# LOW-ENERGY ELECTRON DIFFRACTION

*By Lester H. Germer*

Electron diffraction has become established as a research tool for studying the structure of surface layers and thin films, and it has now been used moderately extensively for this purpose for more than a third of a century. Yet its field of usefulness is not sharply separated from that of x rays. Both require material of considerable thickness. The ordinary electron-diffraction techniques are not sensitive to a single layer of atoms on a crystal surface. This is precisely the sensitivity required to make electron diffraction an indispensable research tool. It is needed in surface physics and surface chemistry; in the most important application, it is needed to understand catalysis. Lacking this sensitivity, as it does now, electron diffraction is not a serious competitor of x-ray diffraction in general usefulness, and it has no unique field as does neutron diffraction. It is often available as an occasionally used attachment of an electron microscope.

I have been speaking of the diffraction of electrons having energies of about 50 keV. It has been known from the very first that the diffraction of low-energy electrons *does* have the sensitivity required to study the structural arrangement of single layers of atoms. In fact, a surface structure of a single layer of adsorbed molecules (probably CO) upon a (111) nickel surface was described in early published papers[1,2] and this structure has been confirmed for CO adsorbed upon this face in quite recent measurements;[3] furthermore, the temperature at which this two-dimensional layer of CO molecules evaporates from the surface was estimated in 1927 and again in 1960, with results in good agreement.

Yet, until recently, the interest in this field has been slight and low-energy electron diffraction has not been greatly developed. Perhaps it was necessary to make substantial progress in understanding solid materials before much interest could be taken in their surfaces. The latter are just now beginning to receive attention, and perhaps low-energy electron diffraction will play an increasingly important role in their study. One should reflect upon the enormous importance of catalytic processes, and upon the absence of basic understanding of these processes. It seems to me that getting to understand catalysis will have a greater impact upon the world than will all the solid-state devices that can ever be developed.

For more than thirty-five years H. E. Farnsworth and his coworkers have used low-energy electron diffraction to study surfaces, but they have worked alone in an unpopular field. Only now has interest in semiconductor surfaces sparked an expansion of effort and development of a new and promising experimental method. This new method is the postacceleration of diffracted electrons so that the entire pattern can be seen on a photographic screen and can be photographed. This method was invented by Ehrenberg in 1934, but he was unable to develop it, and it lay fallow until its revival in the Bell Telephone Laboratories in 1960.

It seems appropriate that low-energy electron diffraction should have been infused with new life in the Bell Telephone Laboratories because electron diffraction, and in particular the diffraction of low-energy electrons, was first discovered

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there. My main theme in this paper is the use of low-energy electron diffraction to study surfaces, but I shall now digress from it long enough to explain how electron diffraction came to be discovered. The facts have not been published and are not generally known. In the year 1964 one would not need to explain why the investigation, that led up to this discovery, was being carried out in an industrial laboratory, but in the 1920's researches as abstract as this were less common outside of universities.

The discovery of electron diffraction was an outgrowth of the Arnold-Langmuir patent suit. The principals in this suit were the Western Electric Company, in whose laboratory H. D. Arnold was director of research although I believe that he did not hold such a title, and the General Electric Company, represented by Irving Langmuir. The suit was concerned with the basic patent of the three-element vacuum tube, and was probably the most famous and important patent suit ever to have come before the courts of this country.

The three-element vacuum tube had been invented by Lee de Forest, and his patent had been bought by the Western Electric Company in the expectation that its use could improve long-distance telephone conversation. Amplifiers used before this had produced terrible distortion, and the improvement from the three-element tube turned out to be fully up to the most optimistic expectations.

De Forest's invention had an oxide-coated platinum filament as its source of electrons. This sort of filament was chosen because it had been used previously by O. W. Richardson in his classic experiments on thermionic emission.

The General Electric Company very shortly devised a three-element vacuum tube having a tungsten filament. This company then claimed that only the tungsten-filament tube was a true high-vacuum tube, and applied for a basic patent. The contention was that the de Forest—Western Electric device did not have a good vacuum and depended for its operation upon considerable air left in the tube. It was claimed that its operation depended upon the emission of electrons from the oxide coating of the filament produced by the bombardment of positive ions.[4]

It was natural, in the course of this law suit, that measurements should have been undertaken in the laboratories of the Western Electric Company (which later became the Bell Telephone Laboratories) of the magnitude of the emission of electrons from oxide-coated platinum when bombarded by positive ions. Almost my first job was the assignment of making these measurements, under C. J. Davisson's direction. Their outcome proved conclusively[5] that the source of electrons from oxide-coated platinum was not the bombarding ions, and this may have influenced the final decision of the Supreme Court of the United States that awarded the patent to Arnold, disallowing the Langmuir claim. The suit had dragged through the courts for about a decade.

The measurements were extended to take in some ordinary metal surfaces, as well as surfaces coated with metal earth oxides. It was found that an oxide coating gives more electrons under ion bombardment than bare metal, although of course by no means enough to account for all the (thermionic) emission from hot oxides. I remember Arnold once talking rather severely to Davisson and myself. The tenor of his talk was that we ought to bestir ourselves and really get to understand just how positive ions produced electrons from metal surfaces. In view of the much later truly monumental work of H. D. Hagstrum in this field, this was certainly asking a lot!

We measured not only the number of secondary electrons but their energy distribution as well, finding all of the energies to be quite low. Some crude observations indicated an angular distribution with something like a cosine law.

In the same apparatus, in which emission of electrons under ion bombardment was being measured, it was possible, just by changing a few potentials on some of the electrodes, to measure electron emission under electron bombardment. In fact, this was easier because electron beams are easier to produce and control than ion beams. So such observations were undertaken as a sort of sideline.

About this time I left these experiments to work in thermionics, also under Dr. Davisson's direction. My place was taken by C. H. Kunsman who worked with Davisson for a considerable time.

Davisson and Kunsman found that most of the electrons emitted under electron bombardment were of very low energy, as were the electrons resulting from ion bombardment. But there were a few electrons having the full energy of the primary electrons! I remember Davisson reporting this observation to Sir J. J. Thomson, who was visiting the laboratories at the time. Sir J. J. was very skeptical. It seems to me now that he almost stood on his great reputation to say that it could not be so. This was, of course, only his natural immediate reaction to a surprising new idea.

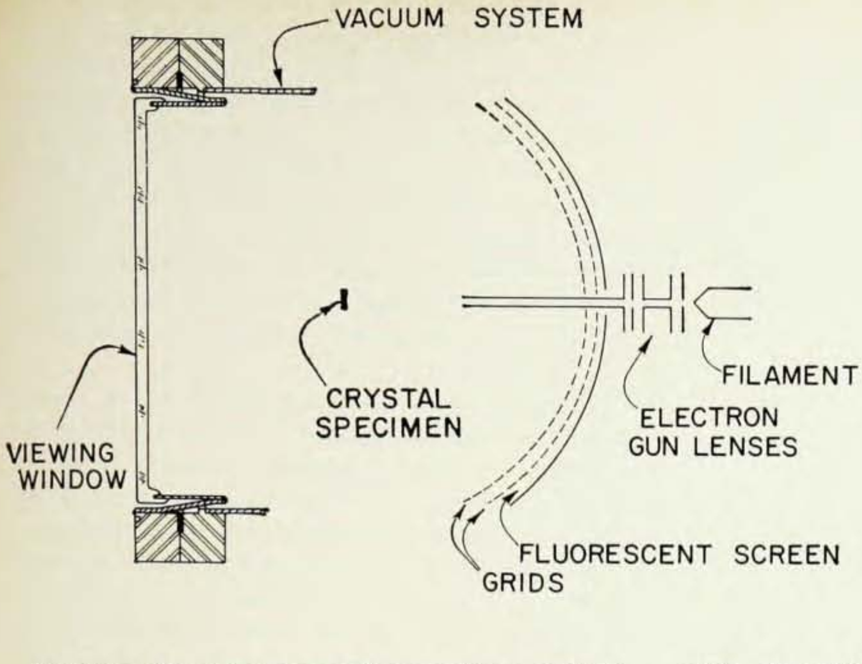


**Fig. 1. Postacceleration low-energy electron-diffraction tube. The space between the crystal and the first grid is field free, and a retarding potential upon the second grid eliminates electrons that have lost energy. A 5-keV accelerating potential upon the fluorescent screen permits the diffraction pattern to be seen.**

Davisson showed great and immediate enthusiasm for this observation that some of the secondary electrons had full energies. He realized that these must be primary electrons deflected through large angles. They seemed to him to offer a tool for exploration of the potentials within atoms. He visualized extending experiments of the Rutherford alpha-particle-scattering type to explore the outer regions of atoms that could not be studied by alpha-particle scattering.

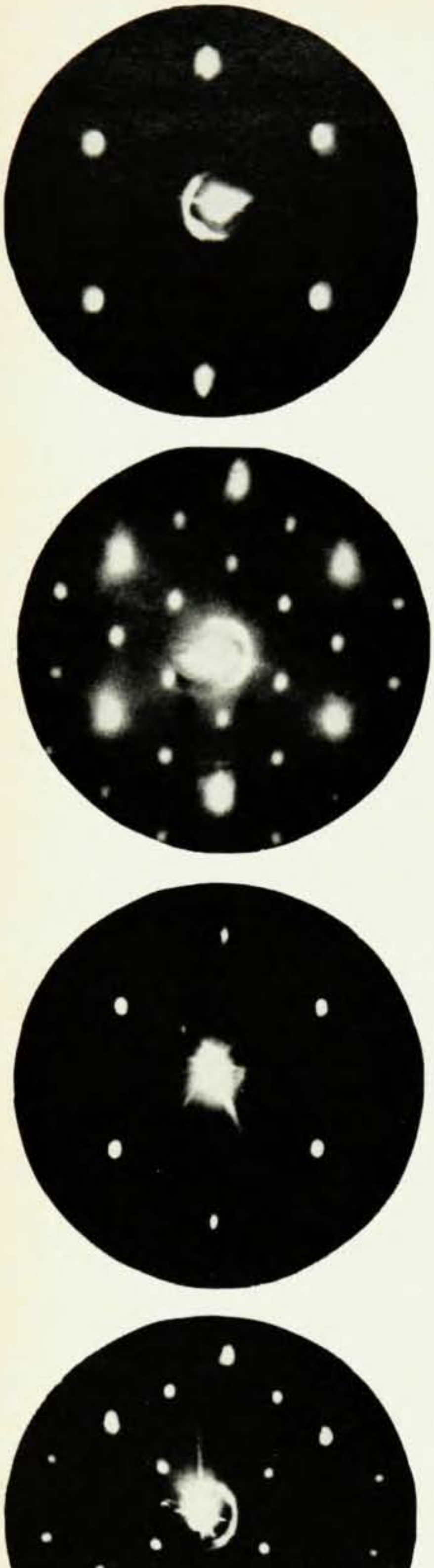
In following up these experiments Davisson corresponded extensively with D. R. Hartree in England regarding the latter's calculations of potentials within atoms. During this collaboration, he was able to calculate, from the Hartree potentials, scattering curves to be expected from atoms of different types. And, of course, he and Kunsman did build more refined tubes in which they were able to make better measurements of angular distributions of scattered electrons. They found that scattering curves of various metals had maxima in the backward direction. Magnesium had no other maximum, but nickel had a secondary maximum at a rather large angle from the backward direction, and platinum had two subsidiary maxima. These were correlated with electron shells within the atoms.

This was about the state of the investigation when Kunsman left; the thermionic experiments were successfully finished, and I came back to the scattering experiments at a very auspicious time. Quite a period of further experimentation elapsed before we had any idea that the scattering pattern from a metal could be influenced by its crystalline structure. The idea was thrust upon us quite abruptly by the discovery of patterns of astonishingly increased complexity, and the immediate correlation of these with a few large crystals in the target. Prior to this each target had been made up of a large number of small crystals. These new and complex scattering curves were certainly diffraction patterns, although naturally they could not be interpreted.

We set about at once to experiment upon a single crystal to discover the nature of the crystalline effect. Experiments on this crystal were well under way before Dr. Davisson, on a visit to England, heard there for the first time about the new de Broglie theory. The experiments were at once guided by the theory and were quickly successful. If de Broglie's theory had been developed three years later, I believe that unguided we would have recognized our scattering patterns as diffraction, but it would have been slower and there would have been considerable stumbling around before the correct interpretation was found.

My digression into the early history is now at an end.

In recent work in different laboratories various arrangements have been used for the postacceleration of the electrons of low-energy diffraction patterns so that they can be displayed on a fluorescent screen. The most widely utilized arrangement has been well developed, and equipment using it is now commercially available for the study of surfaces. A sketch of how this works is shown in Fig. 1. This sketch is drawn to scale, the distance from the crystal under examination to the fluorescent screen on which the diffraction pattern appears being about 6 centimeters.



**2A.** Clean, 98 volts

**2B.** With half monolayer of oxygen atoms, 115 volts

**2C.** With three-fourths monolayer of oxygen atoms, 100 volts

**2D.** With full monolayer of oxygen atoms, 75 volts

**Fig. 2. Diffraction patterns from a tungsten (110) face**

The extent of work currently going on in this field can be gauged from the number of workers involved and the number of papers already published. Some 30 papers, about two-thirds of them from the Bell Telephone Laboratories, have been written by nearly 25 authors. It is still a new type of investigation; interest in it has not yet been aroused in workers in the field of catalysis, which is the field that I think will ultimately profit most from the detailed knowledge of adsorption and surface reactions that will soon be made available.

Up to this time no investigation of any crystal surface has been completed, but nickel and silicon surfaces have been studied extensively by MacRae[6] and by J. J. Lander.[7] Many other metals and semiconductors have been studied less completely.

Examples of diffraction patterns are reproduced in Fig. 2. These were produced by a (110) face of a tungsten crystal, which is the densest plane of atoms in the body-centered cubic structure and presumably adsorbs all foreign atoms most weakly. These four patterns were produced respectively by a clean surface, a surface covered by half a monolayer of oxygen atoms, a surface with three-quarters of a monolayer, and finally a surface having adsorbed on it as many oxygen atoms as there are tungsten atoms in the surface (110) plane. (This, by our arbitrary definition, is a monolayer.)

The pattern of Fig. 2A is a centered rectangular array of spots corresponding very simply to the centered rectangular arrangement of tungsten atoms on a (110) face. The patterns of Figs. 2B and 2C are readily interpreted also,[8] and from the great intensities of the new diffraction features one concludes that they are due to tungsten atoms rather than to oxygen atoms. In other words, the adsorption of 0.5 or 0.75 of a monolayer of oxygen causes rearrangement of the surface tungsten atoms. The surface after adsorption is completely reconstructed. The pattern from the surface covered by a monolayer of oxygen atoms (2D) differs from that of the clean surface (2A) only in diffuseness of the features and in some weak streaks (unobservable in this reproduction) that are not produced by a clean surface. One concludes that a monolayer of oxygen atoms is adsorbed in a structure similar to that of a layer of tungsten atoms but with certain small partially random displacements of individual oxygen atoms attributable to their smaller size.

Reconstruction produced by adsorption is not unique with tungsten. It has been found repeatedly with many surfaces and with many different adsorbed gas atoms. As an extreme example, the nickel atoms on a (110) face are completely rearranged at room temperature by the adsorption of half a monolayer of *hydrogen* atoms;[9] yet hydrogen is held exceedingly weakly upon this surface! Rarely, in the still somewhat limited experience of these experiments, does adsorption of any foreign atom upon any crystal surface occur without the accompanying drastic rearrangement of the atoms of the metal or semiconductor surface. This reconstruction of surfaces by adsorption of foreign atoms upon them is without doubt much the most significant result that has been obtained up to this time from low-energy electron-diffraction studies. It will have a profound influence upon basic ideas regarding chemical reactions which go on upon surfaces. Although it is new, it should not be too surprising, for rearrangement of surface metal atoms is obviously required when oxidation takes place.

There will doubtless be many conclusions of importance following at once from this basic piece of information regarding adsorption. For example, the reaction of molecules coming up to a surface with adsorbed atoms deeply embedded in a matrix of metal atoms must be profoundly different from their reaction with atoms superficially adsorbed upon the surface. Yet the ultimate utility of low-energy electron diffraction in the field of catalysis has not yet been tapped. It is my conviction that this will be its real field of usefulness. This conviction is based on the importance of catalysis and upon the almost ideal adaptability of this technique to that subject.

The reconstruction of surfaces caused by adsorption is partially predictable by a simple rule, and the very existence of this rule makes the entire phenomenon seem at once very reasonable. Thinking of the adsorption of any gas atom upon any metal surface, one generally knows whether the bond between a gas atom and the metal is stronger or weaker than the metal bonds; this can often be found out simply by observing whether metal or gas evaporates first when the metal with gas adsorbed on it is heated. The rule with regard to reconstruction is concerned only with the stronger of these two bonds. According to the rule, among various conceivable reconstructed structures, the structure which occurs is that for which the number of missing nearest-neighbor bonds of the stronger type per unit of area is a minimum. In many cases this rule does not give a unique prediction, and of course there can be superstructures built upon a simple basic structure. The rule cannot possibly be universally true, but nevertheless it holds for a number of observed cases of adsorption and no exceptions are yet known. An interesting discussion of reconstruction has been published by J. F. Nicholas.[10]

One important question has been slighted in the above discussion. It has not been made clear why we can be so confident that rearrangement of surface metal atoms really occurs. The conclusion is based upon intensities of new diffraction features relative to those from the clean metal. We do not know atomic scattering factors for the atoms involved, and without this knowledge the conclusion that the new features are due to metal atoms rather than to gas atoms is purely subjective. This question has been taken up by MacRae[6], and the conclusions regarding reconstruction given here seem to be thoroughly justified. The nonobjective character of the evidence for reconstruction has, however, led to errors in the past. In earlier papers it has been stated more than once that reconstruction of nickel surfaces is produced by adsorption of oxygen upon a (110) face but not by adsorption upon the more dense (111) and (100) faces. The latter part of this statement was an error arising from our conservative treatment of the subjective evidence.

It is quite clear that we badly need good values of atomic scattering factors. Attempts to measure these by at least two different methods are now under way, and success will probably be attained.

In addition, when atomic scattering factors for low-energy electrons are finally available, these can be used to calculate the modern equivalent of the charge distribution inside the scattering atoms. So now we have come full circle to the original experiment conceived by Dr. Davisson. It has been a long and tortuous path that has led far afield for almost forty years.

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