SCIENCE

### CURRENT PROBLEMS IN RESEARCH

# The Fermi Surface

These geometrical surfaces represent the complex gyrations executed by electrons in ordinary metals.

# Walter A. Harrison

The properties we generally associate with metals result from the ability of electrons to run freely through them. These electrons are responsible for easy conduction of heat and electricity, produce the shiny appearance, and act as the glue which holds the atoms together. These properties, common to all metals, have been understood in terms of mobile electrons for a long time. More subtle aspects of electronic motions, which are responsible for many of the differences among metals, have been very incompletely understood until quite recently. These subtleties are now the subject of intense investigation among solid-state physicists.

As long ago as 1900, Drude proposed that the high electrical and thermal conductivity of metals could be understood by assuming that many of the electrons in metals were free and mobile. By clarifying one property, however, he raised a paradox which was not resolvable until 1928, with the advent of quantum mechanics. If these electrons were free to move through a crystal, then they must certainly share the heat energy of a metal. They should, in fact, contribute as much to the thermal energy of a metal as the vibrating atoms themselves, a conclusion which was in direct contradiction to experimental findings. We will see how this puzzle can be resolved by using some of the concepts of quantum mechanics.

In an *isolated* atom the electrons can exist only in certain definite orbits. Only two electrons can exist in each of these

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orbits, and these two electrons spin in opposite directions. Ordinarily an atom has its electrons in the lowest energy orbits. This binding of the electrons close to the atomic nucleus, while giving a very low potential energy, leads to a large energy of motion, for the same reason that an earth satellite speeds up as its altitude decreases. When many atoms are brought together to form a crystal, the electrons can maintain their low potential energy while reducing their energy of motion. This happens when atoms are brought into range of the outer orbits of a neighboring atom. The electrons in these orbits are then no longer bound to a single atom but become free to move, relatively slowly, from atom to atom through the crystal. This lowers their energy of motion and, like the relaxing of a taut spring, holds the atoms together in the crystal.

In what is called "the free-electron model of metals" the metal crystal is thought of simply as a box containing electrons whose orbits are straight lines. In other words, the electrons bounce back and forth between opposite walls. It turns out that electrons can exist in only some of these orbits in the metal, just as only certain definite orbits are allowed in the atom. This restriction of the electrons to discrete orbits is a direct consequence of quantum mechanics and is really understandable only in terms of that theory. The restriction on the allowed orbits is an essential feature of our model of metals.

Just as there can be only two electrons in each orbit in the isolated atom, only two electrons may exist in each of the orbits in the metal crystal. Each of these orbits corresponds to a certain velocity.

In order to discuss which velocities the electrons take, we need a method of mapping the velocities. On an ordinary map, any position can be specified by giving its direction and distance from some central point. A similar system is convenient for mapping velocities. An orbit can be represented by a point whose direction from the center of the diagram is the direction of motion and whose distance from the origin represents speed. Thus, each point on the map corresponds to a particular velocity (Fig. 1).

Just as the surveyor draws contour lines connecting all points of the same elevation, the physicist can draw contour lines connecting all velocities corresponding to the same energy. In this case, "constant-energy" contours are circles around the central point, since an electron with a certain speed has the same energy no matter in which direction it moves. The larger the circle, the higher the speed and corresponding energy.

In a metal, with electrons moving in three dimensions, a three-dimensional velocity map is needed and the contour *line* becomes a contour *surface*. The constant-energy circle becomes a constant-energy sphere.

# The Fermi Surface

Ordinarily, all the electrons have the lowest possible speeds in a metal, corresponding to the lowest energies, and each of the possible velocities corresponding to low energies can be taken by only two electrons. The constantenergy surface "surrounding" the actual velocities which electrons have in a real metal is called the Fermi surface (Fig.

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Fig. 1. Schematic diagram of possible electron velocities in a free-electron metal. Each dot corresponds to a velocity which an electron may have in the metal. The metal has two electrons with a velocity corresponding to each of the dots within a Fermi surface (solid dots) and none corresponding to dots outside (open dots). The further a dot lies from the center, the higher is the speed and energy to which it corresponds. In a real metal there may be of the order of  $10^{22}$  dots within the Fermi surface.

1). We should emphasize again that the Fermi surface is not a real surface in real space but has meaning only in terms of our three-dimensional velocity map, just as, for example, a population growth line has meaning only on a graph showing population changes with time. The Fermi surface is a boundary surface dividing the velocities, on our map, which electrons actually have from the velocities which no electrons have.

At this point we can explain the heatenergy paradox mentioned earlier. If heat energy is added to the metal, only electrons with velocities near the Fermi surface can readily increase their energy by attaining slightly greater velocities. Electrons with lower energy cannot do this because there are already two electrons with each permissible neighboring velocity. It is unlikely that any such low-energy electron would gain sufficient thermal energy to raise its velocity above the Fermi surface. For this reason only the relatively small number of electrons with velocities near the Fermi surface can easily take on energy, and the total contribution to the thermal energy is very small. For the same reason, only electrons near the Fermi surface are important in the conduction of heat and of electricity. Thus, a study of the electronic properties of metals is simply a study of the Fermi surface and of the behavior of electrons with velocities which lie near the Fermi surface.

The description of a metal which we have arrived at is the free-electron model; only one more feature need be added to complete the picture and have a model which describes most of the properties common to all metals. This feature is the collision of electrons with

Fig. 2. The changes in velocities of electrons at the Fermi surface when a magnetic field is applied to a free-electron metal. Each electron keeps the same energy, and therefore stays on the Fermi surface, but continually changes its direction of motion perpendicular to the magnetic field.

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Fig. 3. The shape of the electron paths in the metal, as viewed along the magnetic field, is the same as the corresponding line on the Fermi surface which describes its changes in velocity when the magnetic field is applied. In addition, there may be a drift of the electron along the magnetic field. The distortion of the real-metal Fermi surface by the crystalline lattice is reflected in the distorted electron paths in the metal.

imperfections in the crystal. If there were no such collisions, electrons would traverse the crystal unimpeded and the metal would be a perfect conductor of heat and electricity. Actually there are always defects and impurities in the crystal, as well as vibrations of the crystal due to thermal energy. All of these "scatter" the electrons and, in doing so, are of the greatest importance to the metal's electronic properties. In the purest metals and at the lowest temperatures, the electrons may travel as far as a millimeter before colliding, but generally they travel much shorter distances.

The collection of free electrons in a metal is called an electron gas, since all the electrons speed back and forth, just as molecules do in a gas. They collide with the walls (or metal surfaces), with each other, and with various defects in the crystal. A very important difference between the electron gas and ordinary gases arises from its high concentration and the fact that only two electrons can occupy each orbit. As a consequence, the electrons of highest energy (those near the Fermi surface) move extremely rapidly, at thousands of times the speed of sound.

If a magnetic field is applied to a metal, these straight-line paths are bent (Fig. 2). The bending of a path by a magnetic field is a continual changing of the electron velocity and can be represented as movement of the electrons along a line in the velocity map such that the energy remains the same but the direction of motion changes continuously. Such a line would be a circle for free electrons. Thus, when a magnetic field is applied, the electrons near the Fermi surface change from velocity to velocity around the Fermi surface. As an individual electron is making this circular motion around the diagram, it is also executing a circular path within the metal. If the diagram is drawn to the proper scale (the scale depends upon the intensity of the magnetic field), the lines on the diagram will be of exactly the same shape and size as the real paths the electrons follow in the crystal

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# CHANGES IN VELOCITY

(Fig. 3). This is still true even when the free-electron model is not valid, and it is an important feature of the Fermi surface: The paths followed by the high-energy electrons of a metal in a magnetic field can be drawn as lines on the Fermi surface.

There is one distinction between the true electron paths and the lines drawn on the surface. On the Fermi surface we draw circles, or at least closed lines on more complicated surfaces, but the actual electron paths may be corkscrew shaped. It is the path viewed along the axis of the corkscrew that is the same shape as the line along the Fermi surface.

Fig. 4. The Fermi surface of copper as determined experimentally by A. B. Pippard. Polyhedrons such as that drawn around the surface may be stacked to-gether to fill all space. When a surface is sufficiently distorted to intersect the polyhedron, identical surfaces must be drawn in the adjacent polyhedrons in order to trace out complete electron paths.

### Distortions

This free-electron model has been remarkably successful in explaining the properties common to metals. Even some of the differences between various metals and alloys could be attributed to differences in the numbers of free electrons and the differences in the number of defects scattering these elec-





Fig. 5. A model of the copper Fermi surface, repeated in order to show "extended" electron paths (by D. Shoenberg). Three paths are shown by tapes; one is an extended path.



Fig. 6. The Fermi surface of zinc according to the nearly-free-electron model, showing the fragmentation of the surfaces in polyvalent metals. The various fragments are classified according to energy "bands." The surfaces result from a reassembling of a sphere. As in copper there are extended electron orbits where the surface intersects the polyhedron.

trons. Some properties, however, are completely incomprehensible in these terms. For example, the electrical resistance of most metals increases when a magnetic field is applied, but this would not be expected on the basis of the free-electron model. Peierls first suggested, in a letter to Bethe, that this increase might arise from distortions of the Fermi surface from the free-electron sphere. These suggested distortions have become more and more apparent as the experiments on metals have been refined. As the size of the distortions has been discovered, it has become difficult to understand why the free-electron model was so successful in the first place.

In the free-electron picture we forgot all about the metal crystal and thought of the electrons as completely free in their motions within the crystal. All directions looked the same to the electrons, and an electron of a certain speed had the same energy no matter in which direction it was moving. The Fermi surface was spherical. Actually the atoms of the metal are in a regular repeating array which forms the crystal. An electron which moves along a line of atoms may behave differently from one which cuts across such lines of atoms. An electron with a certain energy may have different speeds depending upon its direction of motion, and the Fermi surface would then be distorted. This in turn leads to distortions of the electron paths in a magnetic field. (In actual study of the distorted surfaces it becomes necessary to think of electron momenta rather than electron velocities, but for purposes of description these are the same.)

Such distortions differ from metal to metal and produce some of the differences between metals, although only a few properties, mostly associated with responses to a magnetic field, depend *only* on the distortions of the Fermi surface.

In the monovalent metals (for example, sodium and copper) distortions of the surface are relatively minor, and many paths taken by the electrons when a magnetic field is applied are very nearly circular. Sodium, in particular, has a nearly spherical Fermi surface. In copper (Figs. 4 and 5) the distortions are relatively large, and it becomes necessary to regard different portions of the Fermi surface as connected to each other; then, in order to draw the electron paths, it is necessary to repeat the distorted sphere over and over in a multiply-connected surface. Silver and gold are also metals in which the electron paths may wander indefinitely perpendicular to the magnetic field, never closing on themselves.

In the polyvalent metals [for example, zinc (Fig. 6), aluminum, and lead] the surfaces are not only distorted but broken up into many pieces. There are a vast variety of electron paths (Fig. 7), many of which have

little resemblance to the sphere from which they were derived. Within the past few years considerable understanding of these more complex surfaces has been achieved by calculating the fragmentation of the surfaces without regard to the accompanying distortions. This nearly-free-electron model has allowed us to unravel many of the complexities and to begin focusing on the distortions which must also be there.

# **Experimental Techniques**

The first metallic Fermi surface to be determined experimentally was that of copper. This achievement, by A. B. Pippard in 1957, gave impetus to the increased recent activity in determination of Fermi surfaces. Most of the experimental techniques used (although not the "anomalous skin effect" used by Pippard) are based on the applica-



Fig. 7. The nearly-free-electron Fermi surfaces of a series of metals of the same crystalline structure but from different valence columns of the periodic table. (From top to bottom) Copper, calcium, aluminum, and lead. 29 SEPTEMBER 1961 919

tion of a magnetic field. The shapes and sizes of the paths of electrons in the metal, which reflect the size and shape of the Fermi surface, are then probed by various techniques, and parts of the surfaces can be deduced. Perhaps the most powerful technique makes use of the de Haas-van Alphen effect. This effect depends upon a restriction in the number of allowed corkscrew orbits in a magnetic field, similar to the restriction in number of allowed orbits in the atom, or in the metal with no magnetic field. This gives rise to fluctuations in many properties at high magnetic fields, notably in magnetic susceptibility, and these fluctuations are related directly to crosssectional areas of the Fermi surface.

None of these experimental techniques could have been used without extremely pure samples of metals. The presence of impurities, as mentioned earlier, causes electron collisions. If these collisions become so frequent that an electron never completes a full path in the magnetic field without a collision, the paths become ill-defined and measurements become smeared-out and useless. Rapid advances in the understanding of Fermi surfaces have been possible only during the past few years, when extremely pure metals have been available. The requirement for long electron paths between collisions also

makes it necessary to conduct these experiments at extremely low temperatures, so that the thermal vibrations, with their concomitant electron scattering, are minimized.

For the same reasons that experimental studies of the Fermi surface have only recently been possible, it is only recently that a need for this knowledge has been strongly felt. The cruder experiments could be explained by the cruder theory if the assumed concentration of electrons and their rate of scattering were chosen to fit the experiments. Only a few phenomena, such as the increase in electrical resistance with magnetic field, signaled the failure of the free-electron model and piqued the curiosity of the physicist.

# **Unsolved Problems**

Intense activity in these highly specialized techniques has led not only to a remarkable advance in our knowledge of electron behavior in metals but also to a number of controversies such as generally arise in an active area of science. Greatly increased knowledge of the Fermi surface in metals, which is central to the whole problem of the properties of metals, has clarified our understanding of some aspects of metallic behavior but has also disrupted what we thought we understood about other aspects, just as Drude's freeelectron model replaced one problem with another.

This step forward has spotlighted our ignorance of the effects of the interaction between individual electrons due to the electronic charge and the interaction due to the presence of the lattice. This latter interaction occurs as an electron moving through the crystal jostles the atoms and as they, in turn, jostle the other electrons. Such an interaction forms the basis for the theory of superconductivity, but also is manifested in metals which are not superconducting.

Whatever the problems that remain to be solved, this recent mastery of some of the intricacies of the motions of electrons in metals has provided an appealing and unusually graphic chapter in solid-state science.

Note added in proof: Various studies during the past few months have indicated that the true Fermi surface of copper is bulged out somewhat more than is shown in the direction of the square faces of the polyhedron.

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# CURRENT PROBLEMS IN RESEARCH

# **Body Composition**

The relative amounts of fat, tissue, and water vary with age, sex, exercise, and nutritional state.

# Josef Brožek

The field of body composition is one of the focal points of contemporary human and animal biology. While the roots of one of the methods of investigation can be traced all the way back to Archimedes, and a baker's dozen of references date from the period 1920-1940, the overwhelming majority of the innovations in method are the contribution of the last two decades. This era was ushered in by A. R. Behnke's essay (1) in 1941. Many developments followed: mathematical body-composition models and calculational formulas (2-5); improvements in the hydrostatic technique (6) and measurements of body volume by helium dilution (7); intensive use of anthropometric methods (8) and the addition of roentgenographic methods (9); gasometric (10) and hydrometric approaches (11), and a multiplicity of means for measuring total and extracellular body water (12); electrolyte-determination methods, especially for potassium (13); methods for the simultaneous assessment of a large number of body compartments (14); and examination of the interrelations between the various approaches (15-17). With the passage of time, these methods were applied in an ever wider context of experimental, clinical, and field studies.

The fact that much of the literature on body composition is the fruit of the last two decades indicates that the field is in the stage of late adolescence rather than of full-blown maturity. A critical analysis of the current status of the

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