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HIGH-TEMPERATURE SUPERCONDUCTIVITY *
(An Overview)

V.L. Ginzburg **
International Centre for Theoretical Physics, Trieste, Italy.

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It is an honour for me to be invited to deliver the introductory report at this Conference. However, it is hard to assess beforehand the usefulness of such a report. Leaving aside the efforts put into this paper, the effect will depend on the composition of the auditorium and the contents of subsequent talks. At the time of preparing this review article, I did not have an inkling to either of these. What is more important, investigations into high-temperature superconductivity are based on new results on metal oxide ceramics and have been carried out mainly for the past six months or so. New results are continuing to pour in. Under such circumstances, it is natural to lay the main stress in the introductory report on the historical aspects of the problem and general theoretical remarks.

1. Let me begin with a brief account of the history of experimental studies on superconductivity. The liquefaction of helium by Kamerlingh Onnes in 1908 was the first milestone in this direction. By the way, liquid helium was produced only at Leiden right up to 1923. In 1911, Onnes discovered superconductivity in mercury (T_c=4.1 K). In 1913, the superconductivity of lead (T_c=7.2 K) was discovered. It was observed in 1914 that superconductivity is destroyed by the magnetic field, the values of the critical field $H_c(T)$ being not very large (for example, in the case of mercury even at $T \to 0$, when H_c has it maximum value, it does not exceed about 400 Oe). Naturally, the critical current I_c was also found to be small.

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** Permanent address: P.N. Lebedev Institute of Physics, Moscow, USSR.

Thus, right after the discovery of superconductivity, two obstacles appeared in the path of its practical application (the first superconducting magnet was constructed by Onnes in 1914). The first obstacle was the temperature barrier (low values of T_c), and the second was the magnetic and current barrier (relatively weak fields H_c and currents I_c). The magnetic and current barrier was overcome by the discovery in the 1930's of alloys which are now called superconductors of the second type. For such materials, superconductivity vanishes only in the field $H_{c2}(T)$ which can assume enormous values For example, $H_{c2}(0) \simeq 200$ kOe for Nb_3Sn. As a result (actually, only in the 1960's) strong superconducting magnets were constructed. For high-temperature superconductors discovered recently, the field H_{c2} is generally still stronger. As regards the critical current I_c, for high values of H_{c2} it is mainly determined by the treatment of a materials, vis. by technology. Therefore, there are apparently no serious reasons to fear that there may be any difficulties in principle in overcoming the magnetic and current barrier for high-temperature superconductors.

Table 1 shows how the critical temperature T_c was raised over the years. I would also like to draw your attention to some values of boiling points and melting points under atmospheric pressure (see Table 2). Of course, these facts are well known but they cannot be left aside.

Let us now outline the endeavours to overcome the temperature barrier since 1973.

In view of the latest achievements, one cannot help mentioning the synthesis and investigation of metal oxide ceramics $BaPb_{1-x}Bi_xO_3$ from 1974 onwards[1]. The maximum value of $T_c \simeq 13$ K is attained in these ceramics for $x=0.25$. The interest to these and other ceramics remained undiminished even before recent discoveries. This is evident from, among other things, the review article[2] which contains over 200 ces. The value $T_c=24$ K (for Nb_3Ge) remained a record until 1986 when Bednorz and Müller[3] detected the appearance of superconductivity in ceramics La-Ba-Cu-O with $T_c \sim 30$-40 K.

But the first paper[3] by these authors under the title "Possible High T_c Superconductivity in the Ba-La-Cu-O System", indeed, did not contain the proof of the disappearance of the resistance R. By mentioning this, I certainly do not intend to undermine the role of Müller and Bednorz. On the contrary, I believe that the caution and restraint exhibited by these scientists speaks in their favour.

Later, towards the end of 1986, the existence of high-temperature superconductors, which can be called "neon" superconductors ($T_c \sim 40$ K) was reliably proved in Switzerland, Japan and USA for the systems La-Ba-Cu-O and La-Sr-Cu-O. Many participants of this conference know the course of events during this period better than I. Therefore, I will remain content by refering to the paper[4] in which a quite distinct transition to the superconducting state was observed for the alloy $La_{1.8}Sr_{0.2}CuO_4$ at $T_c=36.2$ K (corresponding to the midpoint of the transition). Later, in the beginning of 1987, $_{57}La$ was replaced by $_{39}Y$, and this led to the appearance of "nitrogen" superconductors with $T_c \sim 80$-100 K. For example, in [5], superconductivity was observed in alloy $(Y_{0.6}Ba_{0.4})_2CuO_{4-y}$ with $T_{co}=93$ K (under atmospheric pressure) and $T_{co}=80$ K (at T_{co}, the resistance R=0). Similar results were obtained soon afterwards by a number of groups in the USSR (the results of these investigations are published in JETP Lett.). For example, the group led by A.I.Golovashkin at the Lebedev Institute of Physics obtained in the beginning of March a yttrium superconductor with $T_{co}=102$ K. At present, many authors in different countries have obtained, without a shadow of doubt, superconducting metal oxide ceramics of various compositions (in which Y is replaced by Sc and a number of other elements) with $T_c \sim 90$-100 K. I expect that such results will be reported at this conference. On my part, I shall make a few more remarks of historical nature.

Firstly, it is interesting to note that many ceramics which were found to be superconductors, including $La_{1.8}Sr_{0.2}CuO_4$, the optimal material of this type, were obtained in the USSR as far back as in 1978[6]. What is more,

the authors[6] measured the resistance of these ceramics, though not in liquid helium. So, naturally, they did not discover superconductivity in ceramics (as far as I know, there were no "nitrogen" superconductors among these ceramics). The old samples were recently investigated and were found to be superconducting, which indicates that there is little or no "ageing" of these materials. I have heard that such ceramics were also synthesized in France and Japan before 1986, although they were not tested for superconductivity. This may well serve as a lesson. All new materials from the class of metals and semiconductors must undoubtedly be "tested for superconductivity" in liquid helium, and the values of T_c must be determined if a material turns out to be superconducting.

Secondly, a strong anomaly in the diamagnetic properties of CuCl was reported[7] in 1978 and later; in 1980, the same effect was observed[8] in CdS as well, at liquid nitrogen and higher temperatures (see reviews[10a,b]). These results could indicate the existence of high-temperature superconducting phases, although superconductivity itself was not observed from resistance measurements (apparently, this may be due to the absence of purely superconducting channels in the samples). The existence of nonsuperconducting "supermagnetics" also cannot be ruled out[9]. The nature of diamagnetic anomalies in CuCl and CdS remains unclear so far, and sometimes we speak of "nonreproducible superconductors"[10b]. In the light of latest results, it is quite reasonable to assume that superconductivity involving some oxides of copper was observed in CuCl. In any case, it would be interesting to solve the problem of "nonreproducible superconductors". The same holds for the report[10c] which appeared in 1986 even before the paper[3] and revealed the existence of superconductivity with $T_c \sim 40$ K in Nb-Ge-Al-O films (I know nothing about the fate of this paper or, to put it in a better way, of the result reported therein).

By the way, even for new "nitrogen" superconductors, some nonreproducible results were obtained, which could indicate the appearance of superconductivity with $T_c \sim 200$-250K[11].

It can by no means be ruled out that reliable information on the existence of "room-temperature" superconductivity with $T_c \sim 250$-300 K will soon appear.

However, the transition from "helium" to "nitrogen" superconductors is itself an achievement of enormous significance. The striking impression created by this transition is due to three reasons. The foremost among these is the economical and technical factor. A litre of liquid helium costs about 10 roubles in the USSR, while liquid nitrogen is available for just 5-10 copecks. Moreover, the heat of vaporization for nitrogen is an order of magnitude larger than for helium, and all cryogenic equipment for nitrogen is a lot simpler and cheaper than for helium. Besides, helium is obtained from natural gas, and hence it will become scarce with time. Therefore, a switchover to cooling by nitrogen instead of helium is a leap towards a decrease in the cost by a factor of several hundreds or even thousands. At the same time, efforts are being made in electrical and heat engineering to raise the efficiency by a few percent, or even by a fraction of one percent. The second reason behind such a keen interest in highetemperature superconductivity is of purely physical nature. A discovery has undoubtedly been made, although we do come across even more sensational discoveries in physics not infrequently. The third reason is the accessibility of new superconductors. Figuratively speaking, they can be "cooked by every housewife". Personally, although I have firmly believed that high-temperature superconductivity is possible, I consider this accessibility to be most striking.

2. The microscopic theory of superconductivity, which can be called reliable or fairly comprehensive, was first constructed in 1957, i.e. only 46 years after the discovery of superconductivity. Of course, I mean the theory formulated by Bardeen, Cooper and Schrieffer[12]. However, this theory did not grow out of nothing: a lot of work had preceded it[13].

Incidentally, I have participated in the discussion of the following type of question on a number of occasions: what prevents us from creating a new theory (in fact, the discussions concerned problems other than superconductivity)? Do we lack additional facts or information, or are we waiting for the advent of a genius, a "new Einstein"? It is impossible to provide an unequivocal answer to this rhetoric, and all depends on the prevailing situation. But so far as superconductivity is concerned, the following can be stated unambiguously both Einstein and Bohr, and many other leading scientists of a slightly lower calibre, were siezed with the problem of superconductivity and made a number of interesting comments[14]. However, they were not able to formulate the microscopic theory of superconductivity. It seems to me that, in the first place, such a theory had to wait until the discovery of superfluidity of He II, which was presented in a finished form only in 1938. After this, it became more or less clear that superconductivity is the superfluidity of the electron liquid in a metal. In the light of Landau's theory of superfluidity[15], some of the things became clear[15,16], although this did not happen all at once. As a matter of fact, according to one opinion (which was shared even by Landau at one time), superfluidity of helium II has nothing to do with Bose-Einstein condensation (the possibility of such a condensation, nay, its indispensability under certain conditions, was indicated by Einstein in 1925[17]). The connection between superfluidity and Bose-Einstein condensation or, in any case, the Bose statistics of ^{4}He atoms was established beyond doubt only after 1948 when ^{3}He was liquefied and its properties were found to differ sharply from those of liquid ^{4}He (it is well known that there is no λ-point for liquid ^{3}He at $T > 0.1$ K, while T_λ for ^{4}He is equal to 2.17 K). However, this opinion was held by many scientists even before the liquid ^{3}He was obtained. It would seem that under such conditions efforts should be made to find out how the electrons in a metal can be converted into a Bose system, say, as a result of formation of bound electron pairs with zero total spin.

However, it was not easy to actually arrive at such a conclusion. It was difficult to conceive how two electrons, which usually repel each other, can form a bound state. It is quite possible that I am not aware of all the facts, but I know of only one indication before 1954 of the connection between superconductivity and the formation of pairs with their Bose-Einstein condensation. I mean the article[18] by Ogg who believed that he had discovered superconductivity in ammonium-metal solutions. This was an erroneous conclusion, although I am not fully aware of the experimental details. However, Ogg did mention that electrons are bound in pairs and that their Bose-Einstein condensation takes place. In 1952, I studied the properties of a charge Bose-gas and emphasized that Meissner effect must take place in such a gas[19]. However, no mention was made by me[19] of the formation of such a Bose-gas of electrons. I was obviously alien to such an idea. Besides, in the Ψ-theory of superconductivity (this is the term I use for the macroscopic theory put forward by Landau and myself[20] in 1950), we have mentioned while replacing $-i\hbar\nabla$ by $(-i\hbar\nabla - \frac{e}{c}\vec{A})$ that "... e is a charge, which there is no reason to consider as different from the electronic charge." Later, while analysing the experimental results, I came to the conclusion that the agreement between the Ψ-theory[20] and experiment can be improved by introducing[21] an effective charge $e^*=(2-3)e$. Landau, however, opposed such a substitution[21] because observed that the effective charge could depend on pressure, temperature, composition, etc. and as such, must be assumed to be a function of coordinates. But this violates the gradient invariance. At that time, I did not succeed in overcoming this difficulty and introducing the effective charge e^*. Today, the answer to this question is quite obvious: any universal charge $e^*=ne$, where n is an integer, is entirely admissible from the point of view of gradient invariance. Indeed, in superconductors, including the new type of materials[22], $e^*=2e$. Is it not curious (it seems to be sheer blindness now) that such a conclusion was not drawn by me, by Landau, or by anybody else. I have spoken about this problem at length also

in order to appreciate the contribution made by Schafroth who was killed in a plane crash in 1959. Like me, he started by considering a charged Bose gas[23] and then put forth the idea of pairing in the most clear and unmitigated form, suggesting that even the electron-phonon interaction could be responsible for pairing[24]. Schafroth et al.[25] developed their theory but left the question about the nature and mechanism of pairing unanswered. The pair size was assumed to be small (of atomic dimensions) and the critical temperature T_c was determined to a first approximation by the formula for the temperature of Bose-Einstein condensation of an ideal gas:

$$T_c = \frac{3.31\hbar^2 n^{2/3}}{m^* K_B} = 2.9\cdot 10^{-11}\left(\frac{m}{m^*}\right)\left(n_{cm^{-3}}\right)^{2/3} K, \qquad (1)$$

where m^* is the mass of the pair, $m=9.1\times 10^{-28}$g is the mass of a free electron, and n is the number density of pairs with zero spin.

In recent years, and especially now when new superconducting materials have been obtained, Schafroth's model with "tiny" pairs is being widely discussed, and we shall return to it later. Thus, it is obvious that the generally accepted notion about the introduction of pairing in the theory of superconductivity by Cooper[26] in 1956 is entirely unfounded. The merit of Cooper's work and, in the first place, of the subsequent BCS theory[12] lies in the real demonstration of pair formation ("large", or Cooper, pairs) and of their collective "condensation" even under a weak attraction between electrons near the Fermi surface of the electron gas.

The well-known formula in the BCS theory

$$T_c = \theta e^{-1/\lambda_{eff}} \qquad (2)$$

was strikingly successful. Indeed, according to this formula, the value of T_c is determined by only two parameters, viz. θ - the region of attraction between electrons near the Fermi boundary, and $\lambda_{eff}=N(0)V$ - a dimensionless parameter characterizing the intensity of this attraction. In the original version of the BCS theory, $\lambda_{eff}=N(0)V \ll 1$, where N(0) is the density of states on the Fermi boundary and V is the matrix element of the interaction energy. It is not surprising that the BCS theory is indeed the real microtheory of superconductivity for the chosen model. However, the fact that this model provides a fairly accurate description of real superconductors with a weak coupling ($\lambda_{eff} \ll 1$) can by no means be considered obvious. As an example, we can consider the BCS formula connecting T_c with the energy gap 2 (0) in the superconductor spectrum for T=0, which has been confirmed experimentally:

$$2\Delta(0) = 3{,}52\, K_B T_c \qquad (3)$$

This relation might not be satisfied for the simplest model. Of course, the BCS theory was developed and refined (in the USSR, the contributions made by N.N.Bogoliubov, L.P.Gor'kov and G.M.Eliashberg are worth mentioning). The reasons behind the astounding success of the BCS model are discussed in[27].

3. Let us now go over to the calculation of the critical temperature and its possible maximum value *). For the phonon mechanism of superconductivity, i.e. when the attraction between electrons is due to their interaction with the lattice vibrations of phonons, the temperature $\theta \sim \theta_D$ in formula (2) is the Debye temperature. For the normally accepted values $\theta_D \lesssim 500$ K and $\lambda_{eff} \lesssim 1/3$, we obtain $T_c \lesssim 500\, e^{-3} = 25$ K. In general, this explains the fact that $T_c \lesssim 10$-30 K.

In a more realistic theory, and for a weak coupling (under the condition $\lambda_{eff} \ll 1$), we have

$$\lambda_{eff} = \lambda - \mu^* = \lambda - \frac{\mu}{1+\mu \ln\left(\frac{\theta_F}{\theta}\right)}, \qquad (4)$$

*) The following text is based on the material of lecture delivered by me[28] on 26 March, 1987 in Moscow.

where λ and μ are dimensionless coupling constants for the phonon (exciton) and Coulomb interaction respectively, and $\theta_F = E_F/k_B$ is the temperature corresponding to the Fermi energy E_F of the metal. Further, in the commonly used approximation (homogeneity, isotropy, weak coupling), we obtain

$$\mu - \lambda = 4\pi e^2 N(0) \left\langle \frac{1}{k^2 \mathcal{E}(0,k)} \right\rangle , \tag{5}$$

where $\mathcal{E}(\omega, k)$ is the longitudinal permittivity of the material, and the angle brackets indicate the averaging over the momenta $\hbar\vec{k}$.

It has been mentioned in literature that the requirement of stability of a metal leads to the condition $\mathcal{E}(0,k) > 0$. If this be so, then $\lambda \leq \mu$ in accordance with Eq.(5), and superconductivity would be possible only because $\mu^* < \mu$. This would indicate the low upper limit for T_c [29]. Such a conclusion, however, is incorrect since the stability requirement actually has the form $1/\mathcal{E}(0,k) \leq 1$ $(k \neq 0)$, the values of $\mathcal{E}(0,k) < 0$, and hence $\lambda > \mu$ are admissible. This important result was obtained by Kirzhnits[30,27] and is associated with the following circumstance. The response function obeying the dispersion relations is not $\mathcal{E}$ but rather $1/\mathcal{E}$. As a matter of fact, the electric field $\vec{E} = \frac{1}{\mathcal{E}}\vec{D}$, where $\vec{D}$ is the induction satisfying the equation div $\vec{D} = 4\pi\rho_{ext}$. The external charge ρ_{ext} can be controlled, and hence it is $\vec{D}$ that plays the role of the "cause", while the field $\vec{E}$ is the "consequence". We cannot arbitrarily change $\vec{E}$, and hence the function $\mathcal{E}$ in the formula $\vec{D} = \mathcal{E}\vec{E}$ need not obey the dispersion relations. To be more precise, the function $\mathcal{E}(0, k \to 0)$ for small values of $k \to 0$ is also a response function, and hence the necessary condition for the stability of the system is $\mathcal{E}(0, k \to 0) \geq 0$. But in the theory of superconductivity, we are more interested in the large value of the wave vector k. Usually, k is of the order of k_F, and hence we should impose only the requirement $1/\mathcal{E}(0,k) \leq 1$. As mentioned above, this is in agreement with the condition $\mathcal{E}(0,k) < 0$. What is more, just the values $\mathcal{E}(0,k) < 0$ are realised in most metals [31,32]. Usually, $\mu^* \sim 0.1$ (the parameter $\mu \lesssim 0.5$), and in some cases $\lambda \lesssim 3$ (for example, in the PbBi alloys, $\lambda \lesssim 2.6$; see[32,33]).

For intermediate and strong coupling when $\lambda_{eff} \gtrsim 1$, formula (2) under condition (4) is obviously inapplicable. For this case, a number of formulas of type (2) have been proposed with, say,

$$\lambda_{eff} = (\lambda - \mu^*)/(1+\lambda) \tag{6}$$

By way of an example, we observed that for $\mu^* = 0.1$, $\lambda = 1$ and $\lambda = 3$, the temperature $T_c = 0.11\,\theta$ and $T_c = 0.25\,\theta$ respectively in accordance with (2) and (6). In other words, we obtain the values $T_c \simeq 30$ K and $T_c \simeq 75$ K for $\theta \sim \theta_D \sim 300$ K. Many other similar formulas for T_c, obtained on the basis of Eliashberg's equations[27,32,33] and having a semiempirical or model dependence, lead to high values of T_c for appropriately chosen parameters. For example, the following formula has been proposed in[33] (we present it for $\mu^* = 0.1$):

$$T_c = \frac{\theta_{lg}}{5.42}(1 + 0.53\lambda)\exp\left[-1.25/(\lambda - 0.11)\right] \tag{7}$$

where

$$\theta_{lg} = \hbar\omega_{lg}/k_B, \quad \ln\omega_{lg} = \frac{2}{\lambda}\int \ln\omega \cdot \alpha^2(\omega) F(\omega)\frac{d\omega}{\omega},$$
$$\lambda = 2\int \alpha^2(\omega) F(\omega)\, d\omega/\omega$$

(see [27,32] for notation). According to [7], $T_c = 0.07\,\theta_{log}$ and $T_c = 0.74\,\theta_{log}$ for $\lambda = 1$ and $\lambda = 3$ respectively. For a strong coupling when $\lambda \gtrsim 10$, $T_c \approx \bar{\theta}\sqrt{\lambda}$ (here $\bar{\theta} = \hbar\bar{\omega}/k_B$, where $\bar{\omega}$ is a certain mean frequency in the phonon spectrum, see [34] and [27], Chap.4).

In any case, there are no restrictions in principle imposed on the possible values of T_c by the conventional theory of superconductivity. Thus, it is clear that large ("high-temperature") values of $T_c \sim 100$ K can be obtained for $\lambda \lesssim 3$ and $\theta \sim \theta_{log} \sim \bar{\theta} \sim \theta_D$ if at the same time $\theta_D \gtrsim 300$ K. The only question is whether such values of λ and θ_D can be

realised for the phonon mechanism of superconductivity. For each type of material, there exists a maximum value of T_c since the parameters θ_D and λ are not independent. Thus, an increase in the value of the electron-phonon coupling constant λ leads to a decrease in the phonon frequencies (due to the screening by conduction electrons and other reasons). This effect can be approximately described by the formula (see [32] in this connection):

$$\theta_D \approx \hbar\omega_{00}/k_B\,(1+c\lambda), \qquad (8)$$

where ω_{00} is the not renormalised ("pseudoatomic") phonon frequency and C is a constant. As a result, we obtain the maximum value of T_c which is proportional to ω_{00}.

Superconductors obtained before 1986 were characterised by parameters leading to $T_c \lesssim 25$ K. Hence and in view of the rough estimates presented above, it was usually concluded that $T_c \lesssim 30$–40 K for the phonon mechanism of superconductivity (see, for example, [27], Chap.1). It was always stipulated, however, that this conclusion is not general. For example, it was mentioned that $\theta_D \sim 3000$ K for metallic hydrogen and some (though not all) calculations lead to the values $T_c \sim 100$–300K (see [27,32] and the literature cited therein). Many metals are known to have high values of θ_D (for example, $\theta_D(\mathrm{Al}) \approx \theta_D(\mathrm{Ti}) \approx 430$ K, $\theta_D(\mathrm{Os}) \approx 500$ K, $\theta_D(\mathrm{Mo}) \approx 450$ K, and $\theta_D(\mathrm{Be}) \approx 1400$ K). The high value of θ_D for Be even led to the suggestion[35] that a temperature $T_c \sim 100$ K can be attained for beryllium under certain conditions.

The presence of light atoms H and C in organic superconductors raised hopes[36] that the high phonon frequencies in this case might result in large values of T_c. So far, these expectations have not been fulfilled, but such a possibility cannot be ruled out.

4. Naturally, it is especially important at present to explain the mechanism of superconductivity in recently discovered materials, viz. metal oxide ceramics. Let me start with the alloy $La_{1.8}Sr_{0.2}CuO_4$ and similar materials[4,37] with $T_c \approx 36$ K. It is mentioned in [4,37] that the superconductivity in this case may be caused by the usual phonon mechanism described above. The high value of T_c is attributed to the high frequency ω_0 of vibrations in the "subsystem" formed by a Cu ion surrounded by a distorted octahedron of oxygen ions. A comparison with the superconducting metal oxide ceramic $BaPb_{1-x}Bi_xO_3$ (for this alloy, $T_c \approx 13$ K for $x=0.25$, see above and [2]) for nearly identical values of θ_D leads to $T_c \approx 36$ K under the assumption that the density of states N(0) near the Fermi surface is 2-3 times higher for $La_{1.8}Sr_{0.8}CuO_4$ (in [37], where the alloy $La_{1.85}Sr_{0.15}CuO_4$ is investigated, the value of N(0) is 3-5 times higher than for $BaPb_{0.8}Bi_{0.2}O_3$ in accordance with the measurements of the field H_{c2}). Taking $\lambda = 1.2$ for $BaPb_{0.75}Bi_{0.25}O_3$, we get $\lambda = 3.1$–3.9 for $La_{1.85}Sr_{0.15}CuO_4$. Putting $=3.5$ by way of an example and using formula (7) with an identical value of θ_D, we obtain $T_c(La_{1.85}Sr_{0.15}CuO_4) = 3.26\,T_c(BaPb_{0.75}Bi_{0.25}O_3) \approx 42$ K. The same conclusion is drawn in [38] from quantitative analysis based on the calculations[39] of the electron structure for the tetragonal crystal $LaCuO_4$ (such computations have been carried out also in [40]). According to [38,40], the values $T_c \sim 30$–35 K for $\lambda = 2$–2.5 are quite natural for the system $La_{2-x}(Ba, Sr)_xCuO_4$. The light oxygen atom vibrating at a high frequency ω_0 plays an important role in this case.

A distinguishing feature of the metal oxide ceramics is that they are characterised by a high value of ω_0 owing to the presence (associated with light oxygen atoms) of rigid optical modes of lattice vibrations (phonons) which are strongly coupled with conduction electrons. In turn, this is due to a significant contribution of ionic bond in these compounds. About 20 valence electrons per unit cell contribute to the formation of this bond (the metallic bond is formed by just 1-2 conduction electrons which exert a rather weak influence on the lattice). Thus, it can be assumed that there is a tendency towards the optimisation of the contributions from ionic and metallic bonds in metal oxide ceramics (see [27], p. 170).

This, however, does not mean that the nature of superconductivity in the system $La_{2-x}Sr_xCuO_4$ is already clear. The mechanism of superconductivity in $BaPb_{1-x}Bi_xO_3$ is also a subject of discussions (see [2]). But as has been mentioned above, it is quite possible that the normal phonon mechanism is realized in the system La-Sr(Ba)-Cu-O. What is the state of affairs in other cases, especially in the system Y-Ba-Cu-O with $T_c \sim 90$ K and even $T_c \sim 100$ K? No direct information is available for these materials. However, in view of the estimates presented above, it is quite possible to explain the values $T_c \sim 100$ K within the framework of the normal phonon mechanism. As a purely illustrative example, it can be stated that for $\lambda = 3.5$, $T_c = 250$ K, formula (7) gives $\theta_D = 680$ K, which is by no means an astounding value. If the measurements of θ_D, the electronic part of the specific heat, etc. confirm such a possibility, the problem of high-temperature superconductivity for the cases under consideration can be regarded as solved by trivial means, so to say. The restriction $T_c \lesssim 40$ K for the phonon mechanism was never fully justified and was taken quite tentatively on the basis of rough estimates and fairly limited amount of experimental data. At present, from this point of view, materials have been synthesized with values of θ_D and λ leading to high critical temperatures T_c.

5. Firstly, such a possibility has not been proved in any way. Secondly, with a broad approach (which is undoubtedly required), we must analyse superconductivity mechanisms other than the above-mentioned "normal" phonon mechanism. Before going over to such an analysis, it should be emphasized that the list of unconventional mechanisms of superconductivity given below is far from being complete. The important point is that the properties of metal oxide ceramics cannot be explained on the basis of these mechanisms unless and untill the basic characteristics of these compounds are reliably established. Hence, such a list must be regarded only as an illustration of the possibilities which will have to be discussed seriously if the normal phonon mechanism is clearly found to be unsuitable.

Even the simplest formula (2) of the BCS theory, written in the form

$$T_c = \theta \exp\left[-1/N(0)V\right]$$

allows us to elucidate the main factors which can lead to an increase in T_c. Apparently, these factors are an increase in the width of the characteristic interaction region θ, the density of electron states N(0) on the Fermi boundary, and the interaction V responsible for pairing. All the three types of mechanism reflecting the influence of these factors will be discussed below.

Let us begin with the mechanism leading to an increase in the density of state N(0). It is well known that the standard theory of superconductivity which was referred as the conventional theory of superconductivity assumes the density of states N(E) of electrons in an normal material as a smooth and slowly varying function of the electron energy E near the Fermi surface. Hence the final formulas contain only the density $N(0)=N(E=E_F)$ at the Fermi boundary. The situation may change if the superconducting transition temperature T_c is relatively close to the temperature T_g of the structural phase transition, at which an energy gap $2\Delta_g^{(0)}$ of dielectric nature appears in the energy spectrum of the material. This gap may be due to the congruence of different parts of the Fermi surface of the material.*)

Near the gap boundaries, the density of states in the allowed region increases and varies strongly according to the law $N(E) \propto \mathcal{E}^{-1/2}$, where $\mathcal{E}$ is the distance from the gap boundary (in the physical sense, an increase in the density of states is due to their "expulsion" from the gap itself). Let us now suppose that the Fermi level of electrons in a doped semiconductor lies (before their superconducting pairing) in

*) The congruence means that the electron energy spectrum on relevant parts of the Fermi surface with electron momenta $\vec{p}$ satisfies the condition $E(\vec{p}) = -E(\vec{p} + \vec{q})$ for a certain set of vectors $\vec{q}$. Such a situation (or a situation similar to it) is called nesting.

the allowed band just near the boundary of the dielectric gap (see Fig.1). Then the superconducting pairing of the electron due to their phonon attraction (or due to the attraction of some other type, say, of exciton type; see below) will be enhanced on account of the dependence of N on E. Accordingly, the critical temperature T_c will be higher than in the case without a dielectric gap, and will be described, in view of the strong dependence of N(E) on E by a nonexponential formula (see [41] and [27], Chap.5, where the calculations are made in the weak coupling approximation).

Another factor, viz. the increase in the attraction V between electrons, is realised, in particular, in the bipolaron model of superconductivity. According to this model, a strong electron-phonon interaction contracts the rather wide conduction band to a narrow polaron band which corresponds to a fairly large mass of the carriers, viz. polarons. Because of this interaction, pairs of polarons may combine to form a bound state, or bipolaron, with a large binding energy roughly speaking, this corresponds to the confinement of both electrons in the same polarisation well). The aggregate of bipolarons, which are Bose particles, may undergo Bose-Einstein condensation whose temperature is described by formula (1) for a low number density n of bipolarons. In the model under consideration (see [42] and the literature cited therein), this temperature is just the critical temperature of superconductivity. For $n \sim 10^{21}-10^{22} cm^{-3}$ and $m^* \sim 10^2 m$, we obtain $T_c \sim 30-100$ K. The formation of pairs with a small radius (local pairs) and their subsequent condensation form the basis of not only the bipolar on model, but also some other models [43-45]. The pair formation in these models is attributed to the exchange forces of Heitler-London type ("resonating valence bands") and to the electron interaction in general. The critical temperature range is found to be of the order of the temperature typical of antiferromagnetic transition, i.e. may attain values of 100 K and higher. Models with Bose-Einstein condensation of local bound pairs differ in general from the BCS model in that the characteristic interaction is strong in comparison with the Fermi energy. I am not very conversant with these models and cannot describe them in detail. They will be undoubtedly discussed by many speakers.

6. Continuing the line of reasoning outlined at the beginning of this talk, let us now consider the third way of increasing T_c, viz. a broadening of the region of interaction characterized by θ in (2). The interaction between conduction electrons, which leads to superconductivity, may be caused, apart from lattice vibrations (phonons), only by other electrons (let us call them "bound" electrons). In this respect, it would be appropriate to speak of the electronic mechanism of superconductivity. Since superconductivity in metals is an electronic phenomenon, the superconductivity mechanism differing from the phonon mechanism is called excitonic in order to avoid confusion in terminology. However, other terms are also employed. The term "exciton mechanism" has been used by me since long [27,46] because of the clear picture illustrating the phenomenon: in the phonon mechanism, the interacting conduction electrons exchange phonons, while in the exciton mechanism they exchange excitons (excitations) of electron type. In "good" metals (as also in a free electron gas), there is only one type of electron excitation, viz. plasmons, for the energy $E_e = \hbar\omega_e \lesssim E_F$. To a first approximation (for the free electron gas, this is an exact result), the plasmon frequency $\omega_p = (\frac{4\pi e^2 n}{m})^{1/2} = 5.64 \times 10^4 \sqrt{n}$ (the numerical value corresponds to the charge and mass of a free electron). For $n \sim 10^{23} cm^{-3}$, $\omega_p \sim 10^{16}$ and $\hbar\omega_p = E_p \sim 10$ eV (for a degenerate electron gas, $\omega_p = \sqrt{\frac{4\pi e^2 n}{m}} = \sqrt{\frac{16\alpha}{3}}\omega_F$, $\alpha = e^2/\pi\hbar v_F$). The plasmons being considered here are longitudinal vibrations in the system of conduction electrons and their exchange does not take into account the effect of other ("bound") electrons. Hence, it is natural that the plasmons are found to contribute in the simplest case only towards the screening of the Coulomb interaction and influence the parameter μ (see(4)). Some metals or "sandwich"-type systems, however, may contain electronic excitations other than plasmons, having frequencies $\omega_e \ll \omega_F = E_F/\hbar$. In any case, the frequencies ω_e may considerably exceed $\omega_D = k_B\theta_D/\hbar$. For

example, for exciton energies $E_e = \hbar\omega_e \sim 0.1 - 1$ eV, the temperature $\theta_e \sim E_e/k_B \sim 10^3 - 10^4$ K, while for typical metals $\theta_F \sim E_F/k_B \sim 10^5$ K and $\theta_D < 10^3$ K.

The idea of using the exciton mechanism lies just in the replacement of θ_D by θ_e in the BCS formula (2) and in other formulas for the phonon mechanism. Sometimes, a transition from θ_D to θ_e is described with the help of arguments associated with the isotopic effect according to which the typical phonon frequencies $\omega_{ph} \propto M^{-1/2}$, M being the mass of the ions. In the exciton (electron) mechanism, the role of ions is played by "bound" electrons with mass which is generally of the order of the mass m of a free electron. Hence

$$\omega_e \sim \sqrt{M/m}\,\omega_{ph}\,, \quad \theta_e \sim \sqrt{\frac{M}{m}}\,\theta_D \lesssim 300\,\theta_D\,.$$

To my knowledge, the problem of high-temperature superconductivity was first raised at the present-day level (by Little [47] in 1964), within the framework of the exciton mechanism. Little considered the quasi-one-dimensional conducting polymer chains with molecular "branches". In principle, the electron polarisation of these "branches" must increase the value of T_c in the chain or, to be more precise, determine the value of T_c for conduction electrons in the chain. In the same year (1964), Kirzhnits and myself [48] considered the question of two-dimensional superconductivity, let us say, on surface levels, quite independently from the problem of high-temperature superconductivity. Even today, I find this question fascinating, but we shall not discuss it in details here. After the publication of Little's paper [47], I immediately combined both ideas [49] and proposed that T_c can be realized in thin metallic layers or on a surface by covering it with a dielectric. Allied versions of this are the dielectric-metal-dielectric "sandwiches", and various layered compounds. The underlying idea is that the electronic excitons, which can in principle exist and freely move in dielectrics, will be absorbed and emitted by the conduction electrons in the metallic layers (Fig.2). Thus, the excitons play in this case the role of phonons in the phonon mechanism (hence the

term "exciton mechanism of superconductivity"). The possibility of conduction electrons (i.e. their wave functions) penetrating into the dielectic (semiconducting) layers [50] is quite significant. The question of fluctuations was not considered in 1964. But it soon became clear that fluctuations are especially harmful in the quasi-one-dimensional case [47], and their role in the quasi-two-dimensional case is not so significant, but still negative [49]. In any case, one-dimensional conducting chains have still to be created, and such superconductors in truly one-dimensional form are not known to exist. On the contrary, "sandwiches" can be easily fabricated. Numerous types of layered compounds, which are sort of "piles" of sandwiches, exist and can be produced. True, the superconducting layered compounds known until recently had a rather low critical temperature. The new (high-temperature) superconductors also belong to this type of materials.

Of course, the necessary condition for the effectiveness of the exciton mechanism is that an increase in the pre-exponential factor θ in (2) and in other expressions must not be accompanied by a decrease in the parameter λ_{eff}. Can this be achieved? General considerations do not impose any restrictions on the parameter λ for the exciton mechanism also [27]. However, for the exciton mechanism to be effective, it is essential [27,32] that the inequality $\varepsilon_{el}(0,k) < 0$ be satisfied, where $\varepsilon_{el}(\omega,k)$ is the part of longitudinal permittivity associated with the polarisation of electrons (roughly speaking $\varepsilon(\omega,k) = \varepsilon_{ph} + \varepsilon_{el} - 1$, where $\varepsilon_{ph} - 1$ is the lattice contribution). Apparently, it is difficult to attain values $\varepsilon_{el}(0,k) < 0$ for typical metals, since the inequality described above will endanger the stability of the lattice (this is obvious even from the simplest "jelly" model in which the square of the ion frequency is expressed as the ratio of the square of ion-plasma frequency to the quantity $\varepsilon_{el}(0,k)$, and hence becomes negative for $\varepsilon_{el}(0,k) < 0$). In any case, in such calculations we must take into account the exchange-correlation interaction (i.e. the fact that the average electric field differs from the acting or effective field). In other words, we must go beyond the weak-coupling approxima-

tion. A consistent theory taking these requirements into account has not been constructed so far [32,51].

In general, the prospects of using the exciton mechanism from the position of "high theory" are not clear as yet. As far as various heuristic arguments and estimates are concerned, no significant advances have been made during recent years*), and we can refer to the articles [47,49] and Chaps.1, 4,6-8 in the book [27]. From a qualitative point of view, I still believe that it is hard to expect an effective exciton mechanism for good-conducting typical metals (with $E_F > 1\text{-}3\,eV$) with a homogeneous structure. That is why quasi-one-dimensional and quasi-two-dimensional structures offered great promise, as was mentioned above, the latter type of materials having more advantage. It cannot be ruled out, and I think it is quite likely, that the excitonic mechanism of superconductivity plays some sort of a role in the metal oxide ceramics which contain quasi-two-dimensional conducting layers of atoms and a large number of collective electron excitations (excitons). To be more specific, we are speaking of the effect of layers [56] containing Y, Ba (and, to some extent, even Cu and O) on good-conducting layers of Cu and O. The same opinion was expressed by Little in a preprint [53] he sent to me. A more detailed analysis of various models of this as well as other types is beyond the scope of this report.

7. In spite of the importance of metal oxide superconductors, there are absolutely no reasons to believe that only such materials can be high-temperature superconductors. A broad and unprejudiced approach is necessary in this case, and we have always adhered to it [27]. Allow me to reproduce Table 3, which I presented at the plenary session of the World Electrotechnical Congress in 1977. Observe that no question mark is put against sandwiches, layer compounds etc.

*) The only exception to this is the discovery of the so-called "heavy-fermion superconductors" in which the mechanism of superconductivity may not be of phonon type. This [illegible] possibility that non-phonon (electron or [illegible] role in

Such quasi-two-dimensional versions (see [27] p.39 etc.) have always been my favourites, although no breakthrough was made for a long time (by the way, these investigations were carried out by small groups and not persistently). That is why I introduced a mark of interrogation against layered compounds also in the same Table presented by me at the Waynflete lectures [54] in 1982.

What is really important is the absence of any known restrictions on T_c, especially for the exciton mechanism. The condition $T_c \lesssim 300$ K was mentioned in Table 3 and in [27]. In view of the recent experimental results, I would suggest the condition

$$T_c \lesssim 500 \text{ K}$$

I must confess, however, that this estimate is based on the same arguments as the previous one.

If we consider fundamental investigations rather than the practical applications, the main problem today is to understand the physical nature of the high-temperature superconductors that have already been obtained. Obviously, it is necessary to determine the crystal structure and other properties of the new superconductors both in superconducting and normal states. Much has already been done in this direction, but some experimental and theoretical results are not quite clear and contradict each other. It would be a mistake on my part to try to draw any definite conclusions at this stage. I hope that we will hear a lot about this from other speakers. Let me confine to just a few remarks. Thus, it seems fascinating to turn to the study of isotopic effect and, in particular, to replace ^{16}O by ^{18}O in order to determine the role of the phonon mechanism of superconductivity from variation of T_c. Such experiments have indeed been carried out [55] and within the limits of the high degree of accuracy attained in measurements, isotopic effect was not observed in respect of T_c in "nitrogen" superconductors. However, even if we use the dependence $T_c \leftrightarrow M^{-1/2}$, where M is the mass of the nucleus, the effect should be of the order of just 1%. Moreover, the isotope effect may be insignificant or completely absent even in the case of phonon mechanism of superconductivity. Thus,

a dependence of the type $T_c \propto M^{-1/2}$ would indeed be in favour of the phonon mechanism. The absence of isotope effect [55] still does not prove that the mechanism of superconductivity is excitonic (electronic), although it makes such a possibility more probable*). Of course, it should be interesting to verify the dependence (3) and other expressions following from the BCS theory for the weak coupling. However, I have come across only conflicting reports about this question. I would also like to mention that it the model with heavy bipolarons**), and with heavy pairs in general, the penetration depth $\delta = \sqrt{m^* c^2/4\pi e^2 n}$ for the magnetic field must be quite large. Thus, for $m^* \sim 100\ m$ and $n \sim 10^{22} cm^{-3}$, the depth $\delta \sim 10^{-4}$ cm, which is anomalously large (in comparison with known superconductors).

Irrespective of the conclusions at which we may arrive with regard to the details of the mechanism of superconductivity in metal oxide ceramics, our experience of the past forbids us from making absolutely final conclusions. It is quite possible, and even probable, that the high-temperature superconductors discovered so far are of just one or two types. But certainly there can be high-temperature superconductors of several types. In short, a wide and unprejudiced approach towards the search for high-temperature superconductivity is justified as before.

It is quite clear that high-temperature superconductors can find a very wide application in technology. I would like to mention just one point in conclusion. There are reasons to believ that it is possible to create economical superconducting accumulators, i.e. superconducting magnets in which magnetic energy can be stored. If such accumulators are created, thermonuclear reactors can become superfluous. As a matter of fact, according to the existing projects, these reactors are quite expensive and huge (I am speaking of systems with magnetic confinement of plasma), envisage the use

*) It is surprising that isotope effect has not been investigated in La-Sr(Ba)-Cu-O superconductors (see note in the end of the paper).

**) Probably, this version should lead to the isotope effect.

of radioactive tritium (a transition to pure deuterium is a thing of distant future) and, finally, the creation of "blankets" of fissionable materials. In other words, it is a complicated and "dirty" power engineering. At the same time, the use of solar and wind energy, tides, etc. is becoming more and more economical, but raises in the first place the problem of accumulation of energy. If this problem can be solved with the help of superconducting devices, thermonuclear power engineering may indeed become unnecessary and undesirable. Hence, from the point of view of power engineering of tomorrow, the problem of high-temperature superconductivity is of prime importance.

Additional note

According to information received by the author on June 30, in La-Sr-Cu-O superconductors considerable isotopic effect is observed. From this data one can think that in "neon" (LaSr(Ba)CuO) superconductors dominates the phonon mechanism. But in "nitrogen" superconductors ($Ba_2YCu_3O_7$, $Ba_2EuCu_3O_7$; see [55]) exiton mechanism is prevailing.

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TABLE 1

Material	Critical Temperature T_c (K)	Year of Discovery of its Superconductivity
Hg	4.1	1911
Pb	7.2	1912
Nb	9.2	1930
Nb_3Sn	18.1	1954
$Nb_3(Al_{0.75}Ge_{0.25})$	20 to 21	1966
Nb_3Ga	20.3	1971
Nb_3Ge	23.2-23.9	1973

TABLE 2

Substance	He	H_2	Ne	N_2	O_2	H_2O
Boiling temperature T_b (K; under atmospheric pressure)	4.2	20.3	27.2	77.4	90.2	373.16
Melting temperature T_m (K; under atmospheric pressure)	-	14.0	24.5	63.3	54.7	273.16

TABLE 3

Material or system	Superconductivity mechanism (nature of the attraction between the conduction electrons)	Maximum possible value of $T_{c,max}$ (rough estimates in K)
Metallic hydrogen or deuterium, alloys based on them	phonon	100 to 200
Organic metals, hydrogen-containing metals, and so on	phonon	50 to 100 (?)
Materials with electronic structural phase transitions	phonon or exciton	100 to 300 (?)
Three-dimensional metals with exciton bands, and so on	exciton	100 to 300 (?)
Layer compounds and dielectric-metal-dielectric sandwiches	exciton	100 to 300
Filamentary (quasi-one-dimensional) compounds	exciton	100 to 300 (?)
CuCl and CdS with impurities, obtained under pressure and as the result of special processing	?	300 (?)
Non-equilibrium superconductors		There are no clear limits, but in practice it is probable that $T_{c,max} \lesssim 1000$ K.

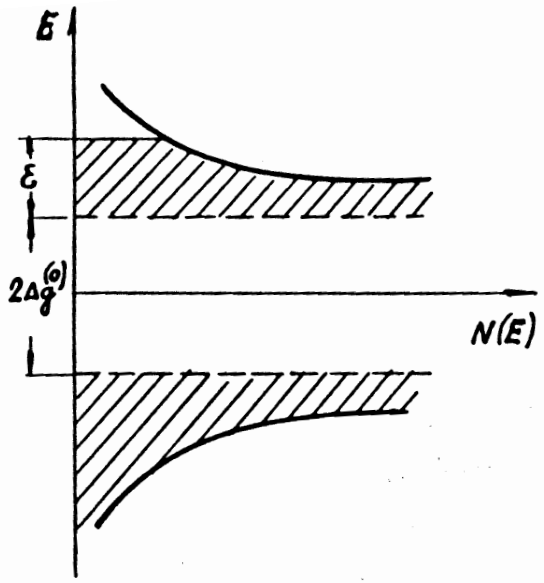

Fig.1

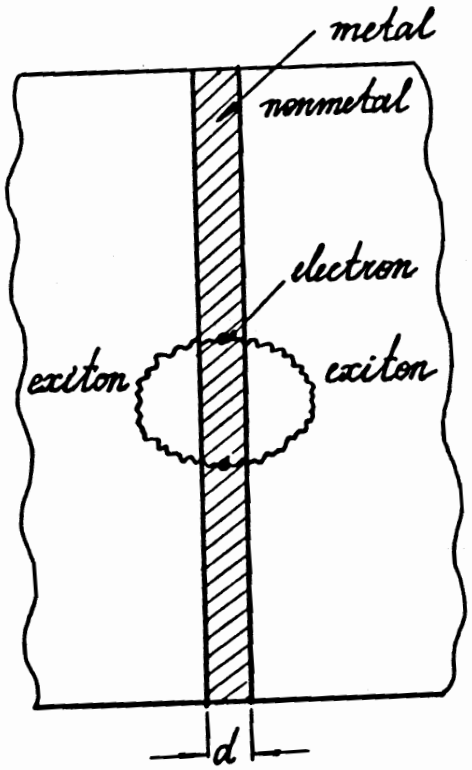

Fig.2