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Superconductivity at Room Temperature

It has not yet been achieved, but theoretical studies suggest that it is possible to synthesize organic materials that, like certain metals at low temperatures, conduct electricity without resistance

by W. A. Little

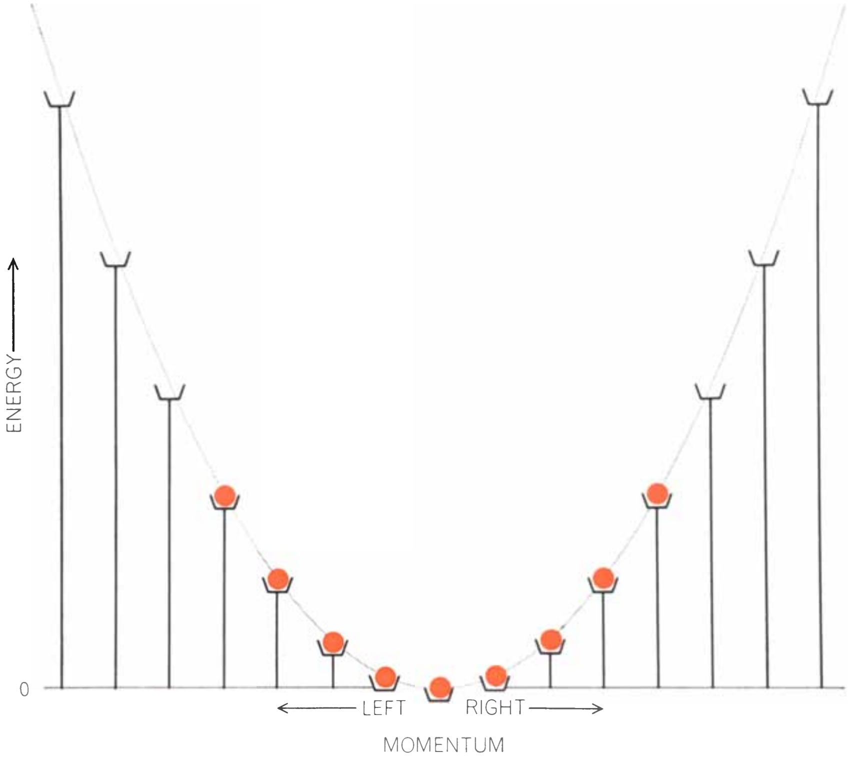
Several years ago an experiment was performed at the Massachusetts Institute of Technology that demonstrated the possibility of constructing a perpetual-motion machine. An electric current was induced to flow around a small ring of metal. The ring was then set aside. A year later the current was found to be still circulating in the material of the ring; what is more, it had not diminished by a measurable amount during this period! Although physicists object instinctively to the idea of perpetual motion and refer to such currents euphemistically as "persistent currents," they are obviously extremely persistent currents.

The secret of this extraordinary phenomenon is of course that the metal must be kept very cold—in fact, within a few degrees of absolute zero (−273 degrees centigrade). Below a characteristic "transition temperature" certain metals spontaneously enter what is known as the superconducting state, in which a stream of electrons can flow without encountering any resistance in the form of friction. Since friction is the cause of the failure of all mechanical perpetual-motion machines, its total absence in this case allows the initial current to persist indefinitely without any further input of energy, thereby violating the traditional doctrine of the impossibility of perpetual motion.

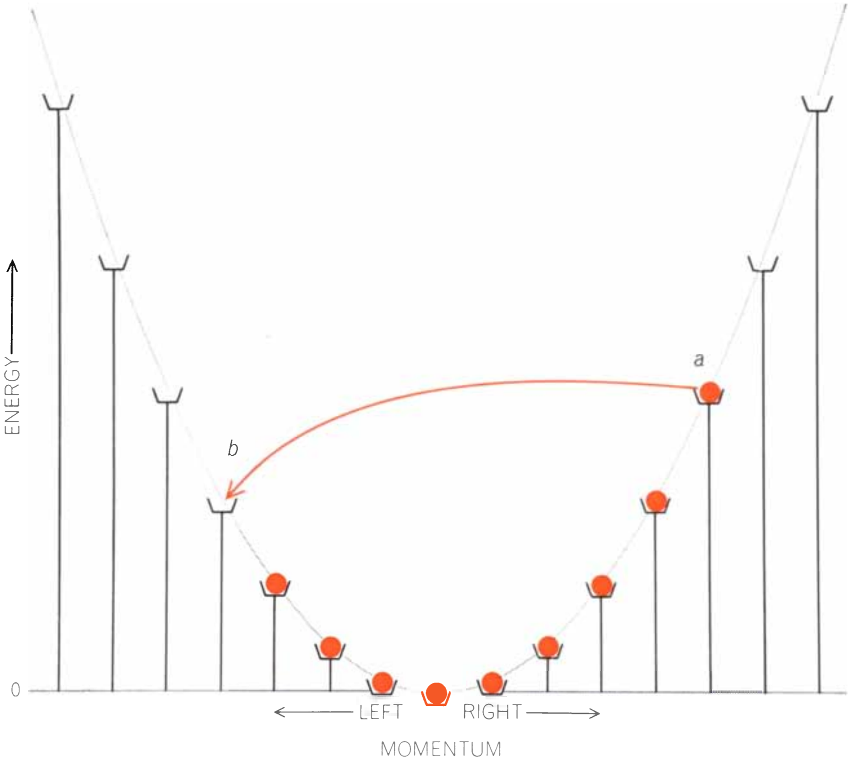
Actually the phenomenon of superconductivity is not at all rare. Since its discovery by the Dutch physicist Heike Kamerlingh Onnes more than 50 years ago many different metals and several hundred alloys composed of these metals have been identified as superconductors. As might well be expected, the technological potential of perpetual-motion machines based on the principle of superconductivity is virtually unlimited. Lossless power transmission, enormously powerful electromagnets, more efficient motors, amplifiers, particle accelerators and even computers are just a few of the serious proposals for the exploitation of superconductivity that have been put forward in the past 50 years. The main drawback of all these schemes involves the very low temperatures typically associated with superconductors; the complex and bulky refrigeration equipment required to maintain such metals in the superconducting state makes most of the proposed applications as yet economically unfeasible. The hope that the problem of refrigeration might someday be circumvented by the discovery of superconductors with higher transition temperatures has led to the investigation of a large number of alloy combinations of the known superconducting metals. Although many new superconducting alloys have been found, the outlook for high-temperature metallic superconductors is not bright. The highest transition temperature recorded so far is only 18.2 degrees Kelvin (degrees centigrade above absolute zero), which is still well below the temperature range accessible to simple refrigeration systems. Moreover, this work has yielded a considerable amount of statistical evidence that suggests that it is extremely unlikely that an alloy will ever be found with a transition temperature appreciably higher than about 20 degrees K.

What about the possibility of discovering some other substance—perhaps a nonmetallic one—that would be superconducting at higher temperatures? As a matter of fact it is an especially opportune time to investigate such a possibility in view of the great theoretical advances that have been made in recent years toward understanding the superconducting state. I have been particularly interested in the possibility of synthesizing an organic substance that would mimic the essential properties of a superconducting metal. My calculations have shown that certain organic molecules should be able to exist in the superconducting state at temperatures as high as room temperature (about 300 degrees K.) and perhaps even higher! In order to explain the line of reasoning that led to this prediction I must first discuss some of the theoretical ideas on which it is based.

An understanding of the true nature of superconductivity has proved to be one of the most difficult problems of theoretical physics in this century. A great stride forward was made in 1957 with the publication of a comprehensive microscopic theory by John Bardeen,



IN AN ORDINARY CONDUCTOR "free" electrons (*colored balls*) can roam in any way consistent with two restrictions: (1) only certain velocities, or energy states, are permitted and (2) only one electron at a time may be in any one of the allowed states. In the most stable energy arrangement all the lower energy states are filled by electrons and all the higher states are empty. No current flows because as many electrons move to left as to right.



CURRENT FLOWS in an ordinary conductor when all the allowed energy states are displaced in one direction (in this case to right); more electrons now travel to right than to left. Current decays when an electron moving rapidly to right (*a*) collides with some imperfection in the metal and is knocked backward (*colored arrow*); it can then occupy one of the vacant states corresponding to an electron moving somewhat less rapidly to left (*b*).

L. N. Cooper and J. R. Schrieffer, then at the University of Illinois. Their theory, now universally known as the BCS theory, has been successful not only in explaining practically all the experimental data that had accumulated over the past half century but also in predicting a number of new superconducting phenomena.

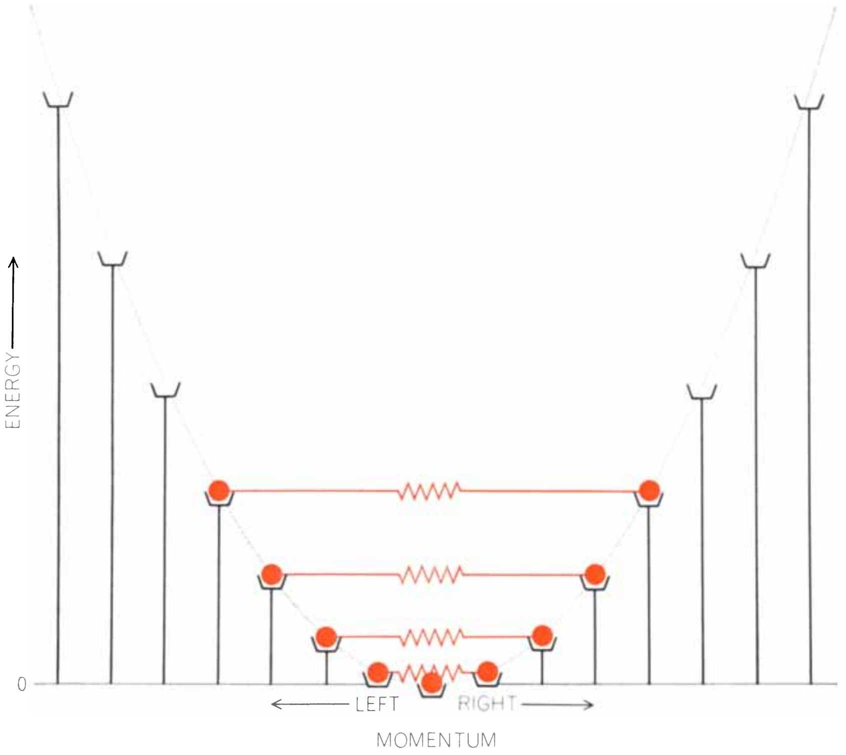
Like most scientific theories, the BCS theory did not appear out of the blue but was built on a firm theoretical foundation established by earlier investigators. In particular, some of the principal features of the BCS theory were outlined many years before by the theoretical physicist Fritz London, who developed a successful macroscopic theory of superconductivity as early as 1950. In so doing London showed an appreciation of the highly organized nature of the superconducting state and an intuitive grasp of several of the essential criteria a successful microscopic theory would have to fulfill. He recognized that each sample of a given superconductor has a unique character peculiar to itself and that in the superconducting state this character remains unaffected by heat or any other external influence. He was also impressed by the extraordinary stability of the superconducting state, a characteristic that figures prominently in the BCS theory.

It was perhaps through his perception of these rough features of a microscopic theory that London was led to suggest that the phenomenon of superconductivity might be significant in areas of science other than the specialized niche of low-temperature physics. He proposed that the existence of such a state in certain large organic molecules, such as proteins, might help to explain some of the unusual properties of these molecules. Unfortunately London died several years before the advent of the BCS theory and so was unable to develop or test his ideas further in its light. Although his other writings have influenced many workers in the field, little attention appears to have been paid to these suggestions in the decade after his death.

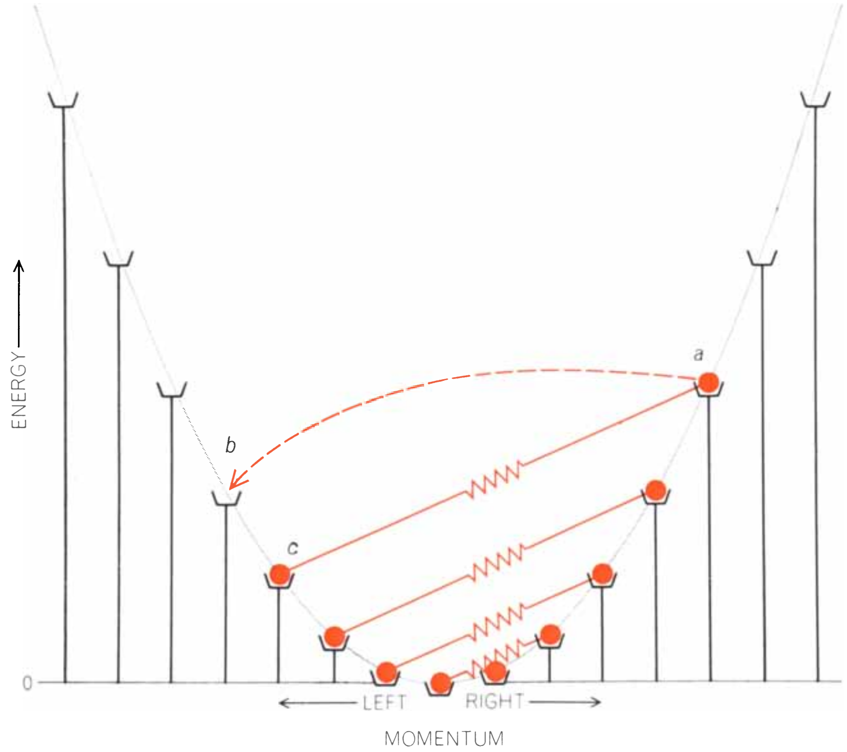
My own interest in the possibility of biological superconductivity was stimulated five years ago while I was working at Stanford University on a rather mundane problem of heat transfer to a metallic superconductor. Like London, I was struck by the great stability of the superconducting state; it occurred to me that if nature wanted to protect the information contained, say, in the genetic code of a species against the ravages of heat and other external influences, the principle of superconductivity would be well suited for the purpose. In view of nature's remarkable record of ingenuity in such matters, I thought it might be useful to determine if the superconducting state could occur in a large organic molecule built along the general lines of the genetic molecule deoxyribonucleic acid (DNA).

One molecule of this general type looked particularly promising in the light of the requirements of the BCS theory. Its structure, incidentally, is quite close to what London appears to have had in mind and suggests that he progressed further along this line of reasoning than his published work reveals. A detailed calculation of the superconducting properties of the hypothetical molecule showed that it should be superconducting at room temperature, and indeed even at temperatures well above room temperature. This bonus, although it is necessary if the phenomenon is to perform any biological function, was quite unexpected. Subsequent investigation has shown that there is a relatively straightforward explanation for this extraordinarily high transition temperature. Before describing how a superconducting current might be transmitted by such a molecule, however, it is necessary to review the mechanisms by which an electric current is transmitted in an ordinary conductor and in a metallic superconductor.

In an ordinary, nonsuperconducting metal each atom loses some of its outer, more loosely bound electrons, which are then free to roam throughout the rest of the metal. The motion of these "free" electrons is not entirely unrestricted: the requirements of quantum mechanics impose the condition that only certain energy states, or velocities, are permitted. Another restriction is imposed on the manner in which the electrons may be arranged in these states. This restriction arises out of the Pauli exclusion principle (named after its discoverer, Wolfgang Pauli), which says that only one electron at a time may be in any one of the allowed states. The electrons are free to arrange themselves in any way consistent with these two restraints. The most stable energy arrangement is one in which all the lower energy states are filled by electrons and all the higher states are empty. For every state that corresponds to an electron moving to the left there is another state of equal energy for an electron moving to the right. Thus in the lowest energy arrangement there are as many electrons moving to the left as to the



IN A SUPERCONDUCTOR an attractive interaction of "free" electrons binds them together in pairs (*see illustration on next page*). The paired electrons cannot move freely in the metal, since it turns out that in order to be bound to each other the momentum of the center of mass of each pair must be the same as that of the majority of the other pairs. When no current is flowing in the metal, the momentum of the center of mass for each pair is zero.



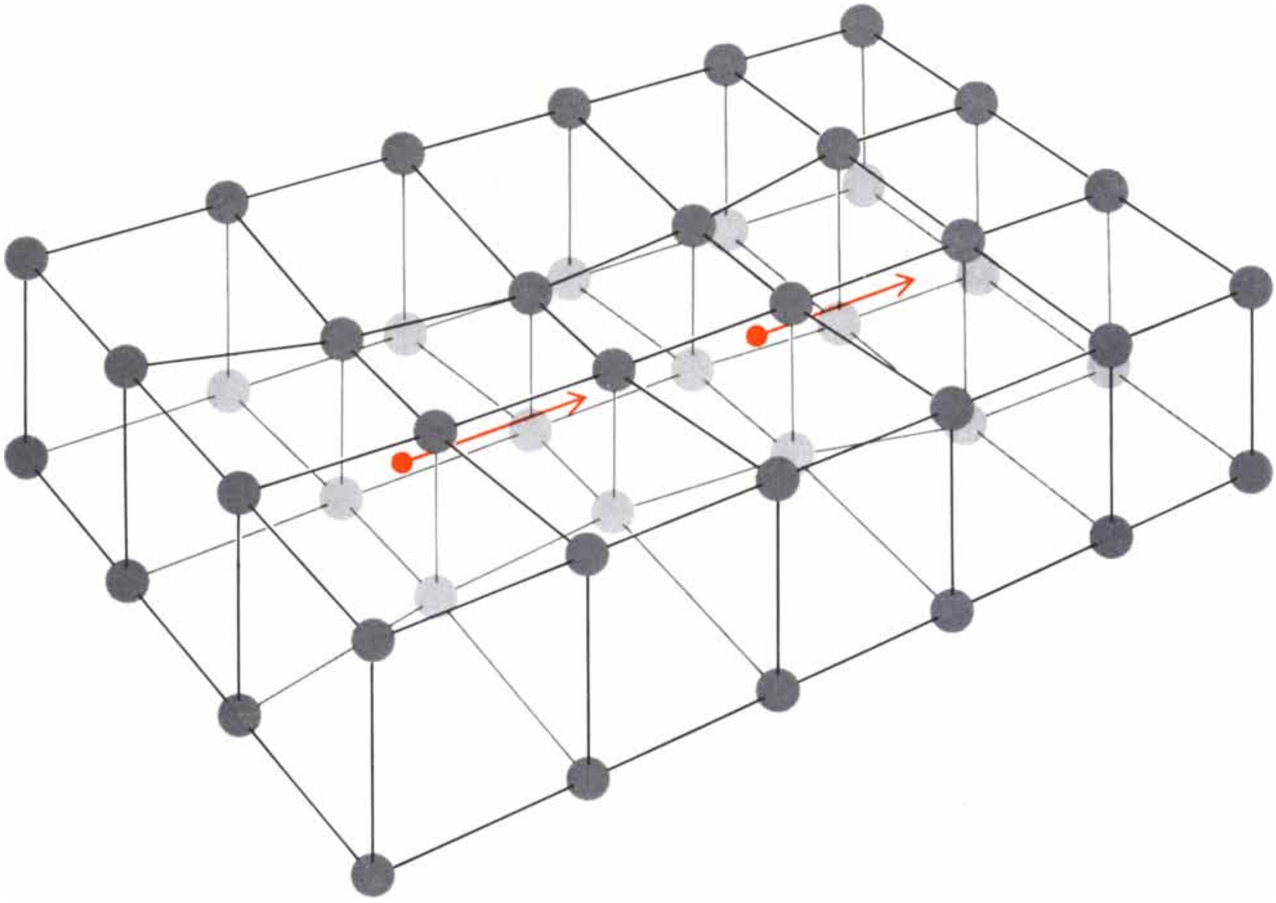
"PERSISTENT CURRENT" FLOWS in a superconductor when more electrons travel to the right than to the left. The current does not decay because if the electron at *a* were now to jump to *b*, both it and the electron at *c* would be left without mates. These two single electrons would not be able to pair up with each other because their center of mass would then have the wrong momentum. Consequently the electron pairs do not as a rule break up.

right and the entire distribution of electrons is symmetric [*see top illustration on page* 22]. In this equilibrium situation the average velocity of the electrons in any one direction is zero and consequently no current flows in the metal.

If a current is now induced in the metal, this is tantamount to saying that all the electrons are forced to move in one direction, say to the right, so to the random velocity of each electron must be added the component of this drift velocity. Electrons moving to the right would therefore have their velocities and consequently their energies increased, whereas electrons moving to the left would have their velocities and energies decreased. On the average this asymmetric distribution of the electrons would have a somewhat higher energy than the original symmetric distribution, owing to the additional kinetic energy of the drifting electrons [*see bottom illustration on page* 22]. The asymmetric distribution does not last long if left to itself in a normal metal, because if one of the electrons moving rapidly to the right should collide with some imperfection in the metal and be knocked backward, it could then occupy one of the vacant states corresponding to an electron moving less rapidly to the left. The states on the left have a somewhat lower energy because of their lower velocity and so would be preferred by the electron. In this way the asymmetric, current-carrying distribution would rapidly rearrange itself to form the lower-energy, symmetric distribution and the current would disappear.

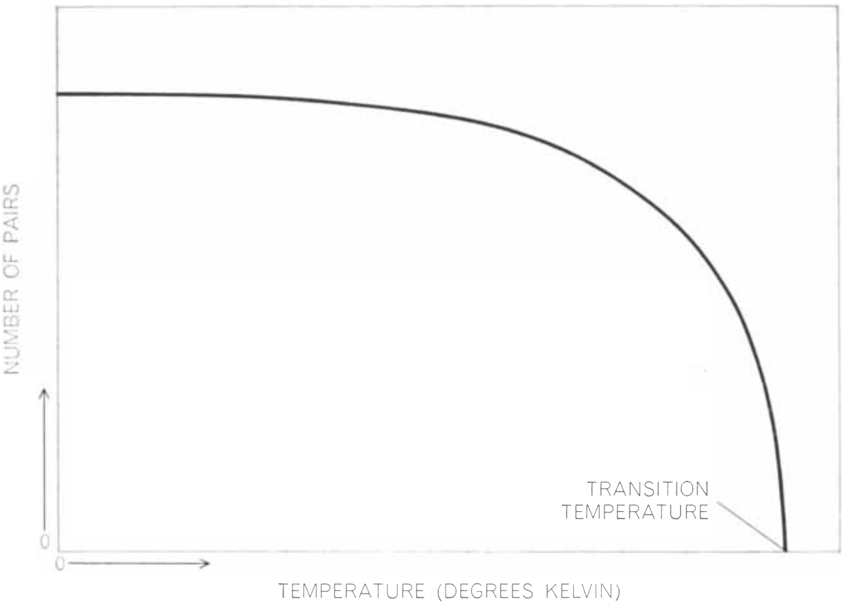
In a superconductor this deterioration of the asymmetric electron distribution does not occur, since there is an attractive interaction of electrons that binds them together in pairs. Each electron in a superconductor has a mate with which it is paired. The paired electrons cannot move freely in the metal; it turns out that in order for them to be bound to each other the momentum of the center of mass of each pair must be the same as that of the majority of other pairs [*see top illustration on preceding page*]. Now, if the electron moving rapidly to the right collides with an imperfection and is knocked into a state corresponding to the electron moving less rapidly to the left, this electron will have no mate and its old mate will similarly be left single. These two single electrons would not be able to pair up with each other because their center of mass would then have the wrong momentum. Consequently if the cost in energy for breaking up the pair is not offset by a sizable reduction in kinetic energy resulting from the collision, the pair will not break up. The asymmetric distribution will remain and the current will persist [*see bottom illustration on preceding page*]. According to the BCS theory, this is the reason why the current in a superconducting ring can persist indefinitely.

Of course the foregoing argument only partly explains why certain substances suddenly become superconduct-



ELECTRON PAIR is formed in a superconducting metal by the attractive mechanism depicted here. As a negatively charged electron moves through a somewhat elastic lattice of positively charged ions it attracts the ions, causing the lattice to "pucker up" in its vicinity. A second electron is naturally attracted to the excess positive charge created by the higher density of ions in this puckered region of the lattice and is thereby indirectly attracted to the first electron. Since the ions move more slowly than the electrons, the puckered region trails a considerable distance behind the first electron and the second electron can follow at this safe distance.

ing at a specific temperature. Why, for example, should the electrons attract one another when we know that electrons have like charges and thus should repel one another instead? Why should the centers of mass of the pairs be correlated in any way with one another? These are subtler questions that cannot be easily answered straightforwardly, but they can be approached in a somewhat more general way with the aid of an analogy.



CATASTROPHIC BREAKUP of electron pairs in a superconductor occurs as the superconducting transition temperature is approached from a lower temperature. Although the pairs begin to break up slowly, the unattached electrons resulting from the just broken pairs interfere with the remaining pairs, causing them to break up and accelerating the entire breakup process rapidly. No electron pairs can exist above the transition temperature.

Imagine a thin elastic membrane stretched over the head of a drum. On top of the drumhead we put two marbles. If we tilt the drum gently from side to side, how do the marbles move? Obviously the weight of each marble depresses the elastic membrane so that when the two marbles come close to each other, one rolls down into the depression made by the other; to all appearances the two are attracted to each other. If we now tilt the drum to one side, the marbles move about on the surface together as a pair—each moving in the depression made by the other. If the tilting is done more vigorously, however, the agitation can eventually become so violent that the two marbles separate and begin to move about more or less independently of each other.

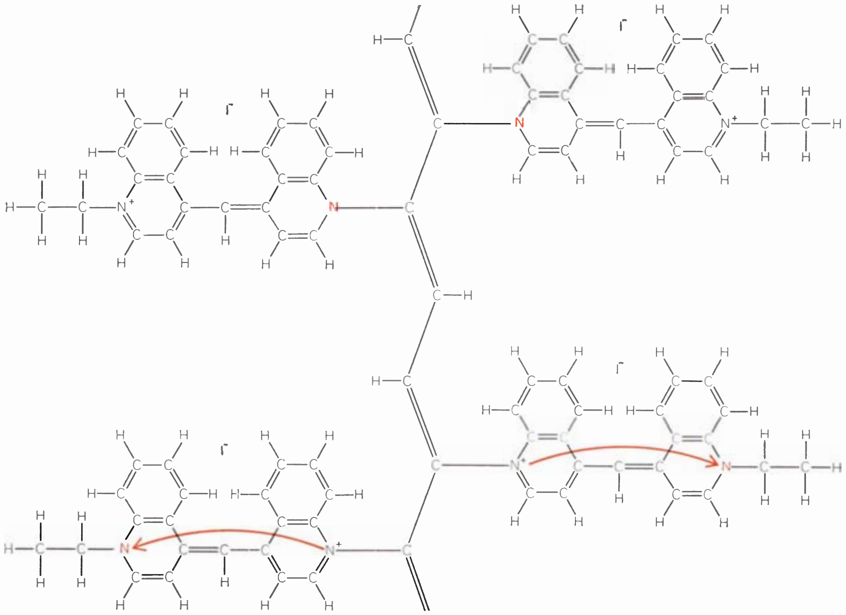
What has this to do with superconductivity? In a metal the positively charged ions, which remain after the atoms are shorn of their outer electrons, are not rigidly fixed at their sites in the crystal lattice but are able to move elastically about these sites. If one of the "free" electrons moves among the positively charged ions, the ions will be attracted to the negatively charged electron as it passes. This distorts the lattice and causes it to "pucker up" in the vicinity of the electron [*see illustration on opposite page*]. A second electron is naturally attracted to the excess positive charge created by the higher density of ions in the puckered region of the lattice and is thereby indirectly attracted to the first electron. The situation is closely analogous to the second marble being attracted to the first by the depression in the elastic drumhead; the puckered lattice and the depression in the drumhead play equivalent roles in the two cases.

In a metal the attractive force produced by this mechanism can be such that two electrons can become firmly bound to each other. The binding will only occur, however, if the temperature is sufficiently low, since at higher temperatures the thermal agitation of the electrons will tend to break up the electron pairs in much the same way as the violent tilting of the drumhead can separate a pair of marbles.

It is useful to look more closely at the details of this process. Suppose the first electron is moving down a corridor of positive ions. The range of the electron-ion interaction is quite short; accordingly the electron will give each ion a short, sharp pull as it passes. This impulse starts the ion moving toward the position of the electron, but since the ions move rather more slowly than the electrons, the electron responsible for the motion will be a considerable distance away by the time the ion has moved as far as it can against the elastic restraints of its neighbors. As a result the puckered region of the lattice trails some distance behind the first electron, and the second electron can follow at this safe distance.

Between the two electrons there is enough space for many other electrons to move. What effect do these electrons have on our theoretical model? If their motion is quite chaotic and completely uncorrelated with that of the first electron, they will interfere seriously with the orderly procedure described above. They too would pucker the lattice in their neighborhood and stretch it elsewhere. If the lattice is stretched where it should be puckered and puckered where it should be stretched by this host of uncorrelated electrons, there will be little left of the puckered region produced by the first electron for the second electron to follow. The scent, so to speak, will rapidly be lost and the pair broken. On the other hand, if the motion of all the other electrons is correlated so that each electron dodges the others and maneuvers in precisely the right way, then each electron can enjoy fully the attraction of its mate and a large number of pairs can coexist with one another.

It turns out that the prerequisite for all the pairs being in harmony with one another in this way is that their centers of mass must all have the same momentum. At low enough temperatures this highly coordinated state of the electrons occurs spontaneously, because the gain in the energy of each pair more than offsets the disadvantages involved in the loss of freedom of the individuals. If the temperature is raised, however, the thermal agitation eventually becomes sufficient for some pairs to break up. The resulting uncorrelated, unattached electrons now become a disruptive nuisance to the electron couples. They interfere with the attractive mechanism and thereby weaken the binding force of the remaining pairs. This in turn causes more pairs to break up. As the temperature is raised still further, the breakup of pairs becomes catastrophic; above a well-defined temperature no pairs can



HYPOTHETICAL SUPERCONDUCTING MOLECULE is built around a "spine" of carbon atoms connected by alternating single and double bonds. Periodically along the spine a side chain consisting of the common dye diethyl-cyanine iodide extends outward. These side-chain molecules are highly polarizable; that is, an electron can move freely from a nitrogen site close to one end of the molecule to another nitrogen site close to the other end. A colored *N* designates the nitrogen atom that contains the resonating electron in the two possible conditions of polarization. Electrons can also move freely along the spine itself.

exist at all [*see illustration on preceding page*].

The superconducting state is obviously distinguished by a high degree of internal organization. It can exist only below the temperature at which the breakup of the electron pairs becomes catastrophic. The temperature at which this occurs is the superconducting transition temperature.

It is not difficult to deduce from the preceding argument the criteria that would have to be fulfilled for an organic molecule to exist in the superconducting state. The molecule would have to be provided with roughly the same essential ingredients that are found in the superconducting metal. A medium is required in which the electrons can move, and a somewhat elastic charged structure is needed to play the role of the ion lattice.

Imagine a long molecule built of a chain of carbon atoms that form what I shall call a "spine." On each side of the spine molecular side chains extend outward rather like the ribs of the human rib cage. As I have mentioned, this structure was suggested by the genetic molecule DNA, the carbon atoms of the spine replacing the sugar-phosphate sequence of DNA and the side chains replacing the bases. If the carbon chain is conjugated, that is, if it has alternating single and double bonds along the chain, it will behave much like a metal, with the electrons moving freely from one end of the spine to the other. For the side chains a molecule such as diethyl-cyanine iodide, a dye commonly used to sensitize photographic emulsions, would appear to be suitable. This is a highly polarizable molecule in which an electron can move freely from a site close to one end of the molecule to a site close to the other end [*see illustration above*]. In an electric field the charge readily shifts from one end to the other and the molecule thus becomes polarized in the field.

Consider now an electron moving along the spine of such a molecule. As the electron passes each side chain its electric field polarizes the side-chain molecule and induces a positive charge at the end nearer the spine. Because of the high speed of the electron in the spine the region of maximum induced positive charge in the side chains trails some distance behind this electron. A second electron is attracted to the region of positive charge and is thereby indirectly attracted to the first electron. This is exactly the same argument we used in describing the superconducting metal and naturally leads to the same phenomenon. When the detailed calculations of the BCS theory are carried out for the organic molecule, however, one finds that the theoretical transition temperature is enormously high—typically around 2,000 degrees K.! This figure is of course much higher than that of any known superconductor and, if it is to be trusted, must be based on some good physical reason. It turns out that it is.

Let us return to the description of the attractive mechanism between free electrons in a conventional superconductor. As an electron passes the ion it gives it a short, sharp impulse and then is gone. The impulse transfers to each ion a certain amount of kinetic energy, which starts the ion moving. The ion continues to move until the elastic restraints of its neighbors stop it. At this point the kinetic energy of the ion is completely converted into potential energy. It is elementary to show that the maximum distance the ion can be displaced is inversely proportional to the square root of the mass of the ion. If the ions are heavy, the displacement is small; if the ions are light, the displacement is large. The larger the displacement is, the larger is the distortion of the lattice and consequently the larger the magnitude of the excess positive charge in the puckered region. Since the second electron is attracted to this region and is thereby bound to the first electron, we should expect the strength of this binding also to depend on the mass of the ions of the lattice. By the same token, the transition temperature, which is determined by the binding energy, should be inversely proportional to the square root of the ionic mass. This is in fact the case. Experiments carried out on samples composed of different isotopes of a given superconducting element have shown that in most cases the transition temperature does depend on the isotopic mass in just this way. This correspondence is known as the isotope effect; its discovery early in 1950 provided an important clue to the understanding of superconductivity.

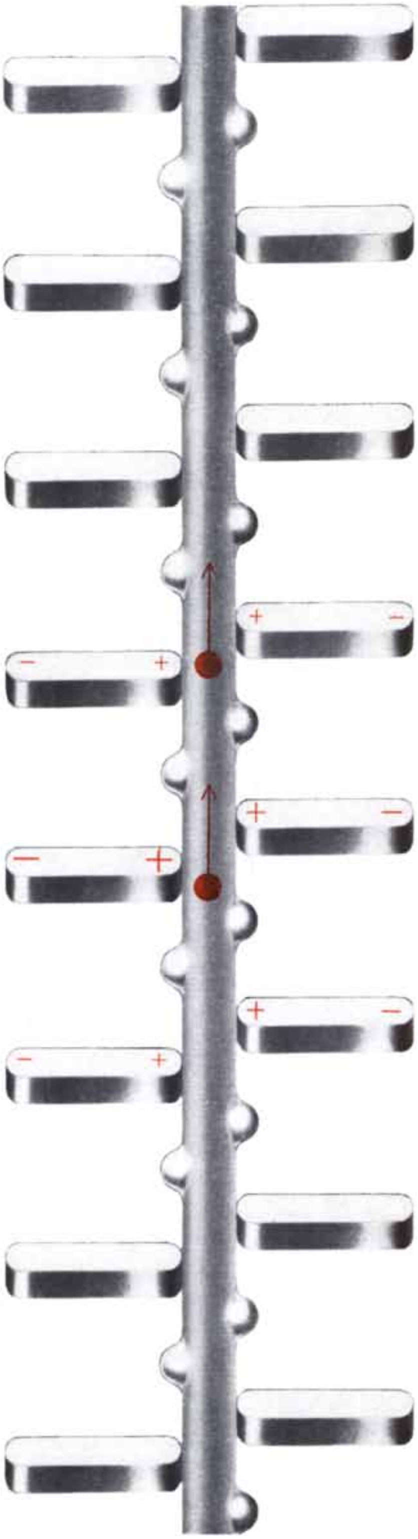
The isotope effect also plays an important role in explaining the tremendously high transition temperatures of our hypothetical superconducting molecules. In these molecules we have replaced the ions of a metal with polarizable side-chain molecules. Under the influence of the electric field of the electron in the spine, the side chains themselves do not move, but a single electron *within* each side chain does move and this produces the polarization. Instead of being an ion, as in the case of the metal, the moving entity is now an electron with a mass only a hundred-thousandth of a typical ionic mass. According to the requirements of the isotope effect, the transition temperature should be on the order of the square root of 100,000 times larger than that for the average metallic superconductor (that is, 316 times 6 degrees K., or roughly 2,000 degrees K.). This figure is almost exactly the same as the one arrived at by our earlier, independent calculation. Obviously the high transition temperature is a result of an attractive interaction that is mediated by an extremely light particle—an electron rather than an ion.

In order for the motion of the ions and the electrons to be in any way analogous it also seems necessary from the theoretical point of view for the electrons to move in a chainlike spine. This is probably the reason why no metal falls into this category of superconductor and why no high-temperature superconductors have been found as yet.

Once we accept the possibility that superconductivity could occur at room temperature in a molecule of this type, a whole new world of science and technology opens before us. Indeed, speculation as to the uses to which such a superconductor could be put reads more like science fiction than any serious scientific proposal. Of course, the chemical problems and eventually, perhaps, the technological problems in the synthesis and production of such materials are immense. After all, we are asking for the synthesis of a molecule to precise, almost engineering specifications, a task that has never before been demanded of organic chemistry. Nevertheless, many chemists feel that this can be done and that given a reasonable amount of time some such molecules undoubtedly will be synthesized. It is to be hoped that when that day comes, our extension of the BCS theory will pass the acid test.

Suppose for the sake of argument we are presented with a plastic material that is superconducting at room temperature. How could we use it? The obvious applications mentioned at the beginning of this article immediately spring to mind, but even more exciting prospects arise from a superconductor's diamagnetism, or impermeability to a magnetic field. Because of the highly coordinated motion of the electrons a magnetic field cannot penetrate the interior of a superconductor. This property can be demonstrated by placing a bar magnet above a sheet of superconducting metal. The magnet floats freely above the sheet, supported entirely by its magnetic field. The field is unable to penetrate the superconductor and so provides a cushion on which the magnet rests. It is easy to imagine hovercraft of the future utilizing this principle to carry passengers and cargo above roadways of superconducting sheet, moving like flying carpets without friction and without material wear or tear. We can even imagine riding on magnetic skis down superconducting slopes and ski jumps—many fantastic things would become possible.

Have we anything of interest to expect from the biological point of view? If it proves possible to synthesize an artificial superconducting molecule, it seems to me that nature would surely have discovered the fact ages ago. Thus we would expect to find molecules of this type playing some unique role in nature, but we can only speculate as to what this role may be. The highly coordinated motion of the electrons within our hypothetical molecule couples the different parts of the molecule together in an extremely intimate way. As a result reactions in one part of the molecule can influence the reactivity of other groups in any part of the entire molecule, however remote. Could this long-range influence explain some of the intricacies of biological molecules? In our molecule the particular value of the common momentum of the centers of mass of the pairs has a very interesting property: it endows the molecule with a unique, preferred three-dimensional folded structure. Associated with each possible value of this momentum there is a unique, intricate shape for the molecule as a whole. Could these structural requirements have anything to do with the large-scale organization of living systems? We cannot be sure at this stage, but the implications of the idea are intriguing. According to our model there is a highly specific attraction between two molecules whose electron pairs have the same momentum but no such attraction between molecules with different momenta for the pairs. Has this anything to do with the extraordinary selectivity and specificity of certain biochemical reactions? Again we do not know, but the idea is suggestive. When one reflects on all these possibilities, the age-old dream of the perpetual motion of mere mechanical devices appears drab and colorless in comparison.



ELECTRON PAIRS are conducted along the spine of a hypothetical superconducting molecule by an attractive mechanism similar to that in a superconducting metal. As an electron passes each side chain its electric field polarizes the side-chain molecule and induces a positive charge at the end nearer the spine. A second electron is attracted to this region of positive charge and is thereby indirectly attracted to the first electron.