



D. Shoenberg and A. B. Pippard
of the planning committee.

THE FERMI SURFACE OF METALS

*A conference report by W. A. Harrison and R. W. Schmitt
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THE last two years have seen remarkable progress toward understanding the electronic properties of metals, but the result of this progress illustrates the dictum of Veblen that "the outcome of any serious research can only be to make two questions grow where one question grew before".

Two years ago it could be said that there were two primary questions in this area: (1) Is a one-electron approach—leading to the band theory—adequate for treating most metallic properties? (2) If so, what are the shapes of the Fermi surfaces in the different metals? The experimental key to the first question seemed to lie in finding if the Fermi surface, determined in several independent ways, was the same. At that time no metal had been analyzed carefully by more than one method.¹ Most experimental efforts had been confounded by the failure to obtain metals of sufficient purity, and the intrinsic electronic properties of the metals were masked by the presence of the impurities and the resultant scattering of the electrons. Physicists had to use many novel schemes to get pure metals. Professor A. Kip and his co-workers at the University of California at Berkeley had found that the purest copper they could get was a natural crystal of it on the shelves of the University's Geology Museum. Their first successful cyclotron resonance experiment for copper was to be done on that crystal.

Since these experiments, metals of remarkable purity have become available and several have been investigated by more than one technique. There is little doubt

that each method of study sees the same geometry of the Fermi surface to within a few percent, and physicists know the general features of the surface in a large number of metals. They are beginning to study the finer details of the surfaces, looking for discrepancies of a percent or two. Many questions have grown where one grew before, and it is too early to tell which of this multitude will grow into the next major advance.

In this atmosphere of rapidly developing knowledge about the electronic structure of metals, particularly the Fermi surface, an international conference was held. The purpose was to review and discuss progress of the last several years with thoroughness and to allow scientists working in the field to get their bearings again. There were about 90 scientists from the United States, Canada, England, France, Norway, Spain, and Japan. The US Air Force Office of Scientific Research and the General Electric Research Laboratory jointly sponsored the conference in Cooperstown, New York, on August 22, 23, 24, 1960. The site was the Otesaga Hotel, on the shores of Lake Otsego. Cooperstown is the legendary home of baseball and is widely known for its Baseball Hall of Fame. However, to the scientific conferees—with a notorious deficiency of interest in baseball—the excellent local museums of early America, Fenimore House and the Farmer's Museum, were infinitely more attractive; a few conferees visited them. For the most part, as the accompanying photographs suggest, the primary occupation was discussion.

The program was planned by a conference committee consisting of M. H. Cohen (Chicago), R. W. Morse (Brown), A. B. Pippard (Cambridge), J. A. Rayne

¹ The "Little Geneva" Conference, a report of which has been given by Roland W. Schmitt and Paul M. Marcus, *Phys. Today* 12 (7), 28 (July 1959).



P. G. Klemens



A. F. Kip

(Westinghouse), R. W. Schmitt (GE), and D. Shoenberg (Cambridge). Sessions occurred during three days; on two days afternoons were open, the second session of the day taking place in the evening in the style of the Gordon conferences. Two or three long papers (30 to 60 minutes) and several short (12-minute) papers were presented at each session, leaving considerable time for informal discussion.

This brief report is intended only to outline the scientific developments which lead up to the conference, some of the questions which have arisen in this field, and a summary of the progress which was reported at the conference. The full proceedings have just been published by John Wiley and Sons.

THE theories developed shortly after the discovery of quantum theory during the 1930's began by neglecting the interactions between electrons. Under this assumption a surface, the Fermi surface, bounds the occupied electronic states in momentum space. The momentum states are quantized and only two electrons, with opposite spin, can occupy each state. For a given density of electrons the lowest-energy state of the whole system will have each quantized state filled with two electrons beginning with the states of lowest energy and ending with the states of a definite, higher energy, the Fermi energy. The Fermi surface is therefore a surface of constant energy bounding the occupied electronic states in momentum space.

For free electrons—electrons without interactions with each other or with the periodic lattice potential—the energy is proportional to the square of the momentum. Surfaces of constant energy are spheres and this is the simplest shape for a Fermi surface. Early theories assumed this spherical shape, thereby neglecting the effects of crystal structure on electron behavior and also making theory incapable of dealing with many subtle but important differences between different metals. However, a spherical Fermi surface was the simplest assumption, and it carried theory far toward understanding the gross electrical properties of metals. But it failed with the magnetoresistance which came out too small to check with experiment by a factor of about 10^4 . Peierls first pointed out, in a letter to Hans Bethe, that small deviations in the sphericity of the Fermi surface would account for this discrepancy. With this

suggestion serious consideration of nonspherical Fermi surfaces began.

It is the periodic crystal potential that distorts the surface from a spherical shape and electrons of the same energy will have different momenta along different crystal directions. Figure 1 is a drawing of the Fermi surface of copper, a surface quite different from a sphere. Since the electrical properties of metals depend primarily on the electrons near the Fermi surface, the shape of this surface is central to our knowledge of metals.

However, for at least two decades after Peierls' observation, ad hoc assumptions about these shapes dominated the electron theory of metals. The transport properties being studied at the time depended both on details of the Fermi surface and on details of the collisions between electrons and crystal defects; these factors could not be sorted out. In most instances, complex expressions containing both collision times and Fermi-surface parameters had to be averaged over the Fermi surface to get the equations describing properties observed by experiment. Unique tests of the ad hoc assumptions were not possible.

Physicists who worked in this field during the last two or three decades couched their theories in analytical terms; if deviations from sphericity of the Fermi surface entered the theory, they entered as analytical expressions for ellipsoids and no one thought seriously of more complex shapes. The object of theory was to do the proper integrals and averages and come out with the correct answer for the resistance or Hall voltage or thermoelectric power. However, during the last five years the mode of thinking has been changing from the

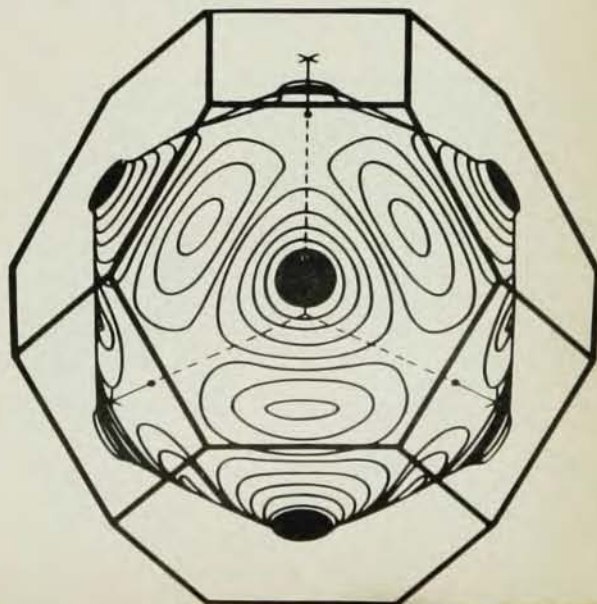


Fig. 1. Fermi surface of copper within the Brillouin zone. (By Pippard.)



Fig. 2. Shoenberg's 1958 Christmas card announcing observations of de Haas-van Alphen oscillations in copper.

analytic to the geometric. This changing style of thought has gone hand in hand with the experimental advances and to it as well as to advanced techniques is due the rapid advance in understanding metals.

The papers presented at the conference illustrated forcefully the new approach; slide after slide, instead of being filled with equations and energy-level diagrams, depicted complex topological surfaces or maps of topologically determined properties on stereographic projections. The reciprocal space of metals has become a wonderland of sculptured forms.

This geometrical thought had its gestation in work on the de Haas-van Alphen effect, the first metallic property investigated that depended critically on the shape of the Fermi surface without being confounded by the effects of collision time. However, geometrical thought as the master rather than the servant of analysis was born with A. B. Pippard's discovery of the Fermi surface of copper. And, it is an amusing fact that he discovered this surface in his pocket!

In 1953-54, Professor Pippard learned that E. Sondheimer was, by a proper theoretical treatment, studying the anomalous skin effect for an ellipsoidal Fermi surface. To the surprise of both men, the answer from this theory agreed with the answer obtained from a phenomenological approach based on Pippard's "ineffectiveness concept". This coincidence made Pippard realize that the anomalous skin effect depended only on the shape of the Fermi surface and that one might be able to discover the real surfaces for simple metals such as copper, even though the shapes were more complex than ellipsoids. Pippard spent the next year in Chicago where there were facilities to prepare the copper samples. The experiments were done, but he then had to invent a shape to fit them. He discovered almost the proper shape in his pocket—a model of the intersection of three perpendicular cylinders that he carried with him to tantalize his colleagues; the plan, elevation, and view drawings of this form are all alike, a circle circumscribing a cross. A few distortions of this shape, and he had the shape needed to fit his data, the shape shown in Figure 1.

For a while only these measurements of Pippard gave

important results for copper. The de Haas-van Alphen effect in copper could not be detected in spite of efforts over a period of five years by David Shoenberg of Cambridge. Eventually, Dr. Shoenberg decided to use whiskers of copper in his experiments. In the summer of 1958 he spent two weeks at the General Electric Research Laboratory where there had been extensive experience with whiskers of metals. Here Shoenberg brushed up on these techniques and also took several choice copper whiskers back to Cambridge with him. But again failure followed failure until just before the Christmas holidays of 1958 when the one remaining, least promising whisker was used in the last experiments before closing for the holidays. This experiment worked and a number of physicists throughout the world were greeted by Shoenberg's 1958 Christmas card showing the photograph of an oscilloscope trace of the successful experiment (Figure 2). Whiskers are proving unnecessary; they were only the key to finding the right experimental conditions.

It is no accident that these two significant advances were made by scientists at Cambridge since that university has unquestionably been the center of activity in this area; not only have Pippard and Shoenberg been active in the field, but Drs. Ziman and Heine along with a number of distinguished students have done a great deal of important work.

The technique used by Pippard in determining the Fermi surface of copper required the preparation of a new specimen for each experimental point. This tedious necessity arises because, in contrast with the other prominent experimental techniques for examining the Fermi surface, the anomalous skin effect measurements use no dc magnetic field. A dc magnetic field serves to specify a transverse plane in which the Fermi surface topology can be studied; because the experimentalist can easily alter the direction of a magnetic field he can obtain several experimental points from each metallic sample. This flexibility is not available when using the anomalous skin effect so each point requires a sample and the surface of the sample specifies the plane that would otherwise be chosen by the magnetic field.

Because many techniques use a magnetic field, we



J. M. Luttinger, W. Kohn, S. H. Vosco. At right, in foreground, J. W. Ziman, V. Heine; in background, J. C. Phillips, M. H. Cohen, B. R. Coles, L. Kleinman, G. F. Dresselhaus, J. Budnick.

shall find it useful to understand the orbits of electrons in a magnetic field.

Write the classical equation for the force on a moving charge in a magnetic field, $\mathbf{F} = \dot{\mathbf{p}} = (e/c) \dot{\mathbf{r}} \times \mathbf{H}$, where $\mathbf{F}$ is the force, $\dot{\mathbf{p}}$ is the rate of change of momentum, e/c is the electronic charge divided by the speed of light, $\dot{\mathbf{r}}$ is the velocity, and $\mathbf{H}$ is the magnetic field; $\times$ represents a cross product. This equation is also meaningful in the quantum mechanical case. It shows that $\mathbf{p}$ changes only in a plane perpendicular to $\mathbf{H}$; furthermore, because the force acts orthogonally to the velocity no work is done on the electron and it moves with constant energy. Thus, an orbit in *momentum space* is the intersection of a plane perpendicular to $\mathbf{H}$ with a constant-energy surface; the orbits of interest lie on the Fermi surface. In metals where the Fermi surface is not a sphere these orbits will not be circular and their shape and dimensions will reflect the shape of the Fermi surface.

Now consider the orbits in real space. By integrating the above equation, we see that the projection of the real orbit on a plane perpendicular to $\mathbf{H}$ is *exactly* the same shape as that of the orbit in momentum space. There may also be a drift parallel to the magnetic field, giving a corkscrew orbit. But, the projection of these electron orbits in real space traces out the shape of the Fermi surface in detail, and the methods used to study the Fermi surface simply measure these orbits and infer topological properties of the Fermi surface from them.

Finally, there is one further striking property of some of the orbits in real metals. If an orbit in momentum space carries an electron to a Brillouin-zone face the electron will be diffracted to the opposite Brillouin-zone face. The electron in real space does not, of course, make any corresponding jump from one part of an orbit to another but instead may sometimes move in a manner which can be reflected in momentum space by repeating the Fermi surface over and over in an extended-zone scheme as shown in Figure 3. These "open orbits" carry the electrons off in directions other than parallel to the magnetic field, contrasting with the corkscrew orbits mentioned above, and lead to distinctive behavior of the magnetoresistance which will be discussed later. It is not surprising that these topological complexities could not be handled by the usual analytical theories of

transport properties and that rapid progress began only after a more geometrical point of view evolved.

THE bulk of the conference consisted of reports of various experimental studies of metallic Fermi surfaces; we shall enumerate and describe these methods before describing what has been learned about different classes of metals.

The de Haas-van Alphen Effect: This effect is an oscillatory variation as a function of magnetic field of the diamagnetic susceptibility of metals. This is a quantum effect associated with the quantization of the electron orbits in a magnetic field. The oscillations are periodic in the reciprocal of the field and their amplitude generally increases with increasing field and decreasing temperature. The beautiful fact about the de Haas-van Alphen effect is that the periods of the susceptibility oscillations measure the cross-sectional areas of the Fermi surface in a plane perpendicular to the magnetic field, those areas that are either a maximum cross section or a minimum cross section. The de Haas-van Alphen effect is a planimeter for the momentum space of electrons.

The Magnetoacoustic Effect: This effect is an oscillatory variation as a function of applied magnetic field of the attenuation of ultrasonic waves; frequencies customarily used are from 30 mc to 150 mc. This effect measures a linear dimension of the Fermi surface perpendicular to the magnetic field and perpendicular, in momentum space, to the direction of wave propagation in real space. The magnetoacoustic effect is a caliper for the momentum space of electrons.

Cyclotron Resonance: This effect is the absorption of energy from an rf field applied parallel to the surface of a metal in the presence of a magnetic field of the

Fig. 3. Fermi surface of copper repeated in the extended-zone scheme. (Model by Shoenberg.)





T. G. Berlincourt and D. Shoenberg. At table, clockwise from rear, W. A. Harrison, B. S. Chandrasekhar, G. A. Alers, H. V. Bohm, S. Rodriguez.

correct intensity and also applied approximately parallel to the surface. The absorption of energy occurs when the period of the electrons orbiting in the magnetic field is a low multiple of the period of the rf field. Cyclotron resonance measurements are usually said to measure the effective mass of the orbiting electrons but another view, consistent with our geometrical outlook, is that it measures the differential area in a plane perpendicular to the magnetic field and bounded by the Fermi surface and another surface of slightly different energy. Cyclotron resonance is a differential planimeter in the momentum space of electrons.

Anomalous Skin Effect: This effect is the high-frequency surface impedance when the classical skin depth has become much smaller than the electron mean free path in the metal. Like all of the previous effects, this one, too, requires long electronic mean free paths and therefore low temperatures and pure metals. It measures the curvature of that portion of the Fermi surface corresponding to electrons moving parallel to the metallic surface. It is a spherometer in the momentum space of electrons.

Magnetoresistance: This effect is the change in resistance of a metal when a magnetic field is applied. At low magnetic fields the effect is complicated by the influence of electron collisions, but as very high fields are applied the resistance change behaves in one of two ways: either it saturates or it continues to increase without bound. When all orbits in momentum space are closed, it saturates. When, on the other hand, there are open orbits in momentum space, it may increase quadratically with field at high fields. Therefore, if with the applied magnetic field pointed along a particular crystallographic direction the magnetoresistance does not saturate, there must be open orbits in the plane perpendicular to that direction. Stereographic plots of the regions of saturation and nonsaturation of the magnetoresistance are important aids for determining the connectivity of the Fermi surfaces.

Other techniques discussed at the conference are less direct but may be applicable to more general systems. The short scattering times for electrons in alloys usually prohibit the use of the above techniques and indirect methods must be used. The Fermi-surface information obtained from the most direct methods does greatly increase the power of the less direct methods because it helps sort out the aspects of the electron behavior that influence the indirect experimental measurements.

MUCH of the discussion at the conference centered around three areas. The first of these became known as the " e^* -controversy". This controversy is centered around a fundamental question: How do the effects of electron-electron interactions modify the simple one-electron point of view used to define the Fermi surface? In particular, as the electrons are deflected by electric and magnetic fields, do they behave as particles with the ordinary electronic charge, or do they have an effective charge, e^* ? Prof. Luttinger (Columbia) has treated electron-electron interactions to all orders of perturbation theory and he concludes, for example, that no effective charge enters the de Haas-van Alphen effect. Drs. Falicov (Cambridge) and Stern (Maryland) independently used different approaches to find that an e^* a few percent different from the electronic charge enters this same effect. Similar controversies arose about other properties such as the cyclotron-resonance periods and the magnetoacoustic oscillations and these questions were not resolved during the conference. The experiments will soon be accurate enough to settle the question, and the e^* controversy may become an amusing memory. During the conference, it was a provocative point.

The second important area of discussion was the Fermi surfaces of noble metals, particularly copper. Copper has been studied by all of the methods listed above. All measurements are consistent, to a good approximation, with the surface originally proposed by Pippard and shown in Figure 1. Only fragmentary reports of this work had been published, and the series of papers describing it was impressive. Not only have the large orbits around the spherical portion of the surface ("belly orbits") been studied, but orbits around the connecting regions ("neck orbits"), orbits which run between adjacent spheres ("dog's-bone orbits", "rosette orbits") and orbits which traverse several spheres ("extended orbits"). Experimentalists are studying discrepancies of a few percent to see if they are experimental error or if they arise from difficulties in the theory; perhaps the e^* controversy bears on this. The work on copper is an outstanding case of an attack on a single problem from many directions and should give a critical test of many of our ideas about electrons in metals. In addition to the work on copper, studies of the other noble metals, silver and gold, have suggested similar Fermi surfaces, but with distinct differences in the area of intersection with the Brillouin zone.

The third important area of discussion was the polyvalent metals. To a good approximation the electrons in most of these metals behave as if almost free and they notice the crystalline structure only when making Bragg reflections at the zone boundaries. This condition can be represented geometrically by cutting the free-electron Fermi sphere with zone boundaries and re-assembling the pieces in a pattern that makes all electron orbits in momentum space continuous. These constructions are essentially a very elementary band calculation and they have been made for almost all of the polyvalent, nontransition metals (e.g., Figure 4).

The geometry of the Fermi surface, determined in this elementary way, appears to be remarkably good and agrees with many experimental results on all of the metals so far studied. There are a few sizeable discrepancies that may be removed by improvements in the band calculations and a few more discrepancies that may not be so removable. For example, the cyclotron resonance periods appear to have a systematic error; this error could reside in the influence of many-body effects that will not be resolved by better band calculations. The polyvalent metals may be the arena for settling questions about many-body effects, such as the e^* controversy, because it is possibly easier to estimate crystalline-lattice effects in these metals than in, say, copper, and thereby to isolate the many-body effects.

The alkali metals, which theoreticians have long considered to be the simplest metals, received little attention, primarily because they are intractable for the experimentalist. None of the principal experimental techniques have been applied to these metals, and only secondary evidence from investigation of the conventional transport properties is available. This circumstantial evidence shows that sodium is probably the simplest metal of any and has an almost spherical Fermi surface that is not distorted by any Brillouin zone boundary. Extensive theoretical calculations have been made on the alkali metals, and theoreticians are threatening to have solved the problem completely if experimentalists don't get busy soon! One of the most serious impediments to experimental work is the low-temperature phase transformations which prevent cooling these metals to very low temperatures in reproducible, single-crystal form.

The semimetals, such as bismuth, are another class of materials that was discussed. In many ways they are

much more like semiconductors than like good metals, and some types of experiments, such as de Haas-van Alphen or magnetoacoustic experiments, are a bit easier with bismuth than with metals. For this reason, bismuth has often been the material studied while expertness was being developed in the experimental techniques. Because of this fact, as well as because of its intrinsic interest, bismuth is one of the most completely investigated materials; its Fermi surface may consist of several ellipsoidal surfaces, but the exact number of ellipsoids is still uncertain. A dispute exists about whether there are three or six electronic ellipsoids, and definite knowledge about the hole surface has just begun to appear.

We have in this report discussed the properties of pure metals almost exclusively. Work on alloys has also been done in several laboratories. Because of the short scattering times in such systems, there is little hope of applying the specific topological techniques which we have emphasized. However, the knowledge of pure metals gives a good starting place for investigation of alloys. Studies of transport properties, optical properties, and crystal distortions under alloying appear to be promising approaches.

Reports presented at the conference displayed the great recent advance in our knowledge of electrons in metals. However, as we remarked at the beginning of this article, the conference dealt with only one portion of the problem of electrons in metals, and the summary we have given shows that much more work is needed in this area. Beyond this area of work there lie whole realms of problems such as the variation of electron velocity over the Fermi surface and collisions of electrons with lattice imperfections. The questions that must be answered about these realms may resemble those asked about Fermi surfaces. The important questions may be, "Does a collision time exist?" and "Is there a unique velocity associated with electrons?"

One could plan a program to get all this worked out in the foreseeable future but, as Professor Pippard mentioned in the last paper of the conference, "... nobody ever takes any notice of ideal programs; they go along in the same pig-headed way they were going along before and so the answer comes out by accident". It shall be extremely interesting to see the new answers that are going to come out—by accident, perhaps—in this field in the next few years.

Fig. 4. Nearly free-electron Fermi surfaces in aluminum (above) and lead (below). (Construction by F. W. Warner, III.)

