were ungrounded. Specifically, a system (a metal) with a negative dielectric permittivity

$$\varepsilon(0,q) < 0 \,, \qquad q \neq 0 \tag{22}$$

can be perfectly stable. Here $\varepsilon(\omega,\mathbf{q})$ is the longitudinal permittivity for the frequency ω and the wave vector \mathbf{q} . When $\varepsilon<0$, the Coulomb interaction $U=e^2/\varepsilon r$ obviously corresponds to attraction. This is precisely what leads to the electron (quasi-particle) pairing. It is interesting that for large q values a negative permittivity is realized in many metals [81, 82] owing to the phonon contribution. Negative ε values due to the electron contribution (mechanism) are only attainable in systems with a strong exchange-correlation interaction (allowance for the role of the local field is necessary). But it should be emphasized that no restrictions are generally known for the use of the electron (exciton) mechanism for raising $T_{\rm c}$ (we do not of course mean temperatures comparable with the degeneration temperature $\theta_{\rm F}=E_{\rm F}/k_{\rm B}$). For

more details concerning this point and the derivation of the stability condition (22) see Refs [71, 81] and the references there

I have permitted myself to discuss here at length the HTSC research carried out by myself and my colleagues working at the P N Lebedev Physical Institute in Moscow [68, 71, 73, 74, 78, 81, 82] not of course to claim priority. We have neither obtained HTSC materials nor given exact prescriptions for the synthesis of such materials which were obtained in 1986-1987 [76, 77]⁵. However, I do not think that a total disregard (see, in particular, Ref. [83]) of everything done earlier in the HTSC research by Little [72], by us in Moscow [35, 68] and by a number of other authors (see, e.g., Ref. [79] and the references in Ref. [78]) is justified. Another standpoint is also possible if cuprates and their superconductivity are assumed to be something quite special, not related to lowtemperature physics. I do not think of such an opinion as grounded, although the distinguished position of cuprates has now become particularly obvious (this fact has even been reflected in the title of the book [29]: 'Superconductivity of Metals and Cuprates').

4. Today (1987–?)

The study of conventional superconductors is of course continued on a large scale. Various nonstationary processes, including thermoelectric effects [38, 37, 28, 29], the study of vortices and different vortex structures [28, 58-61, 84, 85], and the co-existence of superconducting and magnetic ordering [86] can be mentioned as especially topical problems. However, many other interesting questions might also be mentioned. But in the broad context, the most important current problem is everything related to high-temperature superconductors (HTSC). Their discovery in 1986-1987, as is well known, gave rise to a real 'boom', unprecedented attention was attracted to them, and a huge number of papers began to appear (see, e.g., Ref. [83]). But I think nobody could then believe that synthesized oxides — cuprates would turn out to be so radically different from conventional superconductors. Now it has become clear that HTSC cuprates, although I do not think that they should be separated from other superconducting metals by the wall of China, represent a manifestly distinguished class of superconductors. Their properties are elucidated in monographs [28, 29] devoted to superconductivity and in special collections of papers [87, 88] and numerous reviews (I shall only mention a few of them [89 - 93]).

In spite of the fact that HTSC materials have been investigated for 13 years and a great effort has been made (tens of thousands of publications have appeared), the picture in the early 2000 remains on the whole fairly cloudy. This is largely due to complexity of cuprate structure and, mainly, to the difficulties in obtaining perfect single crystals and controlling of the degree of doping, homogeneity of samples, etc. That is why a number of experimental results turned out to be unreliable or insufficiently clear. I do not even want to try to somehow outline the present situation. But at the same time, I cannot but mention the perfection of some of the applied experimental methods, for instance, observations, using a scanning tunnel microscope, of the electron density distribution near individual impurity atoms in HTSC

⁵ I would like to note here that the importance of studying oxides, carbides, and nitrides was pointed out in Ref. [68] and in paper [82].

cuprates [94]. In respect of the theory it suffices to say that there exists no generally accepted view of the mechanism of superconductivity leading to high $T_{\rm c}$ values in cuprates. Here, I shall restrict myself to a few remarks.

The great success of the BCS theory has led to the long-time dominance of the ideology associated with this theory. Thus, at the early stages the HTSC problem was discussed in the framework or, better to say, on the basis of the conceptions of the BCS theory and its extension to the case of strong coupling. Indeed, there were attempts to raise T_c by increasing the temperature θ in the BCS formula (16) through a replacement of $\theta \sim \theta_D$, which holds within the phonon mechanism, by $\theta \sim \theta_{\rm ex}$ for the exciton mechanism of superconductivity. Another way, which is also apparent from (16), is an increase of the coupling constant $\lambda_{\rm eff}$ in passing over to strong coupling, when in the simplest version we have

$$T_{\rm c} = \theta \exp\left\{-\frac{1+\lambda}{1-\mu^*}\right\},\tag{23}$$

where $\lambda - \mu^* = \lambda_{\text{eff}}$ is the coupling constant involved in the BCS formula (16), λ is the strength of the coupling due to the phonon interaction (the phonon mechanism) or excitons (the exciton mechanism), and $\mu^* = \mu [1 + \mu \ln(\theta_F/\theta)]^{-1}$ reflects the role of Coulomb repulsion (for more details see, e.g., Refs [29, 68]). If in (23) we put $\mu^* = 0.1$, then for $\lambda = 3$ we already have $T_{\rm c}=0.25\theta$ and for the phonon mechanism with $\theta=\theta_{\rm D}=400$ K we obtain $T_{\rm c}=100$ K. This example only demonstrates that for cuprates with $\theta_D \sim 600$ K even for $\lambda = 2$ the temperature is already $T_c \approx 130$ K. Thus, to obtain values $T_{\rm c} \sim 100$ K in cuprates is no problem in itself. But this does not, of course, prove that in cuprates we are dealing with the phonon mechanism of superconductivity because T_c is only one of the characteristic quantities. The behavior of cuprates in the superconducting state, for example, the observed ratio $2\Delta(0)/k_BT_c$, does not allow us to identify the mechanism of superconductivity in cuprates as purely phonon. At the same time, a whole number of typical features in the behavior of cuprates in the normal state, which are customarily assumed to be specific, can in fact be well explained within the phonon mechanism [95]. I refuse to understand how the role of the phonon mechanism in cuprates can be ignored ⁶, although this mechanism is not in fact the only one to determine all the properties of these substances.

Undoubtedly, the study of HTSC in cuprates made us realize or rather recall that the phonon mechanism and the BCS approach itself are not the only possible ones for the understanding of superconductivity. Indeed, superfluidity in ³He and in neutron stars definitely has nothing in common with the phonon mechanism. Bose – Einstein condensation (below BEC) leading generally to superfluidity in the case of neutral particles and to superconductivity for charged particles does not depend on the boson formation mechanism (we mean the formation of bosons as a result of pairing of two electrons) ⁷. In my opinion, it would be right to call such a mechanism the Schafroth mechanism [49, 96], although Schafroth had a predecessor [48].

For an ideal Bose-gas of zero-spin particles of mass m^* , the temperature of the beginning of BEC is

$$T_{\rm c} = \frac{3.31\hbar^2 n^{2/3}}{m^* k_{\rm B}} = 2.9 \times 10^{-11} \left(\frac{m}{m^*}\right) n^{2/3} \,[{\rm K}]\,,$$
 (24)

where $m = 9.1 \times 10^{-28}$ is the free electron mass and n is the concentration of bosons (in cm⁻³).

It is interesting that when applied to liquid ⁴He, formula (24) leads to the value $T_c = 3.1$ K for the temperature of the λ point, whereas actually $T_{\lambda} = 2.17$ K. In view of the fact that liquid helium is rather far from an ideal gas, this closeness of T_c and T_λ is evidence of the determining role of the Bose statistics of particles for the superfluidity of ⁴He. According to (24), even for $n \sim 10^{21} \text{ cm}^{-3}$ and $m^* \sim m$, we obtain $T_{\rm c} \sim 3 \times 10^3$ K, and so, from this point of view obtaining the values $T_{\rm c} \sim 100$ K is no problem. In HTSC cuprates the coherence lengths are small, and thus the pairs are obviously much smaller than the typical sizes of Cooper pairs in conventional superconductors. Hence, the Schafroth mechanism or BEC of local pairs in application to HTSC was repeatedly mentioned from the very beginning (see, e.g., Ref. [78]) and was then developed in detail [98]. But such an approach to HTSC cuprates meets with serious objections, as all the other theories of superconductivity in cuprates known from the literature. Among them, the spin mechanism is worthy of note, in which pairing is due to spin interaction (I shall restrict myself to mentioning the first paper [99] and the last review known to me [100] in this field). The exciton mechanism has already been pointed out above [68, 72, 74, 75, 78, 79]; the basis of it is the BCS theory. Let us also mention the electron mechanisms [110, 111].

In a real substance there certainly simultaneously exist electron—phonon, spin, and electron—electron (electron—exciton) interactions. So, strictly speaking, the consideration may be restricted to one of these interactions only in some limiting cases. For example, in conventional superconductors the electron—phonon interaction prevails. But in cuprates, both electron—phonon and electron—electron (and maybe also spin) interactions are probably significant (in this connection see, in particular, paper [114]).

The possibility of applying the notions of a Fermi-liquid and a BCS type theory to HTSC cuprates is called in question [101]. The hypothesis of an electron liquid other than a Fermi-liquid is beyond doubt deep and important [102]. It is in principle possible that non-Fermi-liquid effects are significant and even decisive in HTSC cuprates. The future will show if this is so. But I am not afraid to express my intuitive opinion that the resources of the BCS type theory (including its extension to the case of strong coupling) are far from being exhausted. It is therefore quite possible that cuprates, too, (to say nothing of fullerenes and perovskite type substances like $Ba_{1-x}K_xBiO_3$) are mostly described using the concepts of a Fermi-liquid, the formation of pairs with charge 2e and their collectivization.

Here I however proceed to the section 'Tomorrow'. Today, the situation in the field of superconductivity is primarily characterized by obscurity of the picture of HTSC-cuprates. This is now the main thing.

5. Tomorrow

In the title of the previous section 'Today (1987–?)' there stands a question mark, since as in the sections 'The day before yesterday (1911–1941)' and 'Yesterday (1942–1986)'

⁶ The last known to me confirmation of the important role of phonons in cuprates is paper [112] reporting a strong isotope effect in one of the HTSC cuprates (T_c is not meant, but the temperature T^* at which a so-called pseudo-gap appears in a normal-state underdoped crystal); see, however, Ref. [113].

⁷ The existence of BEC was pointed out by Einstein as far back as 1925 [97] (see also Refs [15, 52]).

some landmarks are understood, for example, the discovery of superconductivity in 1911 and the discovery of HTSC materials in 1986–1987. For this reason, the landmark of 'Today' should not be March of 2000 when this paper is being written, but it should be some event. What event will it be? It is desirable that this landmark be the insight into the mechanism of superconductivity in HTSC cuprates. So many experimental results on cuprates have been obtained in the 13 years and the experimental methods employed have so much advanced (I judge, say, by the recent papers [92, 94, 103, 104, 112]), that a certain clarity may be expected in the experiment in the near future. If this happens, the theoretical comprehension will hardly keep us waiting long. Now I can only make some remarks.

If the phonon mechanism with strong coupling, though not the only one, is still determining, the value of the critical temperature T_c is unlikely to exceed approximately 200 K. [The maximum temperature attained to-date (this happened in 1994) was $T_c \approx 164 \text{ K}$ for the cuprate HgBa₂Ca₂Cu₃O_{8+x} under high pressure; at atmospheric pressure for this material $T_{\rm c}=135\,{\rm K}$.] This is clear from expressions of the type (23) for $T_{\rm c}$ and from the fact that $\theta \sim \theta_{\rm D} \lesssim 10^3$. For spin mechanisms the role of θ is played by Curie or Neel temperatures, and they are no higher than 10³ K either. For the exciton and some related electron mechanisms (the plasmon mechanism is sometimes discussed) $\theta \sim \theta_{\rm ex}$. The natural upper boundary for $\theta_{\rm ex}$ is the Fermi temperature $\theta_{\rm F} = E_{\rm F}/k_{\rm B} \lesssim 10^5$. The electron mechanism is not known to meet with objections of principal character (see Refs. [68, 71]), and from this point of view it may 'do its best' under some conditions. And in this case the dream, i.e., room-temperature superconductivity (RTSC) with $T_c \sim 300-400$ K would come true.

Undoubtedly, many laboratories are engaged in the search for materials with increasingly high $T_{\rm c}$ values. The lack of advances in this direction over a number of years (since 1994) testifies to the fact that the $T_{\rm c}$ of cuprates and many other tested compounds can hardly be raised. But the number of possible compounds is huge, which of course gives hope for finding a substance with higher $T_{\rm c}$ values. I believe, as before, that quasi-two-dimensional (layered) structures are promising; for some ideas concerning this issue see Ref. [105]. Wide possibilities for experiments in this field are known [106].

It should be mentioned here that the current situation in solid state theory cannot yet be thought of as satisfactory. The progress made over the past century is of course great if we look at the distance passed from the idea of electron motion in conductors, suggested by Drude in 1900, up to today's condition of the physics of metals. But on the other hand, the properties of even what seems to be the simplest system, namely, metallic hydrogen cannot be predicted from 'first principles' [107]. Judgements, sometimes encountered, that almost all the principal things in physics have already been done are simply absurd (see, e.g., [108]). There is no doubt that the theory of many-particle systems faces unsolved problems of great difficulty. Not until it becomes possible to calculate the parameters and characteristics of compounds of any prescribed composition and structure will one be able to think of condensed-matter theory as practically accomplished. Certainly, this also refers to superconductors (true, it should be pointed out that for simple metals like Al and Pb, advances have already been made [95]). It is difficult to say how many decades we shall wait for the achievement of this goal. We now have only one natural landmark in view — the year 2011, the centenary of the discovery of superconductivity. Unfortunately, we are unable to make a definite prognosis even for the decade left before this centenary. But I would not be very much surprised if room-temperature superconductors were created by 2011. This is however no more than a dream. But high-temperature superconductivity had also been only a dream before 1986.

6. Supplement

The conference MTSC 2000 (Major Trends in Superconductivity in the New Millennium) and the symposium 'Itinerant and Localized States in HTSC' held on April 1–9, 2000, i.e. immediately after the conference, were rather representative assemblies (nearly 130 scientists were present at the conference). Many experimental data were reported and various theoretical issues associated with superconductivity in cuprates and in some other substances were discussed. However, no essentially new insight into the HTSC in cuprates was proposed. It is surprising that the long discussion of the problem did not contribute to the clarification of the theory of cuprate superconductivity. There exist different points of view, but I hope a consensus will be reached in the near future. The current situation will largely be elucidated in the proceedings of the MTSC 2000 conference (to be published at the end of this year in Journal of Superconductivity) and also in the paper by E G Maksimov [115].

Here I only want to make a few remarks not connected with cuprates. The data [116] reported at the conference testify to the rather probable existence of superconductivity with $T_c = 91$ K on the surface of the compound WO₃ doped with sodium (Na). We are speaking of strongly diamagnetic (at $T < T_c = 91$) small regions localized on the surface. The most significant point here is of course the high T_c value in the absence of copper. At the same time, it is natural to recall here the two-dimensional surface superconductivity which has long been discussed [73, 117]. A two-dimensional conductor may pass over to a superconducting state, and there are different possibilities for that. One of them occurs if a substance (a metal, a semiconductor or a dielectric in the case of volume effects) possesses surface levels. In the case of an appropriate position and occupation of these levels (e.g., Tamm levels [117]) the surface may appear to be metallic and then also superconducting. Another possibility is the coating of a non-superconductive material with a monolayer (of e.g. CuO₂) which may turn out to be superconductive (the technological process is well-known; see Refs [106, 118]).

The report of a possible high-temperature superconductivity in the $WO_3 + Na$ system makes us emphasize once again that there is no reason to assume high-temperature superconductivity (we shall define it as superconductivity with $T_c > T_{b,N_2} = 77.4$) to exist in cuprates only. The search for HTSC in various substances has been and is now being conducted, but the earlier positive results not related to cuprates have not been reproduced and thus confirmed. Nevertheless I believe that there are insufficient grounds to think of all the reported HTSC observations as erroneous. This particularly concerns CuCl (see, for example, Refs [119, 120]; for some other references see also Ref. [78]). Since then, the crucial significance in some cases of even a small doping, i.e. the presence of impurities, especially oxygen, has become clear. Moreover, it has become possible to state the appearance of small superconducting regions not only from measurements of diamagnetic susceptibility (see, e.g., Ref. [116]). That is why some earlier observations, especially with

CuCl, should be repeated. At the same time, the wide-scale search for HTSC in various substances is particularly promising when a material is created using layer-by-layer sputtering (see Refs [106, 118]). The study of non-damping currents in carbon nanotubes [21] also deserves attention.

References 8

- Kamerlingh Onnes H Communication from the Physical Laboratory of the University of Leiden 119B (1911) (below cited as Comm. Leiden)
- 2. de Nobel J Phys. Today 49 (9) 40 (1996)
- 3. Kamerlingh Onnes H Comm. Leiden 120b, 122b (1911)
- 4. Kamerlingh Onnes H Comm. Leiden 124c (1911); This paper is placed as an appendix in paper [6]
- 5. Kamerlingh Onnes H Comm. Leiden 133 a, b, c, d (1913)
- Ginzburg V L Sverkhprovodimost': Fizika, Khimiya, Tekhnika 5 1 (1992)
- Kamerlingh Onnes H Comm. Leiden. Suppl. 34b (1913). This is the Nobel lecture. It is undoubtedly published elsewhere
- Ginzburg V L Sverkhprovodimost' (Superconductivity) (M.-L.: Izd. AN SSSR, 1946)
- 9. Kamerlingh Onnes H, Tuyn W Comm. Leiden 160a (1922)
- Shoenberg D Superconductivity (Cambridge: Cambridge Univ. Press, 1965). The first edition of this book was published in 1938 (Ser. Cambridge Physical Tracts) and the second edition in 1952 (Ser. Cambridge Monographs on Physics) [Translated into Russian: D Shoenberg Sverkhprovodimost' (Moscow: IL, 1955)]
- 11. Kamerlingh Onnes H Comm. Leiden Suppl. 50a (1924)
- 12. Meissner W, Ochsenfeld R Naturwissenschaften 21 787 (1933)
- Kamerlingh Onnes H Comm. Leiden 119 A (1911); see also Proc. R. Acad. Amsterdam 13 1903 (1911)
- Keesom W H Helium (Amsterdam: Elsevier, 1942) [Translated into Russian (Moscow: IL, 1949)]
- London F Superfluids Vol. 2 Macroscopic Theory of Superfluid Helium (New York: Wiley and Sons, 1954)
- 16. Kapitza P L Nature (London) 141 74 (1938)
- Allen F, Missner A D Nature (London) 141 75 (1938); Proc. R. Soc. London Ser. A 172 467 (1939)
- Kapitza P L Zh. Eksp. Teor. Fiz. 11 581 (1941); J. Phys. USSR 4 181;
 5 59 (1941)
- Landau L D Zh. Eksp. Teor. Fiz. 11 592 (1941) [J. Phys. USSR 5 71 (1941)]
- Sommerfeld A, Bethe H A, in *Handbuch der Physik* Vol. 24, Part 2, (Berlin, Springer-Verlag, 1933) p. 333 [Translated into Russian *Elektronnaya Teoriya Metallov* (Leningrad: ONTI, 1938)]
- Wilson A Kvantovaya Teoriya Metallov (Quantum Theory of Metals) (Moscow – L: OGIZ, 1941)
- Lifshitz E M, Pitaevskii L P Statisticheskaya Fizika (Statistical Physics) Pt. II Teoriya Kondensirovannogo Sostoyaniya (The Theory of Condensed State) (Moscow: Nauka, 1978) [Translated into English (New York: Pergamon Press, 1980)]
- 23. Hoddeson L, Baym G, Eckert M Rev. Mod. Phys. 59 287 (1987)
- Einstein A Gedankbook Kamerling Onnes (Leiden, 1922) p. 429
 [Translated into Russian: Einstein A Sobranie Nauchnykh Trudov (Collection of Scientific Papers) Vol. 3 (Moscow: Nauka, 1966) p. 432]
- 25. Gorter C J, Casimir H Physica 1 306 (1934)
- Landau L D, Lifshitz E M Elektrodinamika Sploshnykh Sred (Electrodynamics of Continuous Media) (Moscow: Nauka, 1992)
 See Ch. XI [Translated into English (New York: Pergamon Press, 1984)]
- Tilley D R, Tilley J Superfluidity and Superconductivity 2nd ed. (Bristol: Adam Hilger, 1986) [Translated into Russian of the first edition (Moscow: Mir, 1978)]
- Tinkham M Introduction to Superconductivity 2nd ed. (New York: McGraw Hill, 1996) [Translated into Russian of the first edition: Tinkham M Vvedenie v Sverkhprovodimost' (Moscow: Atomizdat, 1980)]
- Waldram J R Superconductivity of Metals and Cuprates (Bristol, Philadelphia, Pa.: Institute of Physics Publ., 1996)
- 30. Gorter C J, Casimir H Phys. Z. 35 963 (1934)

- London F, London H Proc. R. Soc. London Ser. A 149 71 (1935);
 Physica 2 341 (1935)
- 32. Becker R, Heller G, Sauter F Z. Phys. 85 772 (1933)
- Ginzburg V L, Zharkov G F Usp. Fiz. Nauk 125 19, 750 (1978) [Sov. Phys. Usp. 21 381 (1978)]
- Ginzburg V L Zh. Eksp. Teor. Fiz. 16 87 (1946); J. Phys. USSR 9 305 (1945)
- Ginzburg V L Usp. Fiz. Nauk 167 429 (1997) [Phys. Usp. 40 407 (1997)]
- Ginzburg V L Zh. Eksp. Teor. Fiz. 14 177 (1944); J. Phys. USSR 8 148 (1944)
- Ginzburg V L Usp. Fiz. Nauk 168 363 (1998) [Phys. Usp. 41 307 (1998)]
- Gulian A M, Zharkov G F Nonequilibrium Electrons and Phonons in Superconductors (New York: Kluwer Academic, Plenum Publ., 1999)
- Sverkhprovodimost'. Bibliograficheskii Ukazatel' 1911–1970 (Ed. V R Karasik) (Superconductivity. Bibliographical Index 1911–1970) (Moscow: Nauka, 1975)
- 40. Appleyard E et al. Proc. R. Soc. London Ser. A 172 540 (1939)
- 41. Ginzburg V L, Landau L D Zh. Eksp. Teor. Fiz. 20 1064 (1950). [Soviet journals were not translated into English at that period, and Journal of Physics USSR was closed in 1947. The English translation of the article appeared in the English edition of L D Landau's papers Collected Papers of L D Landau (Oxford: Pergamon Press, 1965) p. 546]
- 42. Pippard A B Proc. R. Soc. London Ser. A 216 547 (1953)
- 43. Bardeen J, Cooper L N, Schrieffer J R Phys. Rev. 108 1175 (1957)
- Bardeen J, in Kältephysik (Handbuch der Physik, Bd. 15, Hrsg. von S Flügge) (Berlin: Springer-Verlag, 1956) p. 274 [Translated into Russian Fizika Nizkikh Temperatur (Ed. A I Shal'nikov) (Moscow: IL. 1959)]
- Ginzburg V L Zh. Eksp. Teor. Fiz. 29 748 (1955) [Sov. Phys. JETP 2 589 (1956)]
- Gorkov L P Zh. Eksp. Teor. Fiz. 36 1918; 37 1407 (1959) [Sov. Phys. JETP 9 1364 (1959); 10 998 (1960)]
- Ginzburg V L Usp. Fiz. Nauk 48 26 (1952); Fortschr. Phys. 1 101 (1953)
- 48. Ogg R A Phys. Rev. 69 243 (1946)
- 49. Schafroth M R Phys. Rev. 96 1149, 1442 (1954); 100 463 (1955)
- 50. Cooper L N Phys. Rev. 104 1189 (1956)
- Ginzburg V L Fizika Tverdogo Tela 2 2031 (1960) [Sov. Phys. Solid State 2 1824 (1961)]
- Landau L D, Lifshitz E M Statisticheskaya Fizika (Statistical Physics) Part I (Moscow: Fizmatlit, 1955) Ch. 14 [Translated into English (Oxford: Pergamon Press, 1980)]
- 53. Ginzburg V L Zh. Eksp. Teor. Fiz. 23 236 (1952)
- 54. Sigrist M, Ueda K Rev. Mod. Phys. 63 239 (1991)
- Abrikosov A A Zh. Eksp. Teor. Fiz. 32 1442 (1957) [Sov. Phys. JETP 5 1174 (1957)]
- 56. Weinan E Phys. Rev. B 50 1126 (1994); Physica D 77 383 (1994)
- 57. Sakaguchi H *Prog. Theor. Phys.* **93** 491 (1995)
- 58. Bethuel F, Brezis H, Helein F *Ginzburg Landau Vortices* (Boston: Birkhauser, 1994)
- Ovchinnikov Yu N Zh. Eksp. Teor. Fiz. 115 726 (1999) [JETP 88 398 (1999)]
- 60. Aranson I S, Pismen L M Phys. Rev. Lett. 84 634 (2000)
- Zharkov G F, Zharkov V G, Zvetkov A Yu *Phys. Rev. B* 61 12293 (2000)
- Bogolyubov N N Zh. Eksp. Teor. Fiz. 34 41 (1958) [Sov. Phys. JETP 7 51 (1958)]
- 63. Valatin J Nuovo Cimento 7 843 (1958)
- 64. Kuper C Adv. Phys. 8 (29) 1 (1959)
- 65. Teoriya Sverkhprovodimosti (Theory of Superconductivity) Collected papers (Ed. N N Bogolyubov) (Moscow: IL, 1960)
- 66. Josephson B D Phys. Lett. 1 251 (1962)
- Eliashberg Zh. Eksp. Teor. Fiz. 38 966; 39 1437 (1960) [Sov. Phys. JETP 11 696 (1960); 12 1000 (1961)]
- 68. *High-Temperature Superconductivity* (Eds V L Ginzburg, D A Kirzhnitz) (New York: Consultants Bureau, 1982)
- Ginzburg V L, Maksimov E G Physica C 235 240 193 (1994); 209 1 (1993)
- 70. Maksimov E G J. Supercond. 8 433 (1995)

- Ginzburg V L, Maksimov E G Sverkhprovodimost': Fiz., Khim., Tekh. 5 1543 (1992) [Superconductivity: Phys., Chem., Tech. 5 1505 (1992)]
- 72. Little W A Phys. Rev. A 134 1416 (1964)
- Ginzburg V L, Kirzhnits D A Zh. Eksp. Teor. Fiz. 46 397 (1964)
 [Sov. Phys. JETP 19 269 (1964)]
- Ginzburg V L Zh. Eksp. Teor. Fiz. 47 2318 (1964) [Sov. Phys. JETP 20 1549 (1964)]; Phys. Lett. 13 101 (1964)
- Proc. Intern. Conf. Organic Superconductors (Ed. W Little) (New York: J. Wiley, 1970)
- 76. Bednorz J G, Müller K A Z. Phys. B 64 189 (1986)
- 77. Wu M K, Chu C W et al. Phys. Rev. Lett. 58 908 (1987)
- 78. Ginzburg V L *Prog. Low Temp. Phys.* **12** 1 (1989)
- 79. Allender D, Bray J, Bardeen J Phys. Rev. B 7 1020; B 8 4443 (1973)
- Cohen M L, Anderson P W Superconductivity in d and f Band Metals (AIP Conf. Proc., N 4, Ed. D H Douglass) (New York: AIP, 1972)
 p. 17
- 81. Dolgov O V, Kirzhnits D A, Maksimov E G Rev. Mod. Phys. 53 81 (1981)
- Dolgov O V, Maksimov E G Usp. Fiz. Nauk 138 95 (1982) [Sov. Phys. Usp. 25 688 (1982)]
- 83. Proc. 18th Intern. Conf. Low Temp. Phys. Part 3 (Kyoto, 1987)
- 84. Crabtrel G W, Nelson D R Phys. Today 50 (4) 38 (1997)
- 85. Palacios J J Phys. Rev. Lett. 84 1796 (2000)
- 86. Amici A, Thalmeier P, Fulde P Phys. Rev. Lett. 84 1800 (2000)
- 87. High Temperature Superconductivity (Ed. J W Lynn) (New York: Springer-Verlag, 1990)
- Physical Properties of High Temperature Superconductors (Ed. D M Ginsberg) (Singapore: World Scientific) [Several volumes, the first of which was published in 1989]
- 89. Ruvalds J Supercond. Sci. Techn. 9 905 (1996)
- 90. Ford P J, Saunders G A Contemp. Phys. 38 1 (1997)
- 91. Goldman A M, Markovic N Phys. Today 51 (11) 39 (1998)
- 92. Timusk T, Stratt B Rep. Prog. Phys. 62 61 (1999)
- 93. Batlogg B, Varma C *Phys. World* **13** (2) 33 (2000)
- 94. Pan S N et al. Nature (London) 403 717, 746 (2000)
- Maksimov E G, Savrasov D Yu, Savrasov S Yu Usp. Fiz. Nauk 167 353 (1997) [Phys. Usp. 40 337 (1997)]
- 96. Schafroth M R, Burler S T, Blatt J M Helv. Phys. Acta 30 93 (1957)
- Einstein A Sitzungsber. preuss. Akad. Wiss., Phys.-Math. Kl., 3 (1925) [Translated into Russian: Einstein A Sobranie Nauchnykh Trudov (Collection of Scientific Papers) Vol. 3 (Moscow: Nauka, 1965) p. 489]
- 98. Alexandrov A S, Mott N F High Temperature Superconducors and Other Superfluids (London: Taylor and Francis, 1994)
- Akhiezer A I, Pomeranchuk I Ya Zh. Eksp. Teor. Fiz. 36 859 (1959)
 [Sov. Phys. JETP 9 605 (1959)]
- Izyumov Yu A Usp. Fiz. Nauk 169 225 (1999) [Phys. Usp. 42 215 (1999)]
- Anderson P W The Theory of Superconductivity in the High-T_c Cuprates (Princeton, N. J.: Princeton Univ. Press, 1997)
- 102. Schofield A J Contemp. Phys. 40 95 (1999)
- 103. Gruninger M et al. Phys. Rev. Lett. 84 1575 (2000)
- 104. Lake B et al. Nature (London) 400 43 (1999)
- 105. Geballe T H, Moyzhes B Y, Proc. M² S-HTSC VI, 2000 *Physica C* (in press)
- 106. Bozovic I, Eckstein J N See Ref. [88] Vol. 5 (1996)
- Maksimov E G, Shilov Yu I Usp. Fiz. Nauk 169 1223 (1999) [Phys. Usp. 42 1121 (1999)]
- Ginzburg V L Usp. Fiz. Nauk 169 419 (1999) [Phys. Usp. 42 353 (1999)]
- 109. Tallon J Phys. World 13 (3) 27 (2000)
- 110. Kocharovsky V V, Kocharovsky VI V Physics C 200 385 (1992)
- 111. Belyavskii V I, Kapaev V V, Kopaev Yu V, Proc. M²S-HTSC VI, 2000; *Physica C* (in press); *Zh. Eksp. Teor. Fiz.* (in press)
- 112. Taprano D R et al. Phys. Rev. Lett. 84 1990 (2000)
- 113. Ohno T, Asayama K Phys. Lett. A 258 367 (1999)
- 114. Bill A, Morawitz H, Kresin V Z *Phys. Rev. B* (in press)
- Maksimov E G Usp. Fiz. Nauk 170 (10) 1033 (2000) [Phys. Usp. 43 (10) (2000)]
- 116. Reich S, Tsabba Y Eur. Phys. J. 9 1 (1999); Levi Y et al. J. Supercond. (in press)
- 117. Ginzburg V L Physica Scripta T 27 76 (1989)

- 118. Bozovic I J. Supercond. (in press)
- 119. Chu C W, Rusakov A P et al. Phys. Rev. B 18 2118 (1978)
- Brandt N B et al. Pis'ma Zh. Eksp. Teor. Fiz. 27 37 (1978) [JETP Lett. 27 33 (1978)]
- Tsebro V I, Omelyanovskii O E, Morovskii A P *Pis'ma Zh. Eksp. Teor. Fiz.* **70** 457 (1999) [*JETP Lett.* **70** 462 (1999)]; see also Tsebro V I, Omelyanovskii O E *Usp. Fiz. Nauk* **170** 906 (2000)