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Superconductivity

Two physicists, P. W. Anderson and B. T. Matthias, approach this important phenomenon from different points of view.

I. A Theoretical Approach

The conditions under which this article is being written are unusual. With the other side of the coin being ably presented by my colleague, B. T. Matthias, I will not have to qualify my statements or judiciously distribute credits and concessions, but can flatly state my opinions, for what they are worth. I suspect that I will be proved wrong in some measure; I hope the fact of my stating these opinions will stimulate other physicists to try to prove me wrong.

The fact is that the theory of superconductivity—to which Bardeen, Cooper, and Schrieffer (*1*) made the most important contribution, which was announced almost exactly 7 years ago (*2*)—has had unprecedented and amazing success in changing this phenomenon from one of the most obscure to one of the simplest and best understood of all the phenomena relating to the properties of matter.

Since this statement appears to contradict what Matthias says in the discussion that follows, and since much—not all—of the disagreement is a matter of semantics and of philosophy, I would like to discuss briefly some of the elementary facts about the nature of scientific theories and of scientific proof which we all think we understand but which, on a little deeper examination, we find are not precisely the way we imagined.

Nature of Scientific Theories

The scientific method advances—we all learned—by induction from experimental facts. The scientist experiments, evolves hypotheses, tests them against more experiment, applies Ockham's razor, and has learned something. That is of course understood, but I suspect many physicists do not think carefully about how the process really goes in a mature science such as the physics of matter. The experiments against which a theory must be tested are not merely those under direct consideration but the ones carried out over the past 50 to 100 years which have given us all-but-absolute, unshakable confidence in a certain structure of fundamental laws: quantum mechanics, relativity, statistical mechanics, the consequences of symmetry, the regular nature of crystals, the band theory, and so on. I could give you tens of examples of the following general rule: a theory which contradicts some of these accepted principles and agrees with experiment is usually wrong; one which is consistent with them but disagrees with experiment is often not wrong, for we often find that experimental results change, and then the results fit the theory.

Here is a simple example: some time ago Heisenberg and Koppe proposed a theory of superconductivity (*3*) which predicted correctly that no transition temperature would be higher than 19°K. It was not a bad theory at the time, but Koppe is the first to agree now that it really was not a very reasonable approach, and that the theory is in disagreement with several now well known principles of solid-state theory. I suspect he would also agree that a theory which was consistent with all the a priori known facts of solid-state theory but did not predict a definite value for the upper limit on the transition temperature T_c would certainly have been more valid than his.

Thus the first—many would say the main—task of a solid-state theorist confronted with a phenomenon (like superconductivity, ferromagnetism, or—an example I shall continue to use—semiconductivity) is to find a way in which the special behavior of matter under consideration can be accounted for in a way that is merely *consistent* with all the things we already know about solids and may already know about the phenomenon. Actually, this is usually, for practical purposes, the end of the story: there is usually only one sensible way to account for the facts about the phenomenon consistently with known principles of physics.

Band Theory of Semiconductivity

Let me take an example which may be familiar to many readers: semiconductivity. The band theory of semiconductivity is mostly attributable to the work of Wilson (*4*) in 1932, and by 1940 or so, Mott and Gurney could say flatly (*5*), "The accepted theory of semiconductors is due to Wilson." If we examine the experimental data up to that time we find that this acceptance rested on little else than the plausibility of the theory; no quantitative, and very

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little qualitative, data existed until after World War II. The theory had certainly predicted nothing quantitatively. The thermoelectric effect, the Hall effect, and the conductivity were found to behave in a manner made plausible by Wilson's theory, and that was about it.

From 1945 to 1950, such detailed *qualitative* achievements as Pearson and Bardeen's wide-ranging experimental study of silicon (*6*) and the various experiments associated with transistor action verified the theory in qualitative detail; but still the quantitative basis of the phenomena was practically untouched: the band structure in all its detail, on which all of the energetics and much of the transport theory depended, and the precise coupling constants which controlled the scattering and thus controlled all transport phenomena. Yet one could hardly find anyone aware of the evidence who would question the basic rightness of the theory. In the final stage of the advances of the past decade or so, two developments typical of an absolutely mature (perhaps even a dying) science have occurred: the correlation of detailed experiment with detailed quantum chemical calculations of band structures, and the beginning of the development of a "rigorous" mathematical theory. (I use quotes because of course the "proofs" in such theories always depend on the intrinsically unprovable convergence of the extraordinarily complicated infinite series which result from perturbation theory as well as on major—and unstated—idealizations of the physical world, as when all crystalline imperfections are neglected.)

Semiconductivity theory is one of the few instances of a theory in which the quantitative aspect—the third stage—has been handled with a reasonable degree of completeness. I have an idea that even though superconductivity theory is so young, it is already entering its third stage—the stage of quantitative energy and transition-temperature calculations, the stage in which there are some pretensions to mathematical rigor.

The BCS Theory

From the very first the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity was remarkably successful in its qualitative and semiquantitative aspects. Perhaps this is as good a time as any to give a brief account of it. The theory stems from an idea of Leon Cooper's, published in late 1956 (*7*). He showed that if the electrons in a metal have an attractive interaction, the commonly accepted state, the so-called "Fermi sea," is not stable, for the reason that two electrons taken from the top of the Fermi sea—the so-called Fermi level—can then always form a bound-pair state, thereby lowering their energy relative to the Fermi level. Since any two electrons may do this, a macroscopic number of bound pairs may form, changing the state qualitatively.

A wave function for a bound pair of electrons may be written

$$\psi(r_1,r_2) = \phi(r_1 - r_2)\exp[iK \cdot (r_1 + r_2)]$$

where $\hbar K$ is the momentum of the center of mass and ϕ is the wave function of the bound pair. Fourier analysis gives

$$\phi(r_1 - r_2) = \sum_k \exp[ik \cdot r_1 - ik \cdot r_2] f(k).$$

Thus, ψ is a superposition of states in which the two electrons simultaneously occupy one-electron states with momenta $(-k + K)$ and $(k + K)$. The most reasonable, and in fact the correct, value of K is zero, hence this is the origin of the famous $k, -k$ pairing. It turns out, also, that the spins of the two electrons are opposite too: the pairs bind in a state whose spin, momentum, and angular momentum are zero.

It was the momentum condition which gave Bardeen, Cooper, and Schrieffer the clue to go farther. They picked out that part of the interaction in which bound pairs of fixed total momentum zero occurred and found that a mathematically tractable—in fact exact—theory of that part could be developed. The resulting theory can be described in physical terms by saying that the entire gas of free electrons condenses into a single state of bound pairs. (One recognizes at once that the occupied electron states deep in the Fermi sea are almost always occupied in $k, -k$ pairs even in the normal state, so that they actually do not change much in this condensation; the properties of both normal and superconducting metals are entirely determined by states only near the Fermi level. This is the main way in which the exclusion principle enters the problem.) To unbind a pair and create an unbound particle or "normal quasi-particle" costs the binding energy of the pair and thus gives rise to the famous "energy gap." But this extra particle is neither a hole nor an electron, because it keeps emitting and absorbing bound pairs into the zero-momentum state, changing from electron to hole when it emits, and vice versa. This is the brilliant and rather tricky new feature of this theory which makes it so successful: the essential discarding, in a sense, of the detailed and exact conservation of particle number.

Electron pairs may be added to or subtracted from the sea of bound pairs; when one metal is in contact with another metal, this is the process which determines the Fermi level. Because these electron pairs occupy the whole metal—their momentum is fixed at zero, usually—they may be added or subtracted anywhere, and the result is infinite conductivity—the superflow. Since the pair state is occupied by a macroscopic number of electrons all acting in concert, any attempt to change the momentum of a single pair will effectively unbind that pair, whereas a change in the momentum of the whole electron gas is a macroscopic process involving macroscopic energy barriers; the "rigidity" of the bound pairs leads to quantization of flux.

The analogy with rigidity of a solid is close and enlightening. Though a bar of steel is full of vacancies, phonons, and other defects, we still are not surprised to find that it transmits a force from one end to the other without loss. That force is transmitted by the lattice of condensed atoms as a whole, the random motions of individual atoms being too small to disturb it. Similarly, supercurrents are transmitted by the condensed electronic state as a whole.

Schafroth, Blatt, Butler Theory

This picture of the superconducting state is rather similar to a proposal made by Schafroth, Blatt, and Butler (*8*), before the BCS theory was proposed: that superconductivity is caused by a Bose condensation of bound pairs of electrons. Just as helium atoms are a bound state of six fermions but obey Bose statistics, they argued, pairs of electrons can act like bosons and condense into the lowest energy state, $K = 0$, as it is suspected helium atoms do in the superfluid. Several years later, in fact, Blatt and others completed the proof that all the results predicted by

the BCS theory can be made, by dint of great effort, to follow from such a picture. I think it is fair to say that this equivalence, and the importance of the ideas of Blatt, Butler, and Schafroth, have been overlooked to some extent.

Why do I then give the lion's share of credit to Bardeen, Cooper, and Schrieffer? Why isn't the BCS theory just a highly convenient working approximation within the Blatt-Butler-Schafroth theory? There are three reasons.

1) A very practical one: it is not obvious that, without the hints of the BCS theory, the mathematical results which correspond so closely to experiment would ever have been obtainable by Blatt and his associates from their very difficult and complicated theory. In any case, Bardeen, Cooper, and Schrieffer were certainly the first, by some years, to give any mathematical results for comparison with experimental results; in the event, the agreement was amazingly good. Before the BCS theory was advanced, electron pairs were merely a plausible hypothesis among other hypotheses.

2) A difference in emphasis which is practically one of principle: according to the BCS theory the thermal breakdown of superconductivity is dominated by the breakup of pairs—the energy gap—and not by their evaporating *as pairs* from the condensate of pairs for which $K = 0$. In metals, pairs in which $K \neq 0$ practically do not exist, because of electromagnetic interaction effects, in contrast to the situation for ^{4}He (*9*). This physical fact was not recognized in the Blatt-Butler-Schafroth theory until much later.

3) The most important difference, one of principle: actually the BCS theory is a better and more useful one than the corresponding theories pertaining to helium II that existed at the time Blatt *et al.* constructed their theory, even better than theories held until very recently, when the usefulness of the BCS type of theory began to be recognized (*10*). A theory of the BCS type, to be workable, had perforce to introduce breakdown of the assumption of exact conservation of particle number, which now turns out to be by far the best way of describing superfluidity as well as superconductivity. Let me make this important point another way.

Photons are bosons. In dealing with microscopic quantum processes we find it useful to deal with photons as particles, and to work with states which we describe as containing a fixed small *number* of photons. In such a state the electric field fluctuates—particularly in phase, and phase and photon number are conjugate variables.

In dealing with "classical"—wavelike—electromagnetic phenomena on a macroscopic scale, on the other hand, we are familiar with the procedure of treating directly with the electric field as a fixed "*c*-number." We know, then, that the number of photons must be uncertain, but that disturbs no one. For macroscopic coherence and interference phenomena it is far better to use eigenstates of the field operator E, not the number operator n. We can of course make transformations from one to the other, because the wave and particle pictures are dual and equivalent; but for classical interference phenomena the description in terms of waves—fields—is far better.

Bardeen, Cooper, and Schrieffer had perforce—though they tried very hard not to—to use states emphasizing the *field* of electron pairs, rather than the *number*, in this same way. Basically, the phenomenon of superfluidity *is* best described in terms of the electron *field*. This choice of coherent states (*11*) in the particle field led directly to the gauge-invariance difficulties which troubled some critics of the theory in the first year or so after it was proposed, but by about 1959 that problem had been cleared up (*9*). Now, on the other hand, it is clear that in such phenomena as the Josephson tunneling effect or flux quantization the phase of the electron wave field has real physical meaning (*12*), and thus a strict interpretation of the requirements of number conservation and gauge invariance, such as was insisted upon by the Australian school, cannot be maintained.

Shortly after the BCS theory was proposed, a number of other theories based on similar ideas appeared. All of these in the end turned out to be essentially equivalent to BCS, although for a computation of a particular kind, any of the four (to my knowledge) others [Bogolyubov and Valatin's quasiparticles (*13*); Koppe (*14*), Suhl, and Anderson's (*9*) pseudospin approach; Nambu's spinor self-energy (*15*); and Gor'kov's Green-function theory (*16*)] might be superior. As I said, Blatt's theory is also equivalent to BCS, but I know of no applications in which it is preferable, and the correct version appeared only much later.

Predictions and Experiment

Let us return to the mainstream of the discussion. The BCS theory led immediately to a number of predictions about the properties of superconductors, which depended on a small number of semiempirical parameters: the transition temperature or the energy gap at $T = 0$; the density of states; the velocity at the Fermi surface. The properties considered fell into two classes, and in both of them the predictions were, on the whole, in excellent agreement with experiment. In the first class were phenomena which depended primarily on the existence of an energy gap and its temperature dependence: the specific heat, the Meissner effect, optical absorption. In the second were a number of phenomena which depended critically on the "coherence factors" of the theory. It was fashionable for a number of years to say knowledgeably that, after all, the BCS theory was not "proved"—that only in the matter of the energy gap was there agreement between experiment and theory. This was not true. In the original paper it was pointed out that the striking difference between nuclear relaxation, which peaks at T_c and then drops, and ultrasonic relaxation, which drops at T_c, was a coherence effect depending delicately on the form of the theory.

This type of coherence effect can be explained in a very simple way. As we pointed out, the BCS assumption is that the pairs have zero spin, zero angular momentum, and zero linear momentum. Another way of saying this is that the paired electrons exemplify time reversal: they are in states in which the momentum and spin of one are reflections of those of the other.

Many perturbing effects—scattering from a surface or a chemical impurity, or from an acoustic wave—are static in nature—that is, "time-reversal-invariant." Such a perturbation does not affect the bound pairs in a superconductor, in the BCS approximation (*17*). A magnetic perturbation, on the other hand—for example, the magnetic field of a nucleus or of a magnetic impurity—has just the opposite nature. This is the source of the two contrasting kinds of effects. One of the most striking predictions of this type to be supported by experiment is that ordinary chemical impurities do *not* lower T_c much and *do* narrow the distribution of energy gaps (*18*), whereas magnetic

impurities *do* sharply lower T_c and "smear out" the gap distribution—effects leading in extreme cases to "gapless superconductivity." The effect on T_c was measured before it was arrived at theoretically, but the effect on the gap was predicted before it was measured (*19*).

According to the BCS concept, these impurity-scattering phenomena are diagnostic for pairing of electrons of the simple type assumed in the theory. So far all superconductors investigated show them. (Because impurities are universally present it is very hard *not* to observe them!)

The one effect which appeared to violate the coherence-factor predictions was the Knight shift. To my mind the violation is more apparent than real, reflecting a failure of communication, in that the theorists have been discussing an idealized, pure system and the experiments are made on some of the most impure and inhomogeneous specimens of metals ever prepared. In investigations of the Knight shift in pure, bulk specimens, experimental results have not yet contradicted theory.

A second qualitative triumph of the BCS theory began in Russia. In 1959 Gor'kov announced that his version of the theory led to the Landau-Ginsburg phenomenological equations of superconductivity, with an effective charge $e^* = 2e$ (*20*). The importance of this discovery was not at that time widely appreciated in the West, mainly because we did not appreciate a 1957 paper of Abrikosov's (*21*) which derived from these equations the entire theoretical apparatus necessary for understanding hard superconductivity—the technologically important superconducting magnets, in particular—and, rather obscurely, demonstrated the quantization of flux through a superconductor in units of $hc/e^* = hc/2e$. As a result of this failure of perception on the part of Western theorists, both of these phenomena were first clearly brought out by the experimentalists (*22*). I am glad to give the experimentalists the credit of discovery if I may at the same time point out that, like a marginal note of Fermat's or a 17th-century anagram, Abrikosov had hidden away the truth, for us all to recognize afterward: the theory was all right, it was just that *we* were stupid.

It is clear from all this that by 1960 or 1961 the experimental support for the theory of superconductivity was overwhelmingly convincing, more so than that supporting, say, Wilson's equally plausible theory of semiconductors at the time the transistor was developed. For some reason—perhaps primarily psychological—physicists were, on the whole, much less ready to accept it than they have been to accept new theories in other, similar cases, but speculation on the precise reasons is hardly appropriate here.

The Third Stage

The first two stages of the development of the theory of superconductivity had, then, been compressed into 4 or 5 years. What about the much more difficult third stage: the quantitative prediction of transition temperatures, for instance, or of the condensation energy? I must again remind you that this kind of question has not been solved in most other cases: we don't have any good theory of melting points, of ferromagnetic or antiferromagnetic Curie points, or of ferroelectric transitions. But we are beginning to understand the superconducting transition quantitatively.

The approximation for the interaction suggested in the original Bardeen-Cooper-Schrieffer paper was admittedly extremely crude. It is known that as an electron passes through the lattice of ion cores in a metal it displaces the ions—polarizes them—in such a way as to attract other electrons. At the same time, its own negative charge repels other electrons. Bardeen and his co-workers assumed that these two mechanisms were independent (they are not, of course, since the electron polarizes the ion cores by electrostatic interaction also) and that the criterion for superconductivity was that the lattice polarization, or "phonon" effect, was the larger. Since that effect was attractive only for electrons differing in energy by less than a largest phonon energy $\hbar\omega_D$, an artificial cutoff (above which no interaction at all took place) was introduced at that energy. The result was the famous equation

$$3.5\,kT_c = \epsilon_g = \hbar\omega_D \cdot \exp[-1/N(0)(V_{phon} - V_{coul})].$$

This equation gives correctly the order of magnitude of the transition temperatures, since it is expected that the coupling constant $N(0)V$ should be considerably less than unity, and it gives the right isotope effect for many metals—the dependence of ϵ_g, and of T_c which is proportional to it, on $\hbar\omega_D$ and thus on the isotopic mass of the ions as $M^{-\frac{1}{2}}$. One could hardly expect that such an admittedly crude approximation could be relevant to the real criterion for superconductivity, and the very first more detailed discussion, by Swihart (*23*), showed that the isotope effect was an artifact of the cutoff assumption. Nonetheless, for a few years this equation seems to have been taken seriously, even to some extent by its authors.

Bogolyubov had already briefly, and Swihart more thoughtfully, approached the problem from a more realistic point of view; but the advance which made the quantitative approach possible was made by Eliashberg (*24*), whose ideas were amplified and clarified by Morel and Anderson (*25*), by Schrieffer, Scalapino, and Wilkins (*26, 27*), and by others.

The new feature brought in by these people was the idea that it was not only more correct but also more useful to emphasize the *retarded* nature of the electron-electron interaction in superconductors. This can be understood very simply if we think about the actual physical interaction between two electrons in a metal.

We know that after an electron has moved rapidly through the metal, the first thing that occurs is a reaction by the other electrons which screens off the electrostatic potential at a very short distance, less than a unit cell radius in most metals. This screening is instantaneous (or may be considered so for our purposes), and so practically no particle beyond the screening radius ever experiences any appreciable potential energy of interaction. Thus, the second electron must be very close in space *and* time to see this part of it.

The second reaction is the slow response of the metal ions which are attracted briefly to the electron's negative charge. The ions move toward the region where the electron was and, in a time equivalent to one lattice-vibration period, return to their unperturbed positions, executing a damped vibration. Their initial, largest swing is such that an attractive potential builds up in the region where the electron had been, but the swing occurs about a lattice-vibration period after the electron, moving with the Fermi velocity, has left the region. Again, most of this attractive, retarded part of the potential is felt only in a volume of space very close to the actual path of the electron. Thus we see that the whole interaction potential between electrons

has a very short range in space but is of a complicated nature in time, with rather long-range parts. The repulsive part is nearly instantaneous, the attractive part is retarded. The partner of the given electron, then, should avoid the space-time region where the potential is repulsive and stay in that where it is attractive.

Eliashberg generalized the equations of the BCS–Gor'kov theory to allow one to use a potential that depended upon both space differences and time differences. The essential result is a single integral equation in space and time —or, when transformed through Fourier analysis, in momentum and energy variables—for an "energy gap" which is a function of momentum k and energy E. The obvious approximation, which turns out to be even better founded than the foregoing discussion indicates, is to neglect the k-dependence—that is, the space-dependence—of this function and to use only the very much simpler equation in one variable, the energy, which results. This single, one-dimensional integral equation is manageable even for very complicated systems; what is more, as Schrieffer has pointed out, this theory is nearly rigorous, in the sense that it includes most of the complicated renormalization effects which might otherwise be large quantitative corrections. I like to call it the "E.A.S.Y." energy-gap equation, for Eliashberg, Anderson, Schrieffer, and Y. Nambu, all of whom contributed—among others—to its development and proper use.

At the same time it happened that developments in experiments on tunneling between superconductors have made it possible to measure the energy-gap function $\Delta(E)$—or at least quantities very closely related to it—in all its detail. The most detailed experiments have been performed on lead by Rowell *et al.* (*28*). By correlating these experiments with the theory we have made the following two advances: (i) it was demonstrated that the tunneling data could result from a gap equation of the given form, and this, in view of the complexity of these data, all but verifies the form of the equation (*29*); (ii) we then showed that the strength of the electron-phonon coupling given from the tunneling data is consistent both with the transition temperature of lead and with the electron-phonon resistivity of lead (*30*). In this way we have realized, in a rather backward fashion, the decade-old hope of Fröhlich and Bardeen that T_c could be calculated from the resistivity; rather, we have calculated both T_c and the resistivity from the much more detailed knowledge of the phonons and the electron-phonon coupling furnished us by the tunneling experiments (with, I should mention, a strong assist from measurements of the phonon spectrum made by means of neutron scattering).

Questions and Answers

A number of questions immediately arise. (i) Can we do the same thing with other metals? Answer: Yes, slowly, when good tunneling data are available, as they are not yet for most other metals; when we know more about their phonon spectra than we now do; and if the spectrum is as easily analyzed as that of lead. (ii) Is there any case in which we know as much from other sources as the tunneling data tell us in the case of lead? There is one: in many semiconductors we have good, detailed information about electron-phonon scattering, band structures, dielectric constants, and so on; and in degenerate semiconductors we can often vary some of the parameters—notably the number of electrons—at will. Cohen has modified the BCS–Gor'kov theory in a manner appropriate to the case of the degenerate semiconductor and has successfully predicted—to everyone's surprise—in what special circumstances degenerate semiconductors might become superconducting (*31*).

A third crucial test for the quantitative theory of the interactions which cause superconductivity is that of the isotope effect. In the absence of detailed information about the electron-phonon coupling one might hope to use the transition temperature as a parameter for determining this coupling and at least predict the isotope effect. In the retarded-interaction theory mentioned earlier, the source of the isotope effect is in the retarded part of the interaction caused by ion displacement, since this part will inevitably scale in time accurately with the lattice vibration period and thus with the isotopic mass. That is to say, the only effect of a change of isotopic mass will be to change the vibration period of the ion. Any deviation from $M^{-\frac{1}{2}}$ must measure the effectiveness of the Coulomb part of the interactions which is instantaneous.

It is well known in the theory of nuclear interactions that particles interacting by way of a "hard core"—that is, a strong, short-range repulsive interaction—can to a great extent avoid its effects by modifying their wave functions in the region of the hard core. This modification brings in very-high-momentum states but does not cost very much energy.

In the case of superconductivity theory we have a "hard core" in time, not in space, but the same principle operates: the electrons can avoid each other in this region by bringing very-high-energy components into their wave functions. But in a solid this may or may not be possible, depending on whether the bands are narrow or wide. When they are wide, as in most simple metals, the avoidance is nearly complete, and the isotope effect is nearly $-\frac{1}{2}$; but in narrow-band metals such as the transition metals the theory, as worked out by Garland (*32*) (after Anderson and Morel, who did not compute the problem accurately enough numerically or include the effect of variable band width), can lead to intermediate, zero, or even, in extreme cases, positive values for the isotope effect. On this issue theory and experiment have fought to a standoff: theory predicted intermediate values—even, fortuitously, the right value for molybdenum!—first (*23, 25*), but experiment found near-zero values before the theory was accurately enough developed to provide a basis for understanding them (*33*).

Matthias brings up some exciting open questions in these areas, which, at the risk of finally ruining my reputation for accuracy, I shall answer here to the best of my ability. (i) Will other mechanisms occur? (ii) Have they occurred? To the latter question, the answer is very probably no. In most of the more complicated mechanisms, electrons seem to be paired in anisotropic or otherwise unusual states, which are broken up by impurity scattering. We must look to very pure metals for anything really new. Will other mechanisms occur? Probably. The requirement for the formation of pairs is that the interaction be attractive not everywhere but simply in some, not necessarily very large, region of space and time. Many interactions—perhaps even screened Coulomb ones—have this property, but the transition temperature may be exponentially low. It is amusing to note that the original BCS criterion—that the interaction be attractive in momentum space—is not necessary or even, in many cases, satisfied; the vital thing is the real space-time

interaction, not its Fourier transform.

Are all metals superconducting? Probably most are; many theorists have accepted for some time the idea that most of them must be. Sodium has an almost vanishingly weak interaction in much of the relevant region, so its T_c may be very, very low; magnetic metals, to be superconducting, must be extremely pure, since their pair states are, perforce, not BCS pairs and will be sensitive to scattering, and the T_c of these metals may be very low. But I can see no reason why *some* component of the interaction cannot be attractive *somewhere* in every case.

P. W. ANDERSON

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II. The Facts

Written discussions between experimentalists and theorists are not too frequent these days, and if they are presented at all, the authors are trying very hard either to agree or to ignore each other. The field of superconductivity is no exception. It is particularly difficult to follow the two sides of an argument when the interval between presentations extends over weeks or months. We hope the argument can be followed more easily in a two-part discussion such as this.

I am indeed fortunate in having the present theoretical aspect of the BCS approach to superconductivity presented by my friend P. W. Anderson, who has been so instrumental and essential in this field. [Another theoretical point of view was given 2 years ago by H. Fröhlich (*1*). While he did not make any detailed quantitative statements, his general approach seemed to reflect the occurrence of superconductivity in a truer way.] For once I will not have the feeling of being unfair when I say that even today the theory cannot in any way predict the occurrence of superconductivity, much less the transition temperature. Reading Anderson's article can hardly lead one to another conclusion. For a long time experiments have indicated the almost general occurrence (*2*) of superconductivity in most metals that were sufficiently pure and cold. We have hoped it could be shown theoretically that a condensation of one kind or another in a Fermi gas should always occur under ideal conditions. Experimentally the answer seems to be in the affirmative. It will be up to the reader to decide whether this answer has now been given theoretically as well.

Theoretical Development

During the last 13 years the theory of superconductivity presented by Fröhlich and Bardeen (*3*) was based on an electron-phonon interaction. Right from the outset in 1950 we were told that this was the final solution to the last unsolved problem in solid-state physics. Since then we seem to have gone through quite a number of "final" stages in the theoretical development. The present one is the BCS theory, named after its three authors, Bardeen, Cooper, and Schrieffer (*4*), and presented in 1957. There has also been a more general theory by Schafroth, Butler, and Blatt (*5*), formulated in 1954, which is based on the Bose-Einstein condensation of electron pairs. As a rule these theories have been preceded by experimental results, and they have in general been unable to predict results. However there are some notable exceptions. Fröhlich predicted a gap in the electron spectrum on the top of the Fermi surface in the superconducting state for a one-dimensional model. This gap was indeed detected optically, by microwave spectroscopy (*6*) as well as by specific heat measurements (*7*). He also predicted the isotope effect, according to which the transition temperature T_c varies with the inverse square root of the atomic mass, thus clearly indicating a correlation with lattice vibrations. In 1957, Bardeen, Cooper, and Schrieffer presented another electron-phonon theory (*4*), which explained the existence of the gap by means of pairs of electrons with opposite spins. They correctly predicted the behavior of nuclear relaxation in the superconducting state. They also predicted the relation between the gap width and the transition temperature for the elements. In 1961 Onsager (*8*) predicted, on the basis of the Schafroth theory, the existence of quantized flux of only half the value of that calculated by London. The factor 2 was, again, due to the formation of pairs of electrons with twice the charge of a single electron. All these theoretical predictions have been verified experimentally.

However, there have been just as many theoretical predictions that have not been verified by experiment. These

include the prediction that the Knight shift in superconductors vanishes, that higher transition temperatures exist, and that the isotope effect, with a value of $M^{-\frac{1}{2}}$ is general; in addition, the theory has also incorrectly predicted the electronic heat conductivity.

Unfortunately, one question remained almost totally ignored in most theories and experiments; namely, What are the critical conditions for the occurrence of superconductivity itself? Derivations of a criterion were first attempted by Fröhlich and Bardeen, and later by Bardeen, Cooper, and Schrieffer. The latter group actually gave an equation for the transition temperature itself; this equation, however, contained an interaction constant that cannot be calculated at present. Apart from this difficulty, the critical conditions for superconductivity could not be predicted by this equation either. For example, according to the equation, yttrium and lanthanum should have the same transition temperature, that of yttrium being possibly a little higher, since both have the same $N(0)$ and almost the same V and Debye temperature. However, yttrium is not superconducting down to 0.07°K and α-lanthanum is superconducting at about 5°K. This difference is discussed later. Moreover, this formula, cited by Anderson, is not only crude, as he says, but also incorrect for the transition elements, since the dependence of T_c on $N(0)$ is in most cases the exact opposite of that stated in the formula. For example, the T_c of yttrium, rhodium, and platinum decreases with an increase in $N(0)$. Since the formula was proposed it seems to have been discarded completely because it does not present the criteria for the occurrence of superconductivity, which, on the other hand, are easily given by a simple empirical rule (*9*).

Theory versus Description

Let me deviate for a moment and explain why I think the word *theory* is really inappropriate. A *theory*, according to the current *Oxford English Dictionary* is defined as "a conception or mental scheme of something to be done, or of the method of doing it. A systematic statement of rules or principles to be followed." According to the same source, a *description* is defined as "the combination of qualities or features that marks out or serves to describe a particular class."

Clearly, since the present "theories" are unable to state the rules for the occurrence of superconductivity, which, in my opinion, are essential in any explanation of the phenomenon, they should really be considered descriptions or at best models of superconductivity. It is, therefore, not surprising that the acceptance of the generality of the phenomenon, which had been considered rather limited until recently, is the result of the *empirical* approach of finding a great number of superconductors. The recent theoretical conjectures of Morel and Anderson (*10*), Casimir (*11*), and Fröhlich (*12*) support the experimentally arrived at conclusion that most metals, if sufficiently pure and cold, will eventually undergo a condensation of one kind or another. In the overwhelming number of cases this will be the onset of superconductivity, but there are rare exceptions, such as ferromagnetism. In the latter case the electron spins, instead of being antiparallel, are all aligned. It is also possible that different and still unknown transitions or condensations will occur in the millidegree temperature range. These might include phenomena such as nuclear ferromagnetism, predicted 25 years ago by Fröhlich and Nabarro, or other types of alignment.

Occurrence of Superconductivity

The conclusion that superconductivity is a rather widespread phenomenon resulted from the discovery, in recent years, of almost 1000 superconductors as compared with the 30 to 40 superconductors known about 13 years ago. Quite early in the experimental studies it was possible to state a simple rule (*9*) for predicting the transition temperature of a given metal. If the metal is a nontransition element, or a combination of nontransition elements, superconductivity almost invariably occurs above 0.3°K and the transition temperature generally increases slightly with n, the number of valence electrons per atom. *All* electrons outside of filled shells are considered valence electrons. While the chemical valence is sometimes related to this number, it has no meaning for $n > 7$ or 8, from a chemical viewpoint. The transition temperatures in systems of nontransition elements are not very high; they reach a maximum of 8.8°K in the lead–bismuth system. All nontransition elements investigated to date show the isotope effect predicted by Fröhlich and Bardeen and later formulated in the BCS theory. Quite frequently the combination of nontransition elements results in semiconductors, in which case an insulator rather than a superconductor is expected as the temperature is decreased. However, even some of the semiconductors, such as doped germanium telluride, become superconducting below 0.3°K, as recently reported by J. K. Hulm at the International Conference on the Science of Superconductivity held at Colgate University.

The transition elements form the second group of metals in the periodic system. The transition temperatures at which these elements and their compounds (with either transition or nontransition elements) become superconducting are strongly dependent on the number of valence electrons per atom for the element and on the average number of valence electrons for the composite systems. This is in sharp contrast to findings for the nontransition-metal group. For the transition elements the maxima in transition temperature correspond to values near 5 and 7 for number of valence electrons per atom, are very pronounced (Fig. 1), and are rather independent of crystal structure. Hamilton and Jensen (*13*) recently found that the distribution of the transition temperature is quite *symmetric* with respect to column VI of the periodic system if lanthanum and uranium are excluded. This means, as far as the *d*-electrons are concerned, that the symmetry is with respect to a *half-filled d*-shell. Although the points shown in Fig. 1 are values for the elements only, the curve was actually traced through many intermediate points not shown in the figure. These points represent the transition temperatures of solid solutions of the elements in each other. The shape of the curve also persists for intermetallic compounds, but for these the height and precise location of the maximum transition temperatures depend somewhat on the crystal structure. No symmetry or regularity of this kind has ever been observed for the nontransition elements. Rather high transition temperatures occur frequently in systems containing a transition element. The maximum transition temperature known today is 18.05°K for the compound Nb_3Sn, which has the rather complicated β-wolfram type crystal structure and a ratio for number of valence electrons per atom of 4.75.

None of the transition elements or their compounds has ever shown an isotope effect proportional to $M^{-\frac{1}{2}}$, the value reported for the five nontransition elements measured to date. In ruthenium (*14*) there is no observable effect at all, and in molybdenum (*15*) the effect is proportional to $M^{-\frac{1}{3}}$. The variations in transition temperature, together with this entirely different isotope effect, would suggest to an unprejudiced observer that there is a drastic difference in the mechanisms causing superconductivity in the two groups of metals. Another difference between the two groups is noticed when their maximum attainable transition temperatures are compared. For alloys of the transition elements this temperature is 18°K, about twice the value for the nontransition elements.

Lanthanum and uranium are exceptions with respect to the symmetrical distribution of transition temperatures in the periodic system. A reason for this has recently been postulated (*13*). Both are the beginning elements of the 4*f* and 5*f* series, without having any occupied *f* levels. However, these *f* levels cannot be far from being occupied, and thus may act as virtual levels. The existence of these virtual levels had previously been proposed as a possible cause of superconductivity by means of a magnetic interaction (*16*), rather than by means of the usual phonon mechanism.

Superconductivity and Ferromagnetism

Many years ago the close relationship between superconductivity and ferromagnetism became apparent in investigations of these phenomena in isomorphous compounds (*17*). Since then we have found many examples which indicate not only that this close relationship exists but also that very often magnetic interactions must be responsible for the occurrence of superconductivity, and the reverse may even be true. This can be illustrated by a few examples: (i) U_6Fe is the superconducting compound of uranium with the highest transition temperature, higher than that of U_6Co or U_6Mn; (ii) iron in titanium raises the transition temperature of titanium faster than any other element does; (iii) however, if iron *lowers* the transition temperature by being *localized,* as, for instance, in molybdenum and some of its alloys, it does this also much more drastically than either cobalt or manganese does.

Scandium is not superconducting above 0.08°K, but solid solutions of chromium in scandium (and, so far as we now know, *only* of chromium) are superconducting near 3° to 4°K. This effect of chromium is presumably due to the magnetic interactions, similar to those of iron in titanium. Iron in scandium, in turn, has a magnetic moment and leads to antiferromagnetism.

The compound $ZrZn_2$ crystallizes in a cubic structure (type C15) which results in superconductivity in most other zirconium compounds. However, $ZrZn_2$ becomes ferromagnetic at 35°K. La_3In is the lanthanum compound with the highest superconducting transition temperature, but the analogous compound with scandium, Sc_3In, becomes ferromagnetic. So far this kind of free electron ferromagnetism has been observed only in these two compounds, which were found among 6000 intermetallic phases. The general rule is that superconductivity will occur.

There never has been any theoretical attempt to link the two phenomena. Yet our results indicate that the mechanisms leading to superconductivity are very often closely related to those causing ferromagnetism. Recently members of the Russian and Japanese schools have presented a number of papers describing magnetic interactions which lead to superconductivity (*18*). Strangely enough, these papers have been ignored thus far. Could it be that history is repeating itself, and that communications on magnetic interaction are receiving the same treatment from Western theorists that the Gor'kov and Abrikosov discoveries received?

Since none of the existing theories can either give criteria for the phenomenon of superconductivity or permit prediction of the transition temperature, it is impossible, for me at least, to understand recent attempts to enforce another consolidation of theory and experiment at any price. Let me illustrate this by the following example. Before the absence of an isotope effect in ruthenium was discovered experimentally, none of the existing theories had ever considered the possibility of the absence of this effect. In their 1961 review article, Bardeen and Schrieffer (*19*), referring to a different Coulomb cutoff in Bogolyubov's theory of superconductivity, stated, "If this calculation were valid, there would be two serious difficulties: (1) the exponent of the isotope effect would be expected to depart significantly from ½, contrary to experiment, and (2) the effect of the Coulomb interactions would be reduced so much that nearly all metals would be expected to be superconducting." Since then we have shown experimentally the absence of an isotope effect in ruthenium and also the deviation from the factor ½. It has also been shown experimentally that most metals are superconducting.

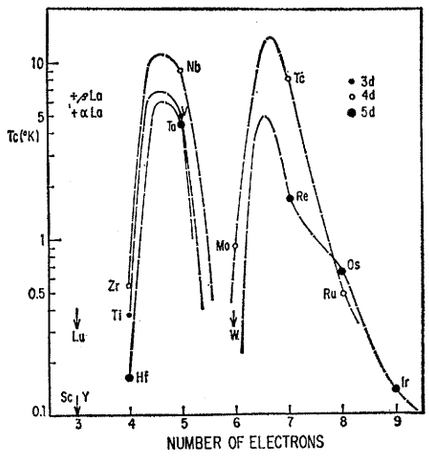

Fig. 1. Variation in superconductivity of the transition elements in the periodic system.

It is not clear to me why suddenly these serious difficulties should no longer exist, as Garland has recently claimed they no longer do (*20*). On the other hand, the different mechanisms for the occurrence of superconductivity, as well as the general existence of the phenomenon itself, have long since been deduced, though purely empirically.

Summary

In summarizing, let me say again that some of the theoretical conclusions have been verified experimentally. These include the gap in the electron spectrum, the nuclear relaxation in the superconducting state, and the lattice-electron interaction for the nontransition elements, as well as the fact that pairs are involved in the condensation, as shown by quantized flux measurements. However, the predictions of the theory, especially those with respect to the Knight shift in superconductors and the isotope effect for the transition elements, have not been borne out. The theory has since been modified to account for the non-vanishing Knight shift found by experiment, and also for

the experimentally determined isotope effect of the transition elements. However, there is no word at all on when and where to find a superconductor in the transition metals.

Unfortunately, the validity of the electron-phonon interaction has been, in my opinion, overstated to the point that a formula for the transition temperature was given which has now failed under the weight of the periodic system. Another result of the BCS formulation of electron-phonon hypothesis is the conclusion that superconductivity is the result of a more or less delicate balance between the electron-phonon interaction and the Coulomb repulsion. For this reason most theories have considered superconductivity an accident rather than the normal ground state of most metals. However, experimental results indicate that superconductivity is indeed a very general phenomenon. In contrast to the BCS formulation, Fröhlich, in paragraph 7 of his review article (*1*), has proposed that the occurrence of superconductivity as well as that of superfluidity might be understood in a very general manner as a result of an appropriate quantum hydrodynamics.

The difference in the transition temperatures of yttrium and lanthanum cannot be understood on the basis of an electron-phonon interaction, but it has been explained on the basis of a magnetic interaction.

The transition elements have many properties which can be symmetrically arranged according to the elements' position in the periodic system. The behavior of the transition temperature at which superconductivity occurs is another such symmetric function—a fact which gives added credence to the generality of the phenomenon. Since the rule that the maximum transition temperatures should occur when the number of valence electrons per atom is around 5 or 7 is fairly simple, it would seem that the correct underlying explanation should be equally simple. I believe that it has yet to be given. Should it ever be stated, we might then expect an answer to our second question: Why has it been relatively easy, within the last 10 years, to reach transition temperatures of 17° to 18°K in many intermetallic systems and impossible to raise this value even by as little as half a degree? It is not that we have not tried. More than 6000 metals have been checked; 18°K has been reached very often but never exceeded.

Another result has emerged from the experimental investigation of all these metals. As stated before, we found ferromagnetism in two compounds which had been expected to be superconducting—namely, $ZrZn_2$, a compound composed entirely of superconducting elements, and Sc_3In, wherein, to date, only indium has been found to be superconducting. The extreme rarity of these occurrences indicates that ferromagnetism is a much less likely kind of condensation than superconductivity. While there are many superconducting compounds formed entirely of nonsuperconducting elements, all ferromagnetic compounds, with the exception of the two mentioned, contain either chromium, manganese, iron, cobalt, or nickel or an *f*-electron element. Superconductivity can be predicted empirically on a routine basis today with very few exceptions. However, prediction of ferromagnetism is not possible at present, since the incidence of 2 in 6000 is rather unfavorable. Perhaps in this case we have not been looking in the right direction, and have thereby given the theory a chance to precede the results of experimental search.

Where do we stand with respect to cooperative phenomena in general? As I have tried to show, ferromagnetism is a rare and restricted phenomenon in comparison with superconductivity. In the field of ferroelectricity there was a superstition for 20 years that the occurrence was due to one specific mechanism, that of the hydrogen bond. Today we know that ferroelectricity is a general phenomenon. We have a great number of ferroelectrics, and the mechanisms responsible for the effect range from order-disorder among hydrogen bonds to the polarization of sulfur. Thus, I think ferroelectricity is better understood theoretically than superconductivity is.

To summarize in the form of a final question, to which the ultimate and final answer must come only from the theory: Will the electrons in any and every metal that is sufficiently pure and cold always undergo a condensation? If so, in a particular metal, at what temperature will condensation occur and of what type will it be? Clearly, we do not yet expect any quantitative answer to the problems of superconductivity. As Anderson mentions, not even melting points can be calculated today. Melting, however, is a universal phenomenon, and every material, when heated above 4000°C, will eventually either melt or sublime. It seems that a similar answer should also be given for electrical conductivity as a general phenomenon. When sufficiently cold and pure, what will a metal do? I think it will usually become superconducting.

B. T. MATTHIAS

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