SOVIET PHYSICS USPEKHI VOLUME 8, NUMBER 3 NOVEMBER-DECEMBER 1965
537.312.6

SUPERCONDUCTIVITY IN NONMETALLIC SYSTEMS

L. V. KELDYSH

Usp. Fiz. Nauk 86, 327-333 (June, 1965)

THERE has been greatly renewed interest in the superconductivity phenomenon in recent years. This is explained to a considerable degree by the fact that after Bardeen, Cooper, and Schrieffer (BCS),[1] Bogolyubov,[2], Gor'kov[3] and others constructed in 1957 the microscopic theory of superconductivity, it became possible, at least in principle, to aim at finding superconductors with various specified properties.

Until recently, superconductivity was observed only in metals and at very low temperatures, not higher than 20°K. In addition, the superconducting state is usually destroyed in even relatively weak magnetic fields (on the order of 10^2–10^3 G), so that the currents flowing through such a superconductor can likewise not be large. All these circumstances greatly limit the possibilities of utilizing superconductivity, and it is therefore natural that one of the central problems of the theory of superconductivity at present is the question of whether one can hope to obtain a substance in which the superconducting state would exist at considerably higher temperatures and higher magnetic fields.

The main result of the BCS theory is that in a system of Fermi particles at a sufficiently low temperature any arbitrarily small attraction between the particles leads to a radical realignment of the state. Particles (we shall henceforth have in mind electrons) stick together to form pairs, and this is furthermore done in such a way that all pairs are in the same state, i.e., they have the same total momentum. In the equilibrium state, i.e., in the absence of current, the momenta of all the pairs are equal to zero. Consequently, the electrons sticking together are those having equal but opposite momenta. In other words, the electron pairs, which have the properties of Bose particles, form a Bose condensate, which behaves like a charged superfluid liquid. It is essential in this case that the pairing is a collective effect: the bound state of two electrons arises only when a large number of other pairs are in the same state, and the binding energy of each pair increases with increasing number of pairs in this state. Therefore any change in the momentum of the pair, connected with its removal from the condensate, should be accompanied by a breaking up of the pair and consequently calls for the expenditure of appreciable energy. It is the latter circumstance which leads to the stability of the superconducting current. The binding energy Δ in each pair at zero temperature, when all the electrons near the Fermi surface are paired, is determined by the width of that electron energy region ϵ_0, in which there is an effective attracting interaction by the density of the electronic states over an energy interval near the Fermi surface N and by the average value of the energy of attraction of two electrons V:

$$\Delta_0 = 2\varepsilon_0 e^{-\frac{1}{NV}}. \qquad (1)$$

With increasing temperature T, the thermal motion breaks some of the pairs, so that their number in the condensate decreases, and at the same time, as noted above, $\Delta(T)$, the binding energy in each pair, also decreases. At some critical temperature T_c, the order of magnitude of which is close to Δ_0/k (k is Boltzmann's constant), $\Delta(T_c)$ vanishes, i.e., the superconducting state disappears.

The binding energy Δ determines also the critical value of the magnetic field H_c in which the superconducting state is destroyed. The point is that in the presence of a magnetic field a superconducting current is produced in the superconductor, the magnetic field of which cancels completely the external magnetic field inside the volume of the superconductor. This effect of forcing out the magnetic field from the superconductor (the so-called Meissner effect) is one of the most characteristic features of the superconductivity phenomenon. The energy of the compensating magnetic field per unit volume of the superconductor is $H^2/8\pi$, where H is the intensity of the external field. It is obvious that in a sufficiently strong field, when this energy becomes larger than the decrease of energy connected with the pairing on going from the normal state to the superconducting state, the existence of the superconducting phase will be thermodynamically unfavorable and this phase will become destroyed. The energy released upon formation of one pair is equal to 2Δ, and the electrons participating in pair production are for the most part in a narrow region of energies near the Fermi surface, with width on the order of Δ. The number of such electrons is of the order of $N\Delta$, and the total decrease in the energy on going to the superconducting state is of the order of $N\Delta^2$. Equating this energy to the energy of the critical magnetic field $H_c^2/8\pi$, we get

$$H_c \sim \sqrt{N}\Delta. \qquad (2)$$

The density of states near the Fermi surface N can hardly be much larger in any substances than in typical superconducting metals. Therefore, an increase in the critical field H_c can be attained in substances with large binding energy Δ, i.e., with a high critical temperature, if such substances can be found.

However, the problem of increasing the critical magnetic field in which superconductivity can still exist has found a somewhat unexpected solution in 1961, when it was observed that certain alloys (Nb_3Sn, NdZr) remain superconducting in magnetic fields up to 10^5 G.[4] This phenomenon was predicted by Abrikosov[5] on the basis of a semiphenomenological theory of superconductivity, proposed by Ginzburg and Landau.[6] He showed that in some alloys, in fields larger than H_c, there can occur the so-called mixed state, characterized by the fact that the magnetic field penetrates into a superconductor in the form of thin filaments which thread through the sample. Between these filaments, the sample remains superconducting, and it is naturally sufficient even for a small fraction of the volume of the sample to be superconducting in order that the resistance of the entire sample be equal to zero. On the other hand, the thermodynamically unfavorable situation for the superconducting state improves radically in this case, since the magnetic field is forced out of the superconductor only partially. By now alloys have been obtained which retain their superconducting properties in fields close to 200 kG. This discovery was of extreme importance for the use of the phenomenon of superconductivity in physics research, and in engineering, especially in the production of strong magnetic fields. Magnets based on superconducting solenoids are already extensively used.

The prospects of further utilization of superconductors in engineering would seem to be unlimited, were it not for the lamentable circumstance that in all the cases known to date the superconducting state is realized at very low, and therefore difficult to attain, temperatures. Thus the question of the future of superconductivity is connected primarily with the problem of increasing the critical temperatures, if this is at all possible.

The magnitude of the critical temperature T_c, which is connected with the energy of pair production Δ, is determined essentially, as can be seen from (1), by the attraction force V which leads to pairing of the electrons. In metals this attraction, according to an idea by Froehlich, is a result of interaction between the electrons and vibrations of the crystal lattice—phonons. Exchange of phonons between two electrons leads to their attraction to each other. This interaction is effective for electrons having energies in a narrow region near the Fermi surface, of width $\epsilon_0 \sim kT_D$, where T_D is the so-called Debye temperature, the order of magnitude of which is equal to the maximum energy of the phonons. The electron-phonon interaction in metals is itself quite weak, i.e., $NV \ll 1$ and there are theoretical indications that it cannot be strong in principle,[7] for when the interaction is strong the crystal lattice becomes unstable, i.e., it is rearranged into some other modification. Taking into account the fact that the Debye temperatures for typical metals are low, on the order of 100—200°K, we see from (1) that the critical temperatures under such conditions should be very small, much smaller than 100°K, as is indeed observed in reality. This raises the question of whether superconductivity cannot be produced as a result of some other stronger interaction, and whether one should not seek such a possibility in other substances, which do not belong to the customary well-investigated class of metals, or else in metals but under unusual conditions.

Recently, there have been published in this direction several theoretical papers, of which the greatest interest was evoked by the paper of Little[8] concerning the possibility of obtaining a superconducting state in long organic molecules. The attraction between the electrons, proposed in this paper, is of the Coulomb type and is therefore connected with energies on the order of 1 eV, corresponding to temperatures on the order of thousands of degrees, two orders of magnitude larger than the energies characteristic of the interaction connected with phonons. The schematic model considered by Little consists of a long one-dimensional chain of atoms, along which electrons move freely, i.e., there is metallic conductivity, and of side chains. With respect to the latter it is assumed that they are strongly polarizable. From the quantum mechanical point of view this means, that the molecules comprising the side chains have at least one low excited level (with excitation energy 1—2 eV) possessing a large dipole moment. In such a model the free electron of the central chain, moving near one of the side chains, polarizes the latter in such a way that a considerable positive charge is induced on the near end of the chain. This charge attracts other electrons from the central chain, as a result of which an effective attraction occurs of these electrons to the electron which has caused the initial polarization of the side chain. According to Little's estimates, the attraction can turn out to be larger than the direct Coulomb repulsion acting between the electrons in the chain, as a result of which the total interaction between them will have the character of attraction with an average neighboring-electron interaction energy $\approx 1.5—2$ eV. Examining further the system so obtained with the aid of the methods of the BCS theory, the author reaches the conclusion that a superconducting state should occur in it, and that the role of ϵ_0 in the formula for the effective region of the energies (1), in which the pairing interaction is effective, is played by the excitation energy of that level of the molecule—the side chain, which possesses a large dipole moment. This energy, as indicated above, is assumed to be of the order of 2 eV, which leads to a critical temperature close to 2000°K for the superconducting transition. This result, if correct, is of phenomenal interest, and it is therefore not surprising that Little's paper has attracted universal attention. Even if we disregard the possible technical applications, the presence of a superconducting state in organic molecules, together with its unique high degree of ordering, can, as indicated by the author, be of cardinal significance for many biological processes.

However, Little's paper has raised many objections, both of fundamental character and with respect to the conclusiveness of its deductions. The initial model itself is reasonable, since metallic conductivity in some organic molecules does seem to exist[10] and examples of molecules which have large polarizabilities and could play the role of the side chains are directly indicated in the article.[8] Moreover, an interesting supplementary result of this article is the statement that the transition into the superconducting state can occur even in the case when the molecule in the initial state does not have metallic conductivity, under the condition that the energy of pair production Δ exceeds the initial binding energy of the electrons in the central chain.

The main objection is connected, however, with the fact that Little's result contradicts the known theorem that in a one-dimensional system there can be no phase transition into an ordered state.[11] From the physical point of view this is connected with the fact that in a one-dimensional chain of atoms, each atom is connected with the others only through its nearest neighbors. Therefore an accidental sufficiently large fluctuation displacement in one point leads immediately to a loss of correlation between the atoms situated on the right and on the left of this point. In two- and three-dimensional cases this obviously is not the case, since the correlation connection between two given atoms which are far from each other is realized not only through the atoms lying on the line joining the two given atoms, but also through a very large number of other atoms, which lie on the side of this shortest path. Therefore for a complete loss of correlation between two remote atoms one would have to have an appreciable fluctuation over an entire plane between these two atoms, an event of very low probability. Formally this circumstance is expressed by the fact that the fluctuations in a one-dimensional system are so large, that they break up the ordered state.

Strictly speaking, this reasoning does not pertain directly to Little's model, since the latter is based on the assumption that the forces have a short-range character, and couple only the nearest neighbors. However, there is a widespread opinion that this result is of a more general character, and that phase transitions to an ordered phase in a one-dimensional chain are generally impossible. Ferrel[12] consider this question especially as applied to Little's model. He showed that the oscillations of the electron density, which take place in a three-dimensional superconductor, but play a minor role there, lead in the one-dimensional case to a destruction of the superconducting state even at arbitrarily low temperatures. In other words, even zero-order oscillations of the electronic density completely destroy the electron ordering characterizing the superconducting state. This result, to be sure, is also not absolutely convincing, since the character of the spectrum or even the very existence of electron-density oscillations in the Little model have not been reliably established. In addition, as indicated by the authors of [13], Ferrel's deduction pertains only to an infinite linear chain, whereas in a macromolecule, which consists of a large but finite number of links, the oscillations of the electron density can lead only to an appreciable decrease in the critical temperature. Assuming that the central chain in Little's model consists of 10^5 atoms, they found that the oscillations of the electron density decrease the pair binding energy Δ by approximately one order of magnitude.

In connection with the question of the possibility of a superconducting transition in a one-dimensional system, interest attaches also to the results of Lattinger,[14] who considered a very schematic example of a one-dimensional electron system, greatly differing from the model used by Little. He showed that an examination of this model by the methods of the BCS theory leads to the deduction that superconductivity exists in it. At the same time, this model admits of an exact solution, showing that the ground state of the system is not superconducting.

Objections of another kind are connected with the insufficiently correct analysis made by Little of the polarization interaction between electrons itself, an interaction which plays the main role in this theory. The estimates made by Little are based on perturbation theory, whereas the energy of interaction between an electron and the polarized side chain is much larger than the excitation energy of this level, which is connected with the occurrence of the dipole moment. It is quite clear that this circumstance should lead to a considerable shift of these levels and to a cardinal realignment of the side chain, and perhaps of the entire molecule as a whole. Therefore Little's calculations show that the molecular model proposed by him is apparently unstable and should rearrange itself spontaneously into some other state. It is not at all obvious here that this new state will be superconducting and not dielectric. From a somewhat different point of view, we can state, that the attraction used by Little is the result of the fact that his model leads to the occurrence of a negative dielectric constant. The stability of such a system, in which like charges (not only electrons in the central chain) attract each other, calls for a careful analysis.

Thus, Little's results can apparently not be regarded as proved with any degree of reliability. However, the ideas on which it is based, and the questions which arise in its analysis, are of exceeding interest, and in this probably lies the main value of this paper. In particular, one cannot exclude the possibility of the appearance of superconductivity as a result of a strong Coulomb attraction in systems which are not one-dimensional but have negative dielectric constants. Systems in which the dielectric is negative at least in some region of the frequency, are known and widespread, and can also be made synthetically. An interesting possibility for the occurrence of additional attraction between electrons was indicated by Vonsovskiĭ and Svirskiĭ.[15]

The main objection against the possibility of existence of superconductivity in Little's model, as indicated above, is connected with the one-dimensional nature of this model. Therefore particular interest attaches to the surface conductivity proposed somewhat earlier by Ginzburg and Kirzhnits,[16] i.e., superconductivity of a solid surface. The point is that on the surface of a crystal, as first shown by Tamm,[17] additional electronic states can arise which attenuate rapidly on going inside the crystal. The electrons situated at such levels can, however, move along the surface. The authors of [16] have shown that in the presence of attraction between the electrons there can arise in such a system also a superconducting state. Formally in such a two-dimensional model the fluctuations are also infinite. However, their divergence is very weak—logarithmic—and therefore for any body with finite dimensions it is quite inessential. It is interesting that superconductivity on surface levels could exist in principle also in the case when by its volume properties the substance is a dielectric.

In this case the interaction of the electrons can also be very specific. It can arise, for example, as a result of interaction between the electrons and the Rayleigh surface waves.

Ginzburg has also indicated that to intensify the attraction between the electrons one can use Little's mechanism, by introducing into the crystal highly polarizable impurity atoms, which in this model can lead to a sharp increase in the critical temperature.

Numerous possibilities are also afforded by an investigation of superconductivity in semiconductors, where the concentrations of the electrons, and also the character of their interaction with phonons and with one another can vary over a wide range. Unlike the preceding cases considered above and so far predicted purely theoretically, superconductivity in many semiconductors has already been observed experimentally. It was first considered theoretically by Gurevich, Larkin, and Firsov[18] and later by Cohen.[19] The first experimental results were obtained with the compound GeTe[20] and strontium titanate, $SrTiO_3$.[21] The latter case is of particular interest, and we shall stop to discuss it in more detail. The point is that strontium titanate is similar in many respects to barium titanate—a typical ferroelectric.[22] Although in strontium titanate itself the ferroelectric transition does not take place, it is very "close" to such a transition. Its dielectric constant at low temperatures reaches tremendous values ($\sim 10^3-10^4$). Therefore the Coulomb repulsion of the electrons from one another—the main factor preventing the appearance of superconductivity—is practically missing in this substance. From the microscopic point of view, the ferroelectric transition, according to present day notions, arises as a result of the fact that the frequency of one of the so-called optical vibrations of the lattice tends to zero. This means that the quasi-elastic force preventing the corresponding type of deformation tends to zero, and the crystal lattice becomes unstable, i.e., rearranged. But on the other hand, from the theory of dispersion of electromagnetic waves in crystals it is known that the frequencies of optical vibrations correspond to absorption lines in crystals, and some region of frequencies, higher than this characteristic frequency, is the region of anomalous dispersion, i.e., in this region the dielectric constant is negative. Therefore, if this region of frequencies makes an appreciable contribution to the interaction between the electrons, then the interaction will be attractive. In essence such an attraction mechanism is analogous to that considered by Little, but in his model the negative dielectric constant is due to the electronic polarizability, whereas here it is due to the polarizability of the ionic lattice. It is therefore essential that in strontium titanate at low temperature one of the frequencies of the optical vibrations turns out to be very low, i.e., the region of anomalous dispersion lies low. It is possible that this is precisely the explanation of the fact that, as reported by the authors of [21], superconductivity appears in $SrTiO_3$ even at very low electron concentrations, $\sim 10^{17}$.

In conclusion we emphasize once more that the presently gained understanding of the nature of the superconductivity phenomenon has made it possible to expand greatly the number of substances in which this phenomenon can exist, and has raised the hope that superconductors which differ greatly in their properties from ordinary metals can be obtained. The number of such possibilities, as we have already seen, is very large, and it is difficult to imagine that all will turn out to be fruitless. However, the main question, whether a superconductor can be obtained with sufficiently high critical temperature (at least on the order of 100°K), still remains open.

---

[1] Bardeen, Cooper, and Schrieffer, Phys. Rev. **108**, 1175, (1957).

[2] N. N. Bogolyubov, JETP **34**, 58 and 73 (1958), Soviet Phys. JETP **7**, 41 and 51 (1958).

[3] L. P. Gor'kov, JETP **34**, 735 (1958), Soviet Phys. JETP **7**, 505 (1958).

[4] Kunzler, Buchler, Hsu, and Wernick, Phys. Rev. Letts. **6**, 89 (1961); J. E. Kunzler, Rev. Mod. Phys. **33**, 501 (1961).

[5] A. A. Abrikosov, JETP **32**, 1442 (1957), Soviet Phys. JETP **5**, 1174 (1957).

[6] V. L. Ginzburg and L. D. Landau, JETP **20**, 1064 (1950).

[7] A. B. Migdal, JETP **34**, 1438 (1958), Soviet Phys. JETP **7**, 996 (1958).

[8] W. A. Little, Phys. Rev. **A134**, 1416 (1964).

[9] W. A. Little, Scientific American **212**(2), 21 (1965).

[10] K. G. Kepler, J. Chem. Phys. **39**, 3528 (1963).

[11] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), Nauka, 1964.

[12] R. A. Ferrel, Phys. Rev. Letts. **13**, 330 (1964).

[13] Dewamec, Lehman, and Wolfram, Phys. Rev. Letts. **13**, 749 (1964).

[14] J. M. Luttinger, Journ. Math. Phys. **4** (1963).

[15] S. V. Vonsovskiĭ and M. S. Svirskiĭ, JETP **47**, 1354 (1964), Soviet Phys. JETP **20**, 914 (1965).

[16] V. L. Ginzburg and D. A. Kirzhnits, JETP **46**, 397 (1964), Soviet Phys. JETP **19**, 269 (1964).

[17] I. E. Tamm, Physik. Z. Sowjetunion **1**, 733 (1932).

[18] Gurevich, Larkin, and Firsov, FTT **4**, 185 (1962), Soviet Phys. Solid State **4**, 131 (1962).

[19] M. L. Cohen, Revs. Modern Phys. **36**, 240 (1964).

[20] Hein, Gibson, Maselsky, Miller, and Hulm, Phys. Rev. Letts. **12**, 320 (1964).

[21] Schooley, Hosler, and Cohen, Phys. Rev. Letts. **12**, 474 (1964).

[22] B. M. Vul, DAN SSSR **4**, 139 (1945).

Translated by J. G. Adashko