

Electron Diffraction

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Diffraction, in light optics, has been defined as “Any departure of the actual light path from that prescribed by geometrical optics” [1]. Contrary to light, where the discovery of diffraction preceded the wave theory, electron diffraction was discovered as a consequence of a deliberate attempt to prove the wave nature of the electron.

In 1924 Louis de Broglie advanced the, for the times, revolutionary view that electrons (or any corpuscles) are accompanied by waves [2]. The origins of that view can be traced back to Einstein’s 1905 theory about the wave–particle duality of light. Starting with this theory of Einstein, de Broglie came to the conclusion that electrons should exhibit the same kind of dual nature as light, where the relation between a particle’s mass m_0 , its velocity v , and its wavelength λ could be expressed as

$$\lambda = \frac{h}{m_0 v}$$

h being the constant of Planck. Today we usually write the de Broglie relation as

$$\lambda = \frac{h}{p}$$

where p is the momentum of the particle; this formulation implies the necessary relativistic correction.

About a year later a young graduate student at the University of Göttingen, Walter Elsasser, surmised that Clinton J. Davisson and Charles H. Kunsman’s work on the scattering of slow electrons by metal surfaces [3] may have shown evidence of the diffraction of the electrons by the crystal lattice, thus supporting de Broglie’s view of the wave nature of the electron [4].

In 1927 came definite evidence for the particle–wave duality through the discovery of electron diffraction by crystal lattices. This discovery was made almost simultaneously by C. J. Davisson and Lester H. Germer, using slow electrons diffracted by a nickel single crystal [5], and by George P. Thomson and A. Reid, using fast electrons passing through a thin celluloid film [6]. Their work was followed by rapid confirmation and extensive further development. Quite early it was shown that the angular dependence of the diffracted beams satisfied Bragg’s law (originally established for x-ray diffraction):

$$n\lambda = 2d \sin \theta$$

where d is the interatomic distance, θ the diffraction angle and n an integer. The de Broglie wavelength λ , as calculated from the relativistically correct equation

$$\lambda = \frac{h}{[2m_0 eV(1 + eV/2m_0 c^2)]^{1/2}}$$

was confirmed with good accuracy. In this equation e is the charge of the electron, c the light velocity, and V the potential difference applied to accelerate

the electron [7]. It was also shown that, while the Davisson–Germer experiment corresponded to the Laue diagram of x-ray diffraction, the Thomson–Reid experiment was a counterpart of the Debye–Scherrer diagram of x rays.

Because of easier experimental requirements (lesser vacuum, less stringent control of the accelerating potentials) the high-voltage, transmission method (Thomson) developed much faster than the slow-electron reflection technique. The original diffraction cameras, consisting of an electron source and an aperture, collimating the beam before it passed through the specimen, were soon replaced by the arrangement first suggested by A. A. Lebedev [8]. In this arrangement an axially symmetrical magnetic field, the axis being parallel to the electron beam, is used to focus the beam on the recording medium (usually the photographic emulsion). This procedure has the advantage of replacing a well-collimated beam with a divergent beam and still attaining a higher intensity of the recorded pattern. At the same time this device allows the use of a larger area of the specimen. The accelerating potentials used by different authors were generally in the 10- to 100-kV range, resulting in electron wavelengths corresponding to $(12.2\text{--}3.7)\times 10^{-12}$ m (0.0122–0.0037 nm).

In the experiments described so far, diffraction was produced by periodic structures, such as crystal lattices. The reason for this is that the discovery of the equivalent to x ray diffraction antedated by about 10 years the discovery of diffraction on opaque edges. In light optics we are familiar with the two kinds of edge diffractions: the Fraunhofer diffraction, produced by a plane wave front; and the Fresnel diffraction, produced by all other wave fronts. Because of the extreme shortness of the electron wavelength, the interference fringes, caused by the diffraction effect, are so closely spaced that their observation required a high degree of resolution of the electron optical system used for recording them. By 1940 the electron microscope was sufficiently developed for the observation of Fresnel fringes, and they were described almost simultaneously by H. Boersch [9] and J. Hillier [10]. By that time, all workers in electron microscopy agreed that the resolving power, as in light microscopy, is diffraction limited and obeys the Abbé relation

$$\rho = \frac{0.61 \lambda}{n \sin \alpha}$$

where ρ is the least resolved distance, n the index of refraction of the medium surrounding the object, and α the semiangle subtended by the object at the lens.

The year 1940 also marks the beginning of another important link between electron diffraction and electron microscopy. Until that time the dominant interpretation of the origin of contrast in electron microscope images was based on mass-thickness scattering by the specimen [11]. B. van Borries and E. Ruska found, however, variations of intensities in chromium oxide smoke images, which could not be interpreted by scattering alone [12]. This finding was followed by the observation of Bragg reflections in images of crystalline specimens [13, 14] and led finally to the theory of diffraction contrast in images of crystalline specimens [15, 16].

Introduced in 1939, convergent-beam electron diffraction started being used

only in the 1970s [17, 18]. Instead of illuminating the sample with a parallel beam, the beam is focused as a convergent cone onto a submicron area in the transmission mode. Advantages are the small-scale analysis area, avoiding twinning and other faults, for example, and microstructure fingerprinting of complex materials.

In the 1980s, electron microscopy started being applied to surfaces, using either samples of submicron thickness with the transmission mode, or submicron-size particles grown on carbon supports in the profile imaging mode [19, 20]. In this manner, deviations from the bulk structure were observed in the first one or two atomic layers of the surface. Obtaining ultrahigh-vacuum conditions is a necessity for control of surface composition [20].

For an understanding of intensity relations in electron diffraction and in electron microscope images of crystalline objects, detailed calculations based on the theory of diffraction phenomena are necessary. There are two theories of electron diffraction: the kinematic (or geometric) theory and the dynamic theory. Both theories were developed originally for x-ray diffraction and adapted for use with electrons. The kinematic theory, in the ideal case, describes the interaction of the electron with a single atom and derives the intensities of the resulting beams. The dynamic theory takes into account the multiple scattering resulting from the presence of many atoms. This theory requires a wave-mechanical treatment, since the scattering produces a background that very considerably modifies the intensity distributions. X rays, which produce much less scattering than electrons, can usually be treated by means of the kinematic theory. In the case of electrons, very thin layers of crystals, roughly below 100 atom layers thick, give diffraction phenomena sufficiently well described by the kinematic theory. Above a thickness of 100 atom layers there is so much scattering that we have to have recourse to the dynamic theory [15, 16, 21]. The thicknesses employed in electron microscopy require the application of the dynamic theory in calculating image intensities [22].

In 1928, however, S. Kikuchi, while observing the diffraction of electrons passing through thin mica sheets, discovered a pattern differing widely from the single-crystal Laue spots or the polycrystalline Debye–Scherrer patterns [23]. He found a system of lines and bands, requiring a modification of the dynamic theory. These Kikuchi patterns consist of a continuous angular distribution of inelastically scattered electrons modulated by lines or band edges at the position of the various Bragg reflections. The energy analysis of the electrons diffracted into a Kikuchi line has shown that, for silicon, the average energy loss was about 450 eV, in contrast to the ten-times-lower loss for the ordinary patterns taken in transmission [24].

Similar effects are found with electrons that have energies on the order of 1000 eV and that have either lost energy to an excitation or have themselves been emitted by, for example, a photon in photoelectron emission. Such electrons radiate outward from the point of interaction and are diffracted by the surrounding lattice. They thereby carry structural information which can modulate the excitation process, as in extended x-ray absorption fine structure (EXAFS) [25]. Near a surface, the electrons themselves can escape to a detector and

deliver surface structure information, as is the case with photoelectron diffraction [26].

For three decades high-energy electron diffraction (HEED) remained the only practical approach to the problems accessible by diffraction methods, although L. H. Germer pointed out quite early [27] the advantages of low-energy electron diffraction (LEED). By 1960, however, two of the experimental obstacles to LEED were removed: high-vacuum technology was radically improved to the extent that the surfaces investigated remained stable during the experiment; and the low intensities of the diffraction patterns, which hampered earlier work, could be enhanced by post-acceleration of the diffracted electrons. The usual energy range of LEED is from 20 to 500 eV, corresponding to a wavelength range of $(274\text{--}55) \times 10^{-12} \text{ m}$ (0.274–0.055 nm). In the case of LEED, multiple scattering is largely unavoidable and the dynamic theory therefore a necessity [28]. Due to strong inelastic and elastic scattering at LEED energies, the electron mean free path is small, 5–10 Å, and the electron–atom scattering cross section is large, comparable to the geometrical atomic size. The LEED theory in common use is an adaptation of the theory of electronic band structure, after inclusion of inelastic damping and of x-ray-like Debye–Waller factors to describe vibration effects. The theory is capable of determining structures within atomic and molecular monolayers to an accuracy of 0.01–0.1 Å. Traditionally a trial-and-error search procedure has been applied to structure determination, but advances such as tensor LEED [29] and the direct method [30] permit rapid and computer-efficient determinations.

The discovery of electron diffraction was followed, within a remarkably short time, by application of the new effect to many other problems. Within the framework of this short survey it is necessary to limit ourselves to an enumeration of some of these applications, without extensive discussion. As with x-ray crystallography, structure determinations have been in the forefront. Because of the limited penetration of electrons, surface structures are much more accessible to electron diffraction investigation than to xrays. Thus surface physics benefits both from HEED reflection observations and from observations by means of LEED. For example [28], it was found that many clean metal surfaces exhibit ideal bulk lattice terminations, but show small relaxations in the first few atomic layers. Other metal surfaces and most semiconductor surfaces, by contrast, reconstruct: one or more atomic layers adopt lattices that differ from the bulk lattice. Also, a few hundred structures of atomic adsorption have been solved. They often involve simple bonding in high-coordination “hollow” sites of the substrate. Increasingly many cases of adsorbate incorporation into or adsorbate-induced restructuring of the substrate are being uncovered. Such results are of direct value in such diverse fields as microelectronic device properties, catalysis, corrosion, and tribology.

HEED in transmission is very widely used for the study of thin films of monocrystalline, polycrystalline, or amorphous materials. In the gaseous phase HEED is very useful for the study of molecular structures [29]. Within 10 years after the discovery of electron diffraction, results were published on more than 150 substances and by 1953 Pinsker’s book [21] tabulated the structures of about

500 molecular species.

Selected-area diffraction has been extended from the high energies [15] to surface-sensitive energies in the low-energy electron microscope [31]. Thus areas of the order of $0.1\text{--}100\ \mu\text{m}^2$ can be selectively examined. Using computer simulations of emitted photoelectrons, Barton has for the first time shown the possibility of performing holography with electrons [32]. This technique will allow one to generate three-dimensional real-space images of a crystalline lattice with atomic resolution. With less than atomic resolution, only perpendicular to the surface, a screw dislocation has in fact been imaged using reflection-electron holography [33]. Electron diffraction on three parallel single crystals, placed at about $0.035\ \text{m}$ distance from each other, was used to create the electron optical analog to the Mach-Zehnder interferometer [34], by means of which for the first time electron interferometer fringes could be observed [35].

See also: Crystal Defects; Crystallography, X-Ray; Diffraction; Electron Microscopy; Gratings; Holography; Interferometers and Interferometry; Low-Energy Electron Diffraction (LEED); Quantum Mechanics; Reflection High-Energy Electron Diffraction (RHEED); Surfaces and Interfaces; X-Ray Spectra.

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