Low-Energy Electron Diffraction - Circa 1968

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Almost forty years have elapsed since the discovery of what has become known as the Davisson-Germer effect [1], namely, the experimental demonstration of the wave nature of the electron. It was obvious at the outset that the diffraction of low-energy electrons (i.e., electrons with energies of the order of 100 volts) could also provide information about crystal lattices, since the diffraction patterns were directly related to the atomic patterns. However, it would probably be mainly a tool for the study of the properties of crystalline surfaces, since the penetration depth of such low-energy electrons is only a few interatomic distances, and hence the distribution and the intensities of elastically back-scattered electron beams contain information that was gathered in, and therefore concerns, the outermost layers of the target-crystal. Nevertheless, the experimental difficulties encountered in the process of obtaining reproducibly low-energy electron diffraction patterns and the theoretical difficulties encountered in interpreting such patterns were so high that in the thirty-five years that followed the discovery of the Davisson-Germer effect only FARNSWORTH [2], together with his students, persisted in this line of work. The technique employed by these workers consisted in measuring intensities and distribution of the scattered electron beams with a movable Faraday box inside a suitable vacuum system. It was with this accurate but time-consuming technique that Farnsworth and his students laboriously laid the firm foundation on which much of the subsequent work would be built.

The situation changed markedly in the years between 1960 and 1968. Many new workers in industrial and academic laboratories started low-energy-electron diffraction studies of crystalline surfaces. The reasons for this revival of interest and activity were primarily experimental. Firstly, ultra-high vacuum technology had by 1960 advanced to the point where attainment and maintenance of pressures in the 10^{-10} torr range became a routine matter in most laboratories. Secondly, several methods were developed that allowed one to clean almost any solid surface *in situ*, the most important being the ion-bombardment technique discovered by the FARNSWOTH school [2]. Thus, the ability to attain, or at least to approach, the atomically clean state of a surface, and to maintain such a state for a reasonably long time, had set the stage for the third, and most important, experimental advance. That was the development, by GERMER, LANDER and co-workers [3, 4] at the Bell Telephone Laboratories, of the post-diffraction acceleration scheme for low-energy electrons that had been proposed earlier by EHRENBERG [5]. This scheme permitted the construction of a

display-type apparatus which allows a large number of dffracted peaks to be viewed at once on a fluorescent screen, so that the symmetries and periodicities of the patterns are readily apparent. This new apparatus enabled the Bell scientists to make rapid advances in the study of surface structure and kinetics. Some of the results previously reported by Farnsworth were thereby confirmed and amplified. It was confirmed, for example, that certain semiconducting materials (Si, Ge, etc.) have surface structures which are different from those found in the bulk, while most other materials have surface structures that correspond to simple termination of the bulk structure. Furthermore, it was found that, whatever the structure of the clean surface, minute amounts of impurities often can cause rearrangements of the surface atoms leading to complicated superstructures (surface reconstruction).

Display-type apparatus for low-energy electron diffraction studies became commercially available in 1964, and consequently the number of its users increased very rapidly. A distinctive short title for the field became popular: Low-energy electron diffraction became known as LEED, and LEED literature grew rapidly. Knowledge of surface crystallography and surface reactivity was thereby extended but, by and large, remained essentially qualitative. There are two reasons for this. In the first place, there was no criterion that could unequivocally establish that a given surface was in fact atomically clean during observation. Hence, the increased activity in the field, while lengthening the list of surfaces observed by LEED, lowered the reliability of the results and the quality of the research. (Indeed, it was proven that the mere observation of a clear LEED pattern does not constitute a sufficient condition for labelling a surface wholly clean [6] or well crystallized [7]. So, a few surfaces were described as clean that were not, and vice versa. In the second place, complete theoretical interpretation of the LEED patterns observed was still lacking. It was easy to draw conclusions from a given LEED pattern about the symmetry and the periodicities of the two-dimensional surface structure associated with that pattern, but what could not be done was to deduce in detail the precise atomic arrangement within the surface layer. The structural problem, in other words, could not be solved. In place of a deductive solution, people were led to speculate on surface-structure models which had the same symmetry and the same periodicities as those obtained from the LEED patterns, but which could otherwise be justified only on crystal-chemical grounds that had nothing to do with the diffraction phenomena observed.

During the past several months, two important advances were made, one experimental, the other theoretical. We give below a brief description of both.

The *experimental* advance provides for the first time a sensitive tool for the identification of impurities on solid surfaces. The method, which may be referred to as Auger-electron analysis, consists in bombarding the surface under study with, say, 1000 V electrons, and observing the energy distribution of the Auger electrons emitted by the surface atoms. When any one such atom is, in fact, ionized by the impinging electron beam in one of its inner shells, a transition may occur in which the inner vacancy is filled by an electron from a higher level. In the course of this transition some energy is released: This energy may either appear as radiation (*x*-rays), or be communicated to another electron of the same atom, in which case this electron is ejected. The latter is called an Auger electron. Its energy is characteristic of the atom

from which it originates: The energy distribution of Auger electrons represents, in fact, something like a fingerprint of the atomic species that was subjected to the initial bombardment. The idea that the study of Auger peaks could provide a tool for surface analysis was advanced earlier by LANDER [8], but HARRIS [9] improved the instrumentation to the point where such analyses became possible. Use of this technique in conjunction with LEED observations is natural, as the geometry of the display-type apparatus is almost ideally suited to studies of secondary electron emission [10]. WEBER and PERIA [11] and PALMBERG and RHODIN [12] demonstrated in fact, within a LEED system, that Auger-electron analysis can reliably detect amounts of surface impurities equivalent to a small fraction of a monolayer. It is clear that the introduction of the Auger technique into the LEED apparatus will improve considerably the studies of clean surfaces and put on a firmer, more quantitative footing all claims about purity of the surface under examination.

The *theoretical* advance that was made recently consists in the development of a complete and accurate dynamical theory of LEED. The need for a dynamical theory, in contrast to the kinematical theory that has been so successful in x-ray crystallography, was evident for a number of years. It was well known, in fact, that, the magnitudes of atomic scattering cross sections for, say, 50 eV electrons, being of the order of 1 Å^2, are approximately eight orders of magnitude greater than atomic cross sections for x-rays [4]. Consequently, multiple scattering effects were expected to play a dominant role in LEED. Experimentally, the intensity of a given reflection reveals, when measured as a function of electron energy, a number of maxima that can be identified with normal Bragg reflections, and are thus called Bragg peaks, *and*, in addition, a number of maxima which are called secondary peaks but cannot be explained on wave-kinematical grounds. McRAE [13] was the first of the new generation of LEED workers to attack the LEED problem systematically. He developed a multiple-scattering theory than can qualitatively explain a number of experimental facts. Several other theorists followed suit with a variety of approaches [14–17]. All theories are very complicated and none can provide complete and accurate results. Very recently, MARCUS and JEPSEN [18] developed a calculation procedure whose physical significance is comparatively easy to understand and whose results appear to be more accurate and complete than those of any previous theory. Conceptually, Marcus and Jepsen's approach is a refinement of the solution to the LEED problem that had already been provided by the first generation of diffraction theorists, namely, BETHE [19] and VON LAUE [20]. Computationally, however, the approach is a very significant innovation[1]).

First review briefly the physical content of the LEED problem: A wave is incident on an interface from the vacuum and reflected waves go back into the vacuum. A partially equivalent optical problem considers a light wave incident on the interface separating two media, giving a reflected and a transmitted wave; the LEED problem is a combination of this and a reflection from a diffraction grating. We should like to know the reflection coefficients, i.e., the amplitudes of the reflected waves, because their squares give the intensities of the reflected waves. In the optical problem, equations relating the reflection *and* the transmission coefficients are obtained by

[1]) In a very recent paper, McRAE [21] developed independently, out of his earlier work, several of the mathematical procedures that were introduced by MARCUS and JEPSEN.

matching the values of the field and the values of its derivative at the interface. Hence, if we can find appropriate expressions for all reflected and all transmitted electron waves, we can apply the same procedure to the LEED problem and thus find the 'reflected' intensities. So, the first step must be to find the reflected and transmitted waves in some suitable representation.

For the wave function on the vacuum side of the interface the task is fairly simple: The wave function is a sum of plane waves with a given energy E and a given tangential component of the wave vector k_t (those of the incident wave). For the wave function on the crystal side of the interface the task is considerably more complicated: The wave function is now a sum of Bloch functions, which are solutions of the 'band problem', i.e., they are solutions of the Schrödinger equation within the infinite crystal with the given periodic potential. We must, however, include solutions in the infinite crystal for which the longitudinal components of the wave vector (k_l) are complex (the so-called evanescent waves). Now for given values E and k_t the solutions fall into pairs, only one of which is needed for the wave function at the surface of a semi-infinite crystal. Of each pair, either one member propagates away from the interface into the crystal while the other member propagates toward the interface, or, in the case of evanescent waves, one member attenuates in the direction away from the interface into the crystal while the other attenuates in the opposite direction, toward the interface. For the semi-infinite problem we are only interested in the former types of solutions, i.e., waves that propagate and attenuate in the direction away from the interface *into* the crystal, since only such Bloch functions can be produced by surface excitations.

To calculate these Bloch functions, MARCUS and JEPSEN introduce a so-called 'propagation' matrix P, which relates the values of the wave function and of its derivative in a given plane parallel to the surface to values in another plane parallel to the surface (actually the values of the Fourier coefficients of the wave function in the plane). The propagation matrix P is central to the procedure because MARCUS and JEPSEN show that the problem can be reduced to finding the eigen-vectors of P, which, in turn, can be calculated with modern high-speed computer techniques. In practice, of course, once calculates with a finite number N of propagating and evanescent Bloch waves (each conveniently represented by N Fourier coefficients), giving an N-th order approximation whose absolute accuracy can be estimated. Once the desired Bloch functions are known the matching procedure mentioned above allows one to calculate *all* reflection and *all* transmission coefficients within the N-th order approximation.

The direct LEED problem relating a given crystal potential to a LEED intensity pattern seems thus solved, at least in some simple cases. However, the inverse LEED problem of deducing the structure from an intensity pattern requires plausible and adjustable estimates of the correct form of the crystal potential to be used in the calculations, including the correct imaginary part of this potential in order to describe properly the absorption effects, and other details. Then, it requires repeated solution of the direct LEED problem. It is no wonder, *a posteriori*, that the LEED problem is so complicated: Thus in order to solve it we have to solve the band problem of the infinite crystal and then do more, i.e., satisfy the boundary conditions. On the other hand, the correlation between reflected intensities, on one

side, and the band structure along the direction normal to the surface, on the other, turns out to be extremely useful to the physical insight into the LEED problem. Both the Bragg peaks and the secondary peaks observed in intensity-versus-energy plots can be traced back to the existence of energy gaps in the band structure of the solid investigated, as was emphasized earlier by HEINE and BOUDREAUX [22, 16]. In general, the 'reflected' intensity rises upon approaching a band edge from within any given band, then, if absorption is neglected, it breaks sharply as the energy gap is entered. It can be said, in retrospect, that what were called secondary peaks are indeed reflections that can be understood in terms of Bragg's theory is multiple-scattering processes are allowed.

Probably the most important single consequence of recent theoretical developments in the field of LEED is that LEED not only is thereby confirmed as a powerful technique for studying surface structure and kinetics, but it may also achieve the status of a very useful tool for investigating the band structure of solids.

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