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IN MEMORIAM

Herman F. Mark – Pioneer of polymer chemistry and initiator of the gas-phase electron diffraction technique of molecular structure determination

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Abstract
Herman F. Mark (1895–1992) was an Austrian-born American pioneer of polymer chemistry. He made substantial discoveries in other areas of chemistry as well. One of them was in 1930, when he and his physicist associate, Raimund Wierl, initiated the gas-phase electron diffraction technique of molecular structure determination. This article follows Mark's path to establishing the new technique, presents the circumstances of the discovery with emphasis on Wierl's contribution, and concludes with mentioning Mark's career in his American life. Mark had a long and most successful professional career and best known for his polymer science. Wierl died young so his role in establishing the technique of gas electron diffraction remained his principal contribution to science.

Keywords Herman F. Mark · Raimund Wierl · Linus Pauling · Gas-phase electron diffraction · Brooklyn Poly

Mark before 1930

Herman F. Mark (1895–1992 [1, 2], Figs. 1 and 2) was born in Vienna, the child of a Budapest father and a Viennese mother. He spoke German, Hungarian, Czech and Polish and had many attributes of a typical citizen of the Austro-Hungarian dual monarchy. He grew up in a loving family of high culture and strict discipline during the last years of the "happy peace time," which ended when World War I, the "Great War," broke out in 1914. He entered military service following his high-school graduation, was thrice wounded in the war, and earned the highest awards for valor. At the end of the war he was captured and spent almost an entire year in an Italian POW camp for officers. There, he studied Italian, French, and English.

In 1919, he enrolled in chemistry studies in Vienna. When his professor, Wilhelm Schlenk, was invited to Berlin to succeed the deceased great organic chemist Emil Fischer, Mark followed Schlenk. Soon, Mark joined the new Fiber Research Institute of the Kaiser Wilhelm Society (the predecessor of today's Max Planck Society) in Berlin-Dahlem. The institute was created to aid the German textile industry, but its activities were broad-based with much emphasis on structural studies. Mark became a member of a research group under Michael Polanyi's leadership. Polanyi was a physician-turned physical chemist who three decades later changed once again his principal area of activities and became a philosopher [3]. Mark participated in the structure determination of a wide range of substances moving eventually to the study of fibrous materials, such as silk, cotton, wool, and others—all being natural organic substances of high molecular weight. In a few years, Polanyi, Mark, and others in Berlin-Dahlem became respected members of the international community of fiber chemists who used X-ray crystallography as their main research tool. They determined interesting and important structural characteristics of materials, among them, metals. Their achievements paved the way for future structural studies of other high-molecular-weight materials—large biological molecules—that at the time were not yet amenable to detailed structural characterization. Mark was also involved in professorial activities. The future physics Nobel laureate Eugene P. Wigner studied chemical engineering at the *Technische Hochschule* in Berlin and he prepared his Diploma work (Master's degree equivalent) with Mark's supervision. Mark suggested to Wigner to investigate the symmetries of the rhombic sulfur crystal for Wigner's thesis. According to a Polanyi biography,

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Fig. 1 Herman F. Mark (photograph courtesy of the late Herman F. Mark)

Fig. 2 Bust of Herman F. Mark by unknown sculptor at the Jacobs Building of Brooklyn Poly (photograph by I. Hargittai)

this was the first step in Wigner's interest and spectacular career in symmetry studies [4]. They published a substantial study [5]. Toward the end of Wigner's life, he remembered Mark [6]: "He was a pleasantly vigorous man who liked food and wine, games, and song. Mark's father, like my own, was a Jew who had converted to the Lutheran faith. Herman Mark had a bit of the Hungarian kings in him. Like a king, he was scrupulously honest, ready to act, and fond of those in his care; but again like a king, he saw no need to consult others closely or to justify his actions." As for Mark, as his thesis advisor, Wigner noted [7]: "Mark chose not to closely supervise my thesis. We talked generally about my topic. Crystallography, the science of crystal structure, is wonderfully full of symmetry, and I told Mark how fascinated I was by the crystal structure of sulfur. … Mark assured me that he was quite pleased to see me so fascinated with my work, but I must pardon him if he was somewhat less fascinated with it. Mark was not an easy man to impress." For doctoral dissertation, Polanyi acted as Wigner's "Doktor-Vater." It was about the mechanism and reaction rates of chemical reactions.

Mark's principal research interests were in cellulose and rubber. He studied their mechanical properties and was looking for their interpretation at the molecular level. This research was a good example of demonstrating the preeminence of novel instrumentation, in this case the powerful X-ray diffraction apparatus. Again, the work was broad-based and along with solving problems of chemistry, they interacted with leading physicists, invoking their help as well as providing assistance to their research. A conspicuous example was when in 1924, Albert Einstein asked the Berlin-Dahlem physical chemists to see if they could verify the existence of the "Compton effect." It was about the scattering of X-rays by free electrons, and Mark and his colleagues verified it.

In 1926, Mark made another move. At the suggestion of Fritz Haber, a leader of the Kaiser Wilhelm Society at the time, Mark left the Fiber Institute and took an important position at the research laboratory of the giant company, I.G. Farbenindustrie. Under the Nazi rule this company gained terrible notoriety. It exploited slave labor in Auschwitz and elsewhere and one of its subsidiaries provided the poison gas Zyklon B to murder concentration camp inmates during the Holocaust. In the 1920s it was still benevolent research for which Mark was enthusiastic to join it. He received assurance that he would be able to continue his fundamental research in the industrial laboratory. From the end of 1926 Mark spent 6 most fruitful years in Ludwigshafen, working for the company. Not only could he continue his fundamental research along with solving the immediate tasks of industrial importance, he could even initiate a new tool for molecular structure determination: the technique of gas-phase electron diffraction.

Gas-phase electron diffraction

The discovery of the technique of gas-phase electron diffraction was preceded by two profound theoretical discoveries. One was in 1915 when Peter Debye examined the X-ray scattering by a rigid system of electrons that can occur in all possible spatial orientation (either in time or at once if supposing a large number of such rigid systems) [8]. The finding was that the interference pattern does not extinguish completely despite the presence of all possible orientations of the system. On the contrary, there will be a characteristic interference pattern in the average intensity distribution of the X-ray scattering as a function of the scattering angle. This average intensity distribution will depend on the distances between the electrons constituting the rigid system of electrons. If substituting the electrons by atoms, the X-ray scattering of rigid molecules in all possible orientations can be considered—as if they were in a gaseous sample. Even lacking a preferred orientation, the geometry, i.e., the mutual distances of the atoms constituting the molecules, could be determined on the basis of the average scattering intensity distribution. Still this discovery did not bear practical fruit, because the free molecules, that is, a gaseous sample, would need an impractical long exposure time, and a gaseous X-ray diffraction technique of molecular structure determination never took off. The other theoretical discovery was by Louis de Broglie [9] who recognized the wave nature of moving electrons and established the interrelationship between their wavelength, λ, mass, m, and velocity, *v*,

$$\lambda = h/mv \tag{1}$$

where h is Planck's constant (and, in this simplified expression, the relativistic correction is ignored).

In 1927, electron scattering experiments verified this relationship, by slow electrons [10] and fast electrons [11]. Whereas X-ray diffraction is a consequence primarily of the scattering by electrons, electron diffraction is primarily caused by the atomic nuclei and only in small part by the electrons. Hence, the intensity of the matter and irradiation in case of electron diffraction may be many thousand times higher than in case of X-ray diffraction [12]. Accordingly, the tremendously long exposure time necessary for X-ray diffraction of a gaseous sample can be reduced to minutes, even seconds for electron diffraction. In hindsight, all this is common knowledge, but Mark was the first who recognized that these differences might lead to the creation of a new technique for the determination of molecular geometry. (Later, of course, consideration of molecular vibrations became also part of the utilization of the technique.)

Mark asked one of his physicist associates, Raimund Wierl (1903–1932), to join forces with him. Wierl soon performed the first gas electron diffraction experiment on a gaseous sample of carbon tetrachloride, CCl_4. That this molecule was selected for their first trial shows once again how much deep thinking went into this project. The choice was dictated by the presence of the four relatively heavy chlorine atoms in a tetrahedral structure, so there was hope for the diffraction pattern being dominated by the Cl…Cl distances. From them, supposing tetrahedral geometry, the C–Cl bond length could be calculated. This was the first direct determination of the length of a covalent bond. It pointed the way toward heretofore unreachable possibilities of molecular structure determination by this new technique. In their first publications [13–16] demonstrating gas electron diffraction, Mark and Wierl communicated bond length data for several simple molecules.

As a tribute to Wierl and to appreciate the circumstances of the first gas electron diffraction experiment, I quote Mark's words about them [17]. First about Wierl: "When I asked Dr. Raimund Wierl, one of the three high level physicists in our laboratory of his opinion he agreed that such experiments would be very interesting but certainly not easy. Wierl had received his PhD summa cum laude with Professor Willy Wien in Munich and had an excellent training in the physics of high vacuum and high voltage." Here the reference was made to the Nobel laureate (1911) physicist Wilhelm Wien. Then, here are Mark's words about the experiment, and it is remarkable how well its conditions and requirements could be anticipated [17]: "The electron beam had to be *narrow* and well *collimated*, which is difficult to achieve because the negatively charged electrons repel each other as they travel together close to each other over a distance of a few centimeters. The beam has to be *monochromatic*; according to Eq. (1) that means that all electrons should have the same velocity distribution, which, for the purpose of this test would have to be narrowed as much as possible. This electron beam would have to impinge perpendicularly on a jet stream of the gas which had to be as narrow and as dense as possible in order to give a maximum of interaction between the electron and the scattering molecules. All this had to happen in a vacuum camera in order to avoid any scattering of a gas which did not belong to the jet stream. Evidently the execution of this experiment required inventiveness in instrument construction and extreme care and skill in the execution." (italics in the original) Apparently, Mark participated in the planning, but left the realization to Wierl. To continue with Mark's words [17]: "Fortunately Wierl had both to an admirable degree and already a few weeks after our first conversation he came with a beautiful photograph of carbon tetrachloride produced with 45 kV electrons in 1/10 of a second. What a tremendous difference between this test and the daylong exposure with x-rays with more diffuse patterns of lower contrast." It was of historic importance when Mark and Wierl announced the new technique in a 1-page communication in the prestigious journal Naturwissenschaften [14]. The example they demonstrated their experiment was carbon tetrachloride, the accelerating electron voltage was 36 kV, and the exposure times were 1 to 3 s. Considering the 20-h exposure time for a similar X-ray diffraction experiment, it was an at least 24,000-times reduction. Mark and Wierl were true pioneers, but they were also meticulous not to claim absolute priority for the idea. They noted that Walther Bothe already in 1929, on the occasion of a discussion of X-ray irradiation, raised the possibility of electron diffraction investigation of gases [14, foot note 2]. Bothe was a future (1954) Nobel laureate physicist.

Incidentally, by the time Mark and Wierl' first publications had appeared, Wierl' attention had moved to the investigation of crystalline surfaces by electron diffraction in line with the interests of the laboratory. He died very young, at the age of 29. He is buried in a family grave in the cemetery *Waldfriedhof,* Munich.

Whereas the investigation of crystals fit the research program of the industrial laboratory, the study of the structure of gaseous molecules did not, and there were no plans to continue this line of research. Fortunately, however, it was at this time that Linus Pauling visited Herman F. Mark and his laboratory and Pauling recognized at once the perspectives offered by this new techniques: "I was overwhelmed by my immediate realization of the significance of this discovery" [18]. Pauling's main interest at the time was in the nature of chemical bonding and he was in need of reliable structural information of free molecules. The coincidence of his visit and Mark's desire to see his discovery to be utilized elsewhere led to Pauling's taking with him the technique of gas electron diffraction to Pasadena, and not only the idea of the new technique but much valuable information about its technical realization. Mark even supplied Pauling with the blueprint of the design of the apparatus he and Wierl had developed. In Pauling's opus magnum, *The Nature of the Chemical Bond*, there is a plethora of information from his and his students' gas electron diffraction studies [19].

Pauling and his doctoral student, Lawrence O. Brockway, at the California Institute of Technology in Pasadena, introduced innovations in the application of the new technique of molecular structure determination. The most significant was the Fourier transformation of the intensity data thereby having produced a probability density distribution of the intramolecular interatomic distances [20]. Whereas the average intensity distribution of electron scattering did not display any direct information about the geometry of the molecule, its Fourier transform showed individual peaks corresponding to individual interatomic distances. Even for didactic purposes this became a great tool in demonstrating information about molecular structure. Brockway went on and established his gas electron diffraction laboratory at the University of Michigan, Ann Arbor. Two of his former graduate students, Isabella Karle and Jerome Karle, eventually, added considerations of molecular vibrations and made great strides in making the structural information yielded by the technique even more quantitative. By then, other laboratories had also developed, further improving the technique and producing valuable structural information. Perhaps the most brilliant of them was the Norwegian group [21], and the technique became a choice method in structural chemistry. The Nobel laureate Jerome Karle, himself a pioneer of the field succinctly summarized its significance in 1988 [22]: "As a result of the dedicated efforts in a relatively small number of laboratories, gas electron diffraction has served as a valuable tool in the investigation of molecular structure. Much information has been obtained concerning molecular configuration, bond distances and angles, internal motion (including hindered internal rotation and barrier heights), preferred orientation in conformers, and conjugation and aromaticity. Investigations have also concerned mixtures in equilibrium, including evaluations of thermodynamic quantities, free radicals, a wealth of high-temperature studies, clusters, isotope effects, and the joint use of other techniques such a laser excitation, microwave spectroscopy, and mass spectrometry." The technique never became a tool utilized in many laboratories; even at its height, perhaps in and around the 1980s, it was being practiced in no more than 25 laboratories in Europe, the USA, and Japan. By now, in the 2020s, only a handful of laboratories carry on as increasingly more efficient and reliable as well as considerably less labor-intensive computational studies have overtaken much of the related research. But this is a whole other story. Here the aim was to show Herman F. Mark and Raimund Wierl's contribution and have a glimpse into its immediate consequences.

Mark at Brooklyn Poly

Herman F. Mark had spectacular successes in his I.G. Farbenindustrie laboratory in Ludwigshafen. He reached important results in his studies of cellulose, rubber, and synthetic polymers. In addition to his achievements of industrial significance, he had findings of fundamental character, including structural aspects of the polymers. At the time the existence of long-chain molecules held together by covalent bonds was still not considered proven. Hermann Staudinger had postulated that rubber and some other substances consisted of covalent very long chains with molecular weights in the hundred thousand order of magnitude. However, the evidence Staudinger and his associates provided were not convincing. Eventually, X-ray diffraction data obtained in Berlin-Dahlem and Ludwigshafen by Mark and his colleagues as well in

Leeds, England, by William T. Astbury provided unshakeable evidence of the existence of covalently bonded macromolecules. Mark and his colleagues worked on cellulose, starch, silk, rubber, and others and Astbury worked on hair and wool. It is regretted that Staudinger never properly recognized Mark's crucial scientific contribution to show the validity of his, Staudinger's, hypothesis. Staudinger, alone, was the recipient of the 1953 Nobel Prize in Chemistry "for his discoveries in the field of macromolecular chemistry."

Mark was interacting with universities and not only by involving famous professors as consultants but also acting as lecturer and consultant himself. Thus, for example, Mark was Edward Teller's favorite professor at the University of Karlsruhe. There, Teller was still studying for his chemistry degree, and he signed up for Mark's course on wave mechanics. The subject was almost as new for the young professor as it was for his students, and it was Teller's introduction to modern physics. Mark and Teller became life-long friends despite their age difference [23].

As time went by, he was feeling increasingly the looming Nazi threat, but the most frightening action against his and his family's lifestyle did not come from street fights of Nazi thugs. Rather, I.G. Farbenindustrie did not wait for the Nazis to take over Germany in 1933, which would start its rein with enacting legislation leading to the dismissal of Jewish scientists. As early as the summer of 1932, Mark's company superiors told him that on account of his father's Jewishness, he could not expect promotion or advancement and they advised him to leave the company and to move out of Germany. Mark and his family returned to his native Vienna in 1932, and he became a Professor of Physical Chemistry at the University of Vienna. He gave the main course of physical chemistry, introduced a state-of-the-art curriculum in polymer chemistry, conducted research in the structure and properties of polymers, and invigorated the international contacts of the university. This creative period came to end in March 1938 with the *Anschluss*, Austria's annexation by Nazi Germany. For a brief period, Mark was even incarcerated by the Gestapo. He was subjected to days of interrogation because of his prior friendship with Austria's former chancellor Engelbert Dollfuss who was assassinated by the Nazis in 1934.

In April 1938, Mark and his family were already on the road to emigration. They spent two years in Canada, where he worked in an industrial laboratory. In Fall 1940, he joined the Polytechnic Institute of Brooklyn (as it was then, "Brooklyn Poly") and during the war he worked for war-related research. After the war, he was much involved in international cooperation and assisted the development of the Weizmann Institute, which began some time before the birth of the State of Israel. He had other fruitful interactions with many other international institutions and organizations. In the focus of his activities was the establishment what became the Polymer Research Institute in 1946. It is not the purpose of this note to detail the achievements of Mark and his Institute. Instead, I quote from the plaque of National Historic Chemical Landmark erected on the wall of Polytechnic University (as it was at the time) by the American Chemical Society on September 3, 2003: "The Polymer Research Institute was established in 1946 by Herman F. Mark, a pioneer in the study of giant molecules. The Institute brought together a number of polymer researchers to create the first academic facility in the USA devoted to the study and teaching of polymer science. Scientists associated with it later went on to establish polymer programs at other universities and institutions, contributing significantly to the development and growth of what has become a vital branch of chemistry, engineering and materials science."

To give a feeling of proportion of Herman F. Mark's achievements, I note that of the close to 150-page book of his autobiography [1] less than 2 pages are devoted to the discovery of gas electron diffraction and one of the 2 pages is a long quote by Linus Pauling [24].

I augment this note by mentioning my only personal encounter with Herman F. Mark. It happened in 1987–1988 when we were organizing our two-volume edited treatise, *Stereochemical Applications of Gas-Phase Electron Diffraction* [25]. We invited Mark to prepare its Introduction, which he did. It was quite detailed and factual with the necessary references. He wrote about the history of the discoveries that led to establishing the technique of gas-phase electron diffraction, about the design of the first apparatus, and about the initial structural results yielded by their first experiments. He concluded with a brief summary of the contents of our two volumes. At the time, Mark was 92 years old.

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