

Chapter 2

Ionizing X-rays

2.1 Luminescence

The emission of light by a hot or heated object is called incandescence. In the nineteenth century, city, factory, and household lighting were dominated by the gas light industry. Efforts to produce better incandescent lighting, powered by electricity, started after the development of large batteries, known as voltaic piles, in 1800. Further interest in electric lighting was sparked when the electromagnetic generator became available after 1831. A practical incandescent lightbulb and electrical supply system was created by Thomas Edison during 1878–1880 [1, 2]. Another incandescent light source was the Welsbach gas mantle made in Germany from 1891 to the present (see Chap. 4). Chemist Carl Freiherr Aurer von Welsbach produced a knitted cotton fabric (mantle) soaked in thorium oxide with trace amounts of a “rare earth” element (REE) like cerium. This Aurer Mantle was placed in a gas flame and could burn for 3000 h compared to 1000 h for an incandescent bulb. The Aurer Company claims that 75,000 of their gas streetlamps are still in use worldwide. A portable gas mantle lamp is available for sportsmen and for outdoor family recreational use [2, 3].

A substance is luminous or luminescent if it emits visible light for any reason other than a rise in temperature or by heating. The element phosphorus was discovered in 1669 by the physician and alchemist Hennig Brand of Hamburg. He extracted it from urine as a waxy white substance that glowed (was luminous) in the dark! The element was named “phosphorus” after the Greek word meaning “light bringing” which was used to indicate the morning star, usually Venus, which appeared at daybreak. During the late eighteenth century, phosphorescent came to mean the property of being luminous at temperatures below incandescence, such as (a) from the slow oxidation of phosphorus or (b) after exposure to light or other radiation [1, 2, 4–6].

Different tetrahedral configurations of phosphorus and oxygen give us white, red, and black phosphorus. White phosphorus is luminous in the dark, poisonous and flammable, igniting spontaneously in air unless stored under water. Red phosphorus is less flammable and less poisonous and black is insoluble and least

flammable. “Self-igniting matches,” which used white phosphorus, were developed during the early nineteenth century. They required confinement in a glass vial that was then broken to produce a flame. By 1830, “friction matches” known as “Lucifer’s” were invented. The match head, impregnated with white phosphorous, was drawn between folds of sandpaper to ignite. Airtight metal boxes were used to prevent spontaneous or accidental ignition. In World War I, the doughboys were still using Lucifer’s to “light their fags.”

White phosphorus was toxic for those workers manufacturing the matches as its chronic absorption caused bone necrosis (“phossy jaw”), and it was poisonous to those accidentally or purposely eating the match heads. These matches were gradually outlawed in most countries between 1872 and 1925. “Safety matches” were developed which used red phosphorus on a separate specially designed striking surface instead of inside the match head [1, 2]. In the 1920s, “phossy jaw” was often confused with the jaw (mandible) necrosis seen in radium poisoning (Chap. 6). Both phosphorus and radium are deposited in bones.

“Fluorspar” had been coined in 1530 by Agricola (George Bauer, 1494–1555) as a Latinized version of the German “Flussspat,” a mineral which was used as a flux for smelting metals. Fluorspar lowered the melting point and decreased the viscosity of solutions making them more fluid. “Fluo” or “fluores” means “to flow” in Latin. Fluorspar was made into an acid and was used for etching glass in the eighteenth century. By 1771, Swedish apothecary Carl W. Scheele began to study what was now called fluorine acid. By 1810, fluorspar was suspected to harbor a new element. By 1824, other fluorite minerals had been discovered. This confirmed that a new element would be found that would be similar to chlorine, iodine, and bromine [4–6].

Humphrey Davy (1778–1829), who had correctly identified chlorine as an element, suggested the name fluorine. By 1869, fluorine was included in the periodic table [7]. Because of its toxicity, many chemists were injured or died, trying to isolate fluorine. Henri Moissan (1852–1907), a chemist at the Sorbonne, isolated fluorine in 1886. He earned the December 1906 Nobel for his work. After returning from Stockholm, Moissan died, 2 months later, of what was thought to be an acute case of fluorine poisoning [8]. The term fluorspar was replaced by fluorite as the new mineral name and “fluorspar” was identified as the mineral compound calcium fluoride (CaF_2), which was first studied for its fluorescence in 1824.

The phenomenon of fluorescence had been observed for centuries before it came under scientific study in the nineteenth century. In 1824, a German mineralogist, Frederick Mohs (1775–1859), observed that, when viewed under ultraviolet light, calcium fluorite (CaF_2) crystals appeared a completely different color than when viewed in daylight. Alexandre Edmond Becquerel (1820–1891) in 1842 reported light emission from calcium sulfate crystals after exposure to ultraviolet light. He found that the emitted light was of a longer wavelength (visible light) than the inciting ultraviolet light, which was invisible. Sir John Frederick Wm. Herschel (1792–1871) found the same luminescence after quinine sulfate crystals were exposed to ultraviolet light. He dubbed it “epipolic dispersion”; a term which was fortuitously rejected [5, 6].

At Cambridge, George Gabriel Stokes (1819–1903) published a 100-page monograph on the subject in 1852. Since fluorspar, a fluorite mineral, also exhibited the

luminescent phenomenon, Stokes coined “fluorescence” to describe the emission of visible light by a substance *during* exposure to external radiation such as invisible ultraviolet light. Fluorescence occurred because of the absorption of incident radiation and it persisted only as long as the stimulating radiation was continued. The noted shift in wavelength, from invisible to visible, became known as the Stokes shift. By 1989, it was estimated that 566 of the 4200 known minerals exhibit fluorescence [5, 6, 9].

Color in minerals was found to be due to the presence of trace elements inside the crystalline structure; a trace element being one with a concentration less than 1000 parts per million (ppm) or 0.1 % of a *rock*’s composition [6]. Trace elements exist in an electronically unstable state as a result of not fitting perfectly within the crystal structure they currently occupy. When exposed to any kind of light, the atoms of the trace elements absorb energy and move into a higher energy level or state of excitation. This lasts for only a fraction of a second before the previously absorbed energy is released and the atoms return to their prior energy level or state of excitation. The excess energy is released as visible light. The color of the visible light, which is released by fluorescent minerals, will differ depending on the energy difference of the inciting light: daylight or ultraviolet [9].

The term “fluorescence” came into use in order to differentiate it from “phosphorescence.” Fluorescence was defined as the emission of visible light that occurs only during the exposure to inciting energy. If the luminescence does not persist after the exposure has terminated, it is called *fluorescence*. Any luminescence which persists for any time after removal of the exciting agent is called *phosphorescent*. A mineral from Connecticut was reported to phosphoresce for 36,000 h after ultraviolet exposure ended [5]. Technically, if light persists over 10 ns (10^{-8} s), it is phosphorescence. If the light persists for only 10 ns or less, it is *fluorescence*. The distinction has become rather arbitrary and the terms are often interchangeable for the average person [5, 6, 9].

2.2 Fluorescence

The discovery of both X-rays and radioactivity during 1895–1896 was due to the observation of fluorescence, caused by unknown invisible light rays. The discovery of X-rays came about during the investigations of the discharge of electricity through gases which were confined within sealed glass vacuum tubes. After 1800, electricity from voltaic piles was used to separate chemical compounds into their individual elements, a process which became known as electrolysis. During 1807–1808, English chemist Humphrey Davy (1778–1829) passed an electric current through various molten or liquid mineral compounds and was able to isolate six new elements: *sodium*, *potassium*, *calcium*, *magnesium*, *boron*, and *barium* (Na, K, Ca, Mg, B, and Ba) [1, 4].

Davy found that his greatest discovery was his student, Michael Faraday, in 1813. Faraday went on to establish the basis of electrolysis, electrochemistry, and electromagnetism. In 1838, Faraday (1791–1867) passed electrical currents through rarefied or low-density gases. The gases were contained within a sealed glass tube

which had been only partially evacuated due to the poor vacuum pumps of the time. Faraday described the luminescent glow that developed in the glass tubes when the current flowed through the gases. “The rarefaction of the air wonderfully favors the glow phenomena.” The luminescence that Faraday described in his discharge tubes was considered to be due to electromagnetic radiation acting upon the *gases* in the tube in the same way as ultraviolet light acted upon various mineral crystals. Faraday’s work sparked the interest of nineteenth-century physicists in the passage of electricity through rarefied gases in a vacuum tube [1, 10–12]. Those involved in vacuum tube research in Germany and the UK included:

1838	Michael Faraday (1791–1867), UK
1855	Heinrich Geissler (1814–1879), Bonn
1858/1859	Ulius Plucker (1801–1868), Bonn
1869	Johann W. Hittorf (1824–1914), Munster
1876	Eugen Goldstein (1850–1930), Potsdam
1877/1879	Sir Wm. Crookes (1832–1919), UK
1892	Heinrich R. Hertz (1857–1894), Germany
1893/1894	Phillip Lenard (1862–1947), Breslau, Kiel

In Germany in 1855, a Bonn instrument maker named H. Geissler invented a mercury vacuum pump which achieved a greater vacuum than previously possible. He was able to seal the electrical anode and cathode at opposite ends of the glass tube. Bonn physics professor J. Plucker utilized the Geissler tube in 1858/1859 and reported a bright green *fluorescence* glow in the glass wall of the tube, near the cathode. He was able to change the position of the glow inside the tube by the use of a simple magnet, which suggested an electric charge. Edmond Becquerel (1820–1891) in 1859 applied coatings of luminescent materials on the inner surface of the tubes to produce fluorescence.

J. W. Hittorf, a student of Pucker’s, then made a significant advance by designing an L-shaped tube in 1869. The anode was moved off at a right angle from the cathode so that they were not in the same plane (Fig. 2.1, Tube I). The glow now appeared only within the cathode section and objects *placed in* front of the cathode cast a shadow. This showed that mysterious electromagnetic rays were coming in a straight line from the cathode end of the tube. That was evidence enough for E. Goldstein, an astronomer at the Potsdam Observatory, to coin “Kathodenstrahlen” (cathode rays) in 1876.

In England, Sir William Crookes was already renowned for originating the *Chemical News*, a science magazine, in 1859 and for the discovery of the element thallium in 1861 and its atomic weight in 1873 [10–12]. In 1873–1879, he adapted the L-shaped Hittorf vacuum tube for his investigations on the passage of electricity through rarefied gases. His experiments confirmed that the kathodenstrahlen had mass and charge. By 1897, the cathode rays would be identified as electrons. The fluorescence observed within the discharge tubes was found to be the result of ionization by the cathode electrons of the trace amounts of gas remaining in the incompletely evacuated tubes.

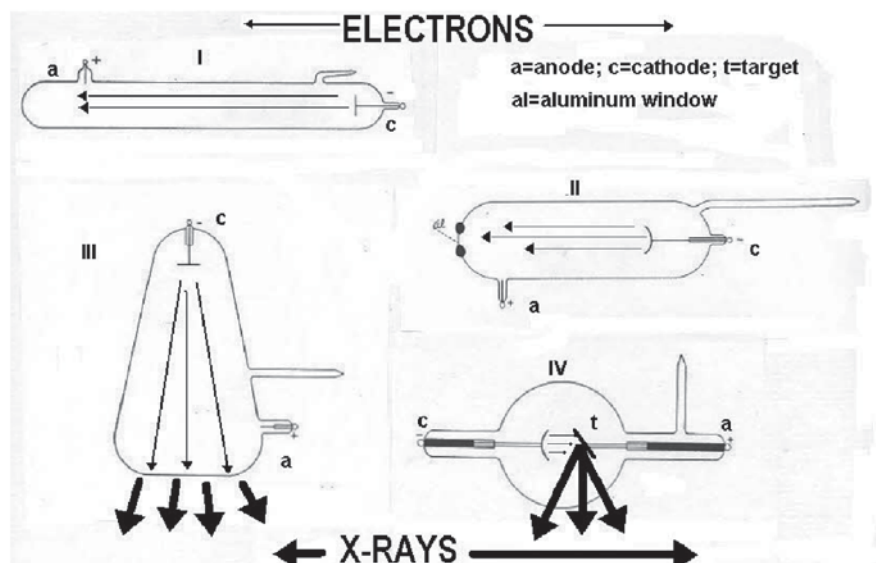


Fig. 2.1 Sealed glass vacuum tubes of Hittorf, Lenard, Crookes, and Röntgen. (Author)

The Crookes tubes used stronger batteries and had an improved vacuum, but they also produced a brilliant *fluorescence* within the tube. This occurred despite the better vacuums which left fewer gas molecules in the tube to interact with the cathode electrons. With less collisions to slow them down, the electrons accelerated more rapidly through the tube to strike the opposite glass wall, where they produced fluorescence by causing ionization when they struck the glass wall. And at the point of impact with the glass wall, the cathode electrons were also producing invisible X-rays, which were undetected until 1895. The Crookes and/or Hittorf tubes became ubiquitous in college laboratories the world over. After the discovery of X-rays, the Crookes/Hittorf gas tubes were used to produce X-rays until the invention of the Coolidge hot cathode tube in 1913 [11, 12]. The hot tungsten cathode generated the necessary electrons and made the gas tubes obsolete. Cathode ray tubes are used today to illuminate our television and computer screens.

The Geissler tube had a poorer vacuum than the Crookes tube and the cathode electrons could not travel far before colliding with a gas molecule. This led to a colorful fluorescent glow, which proved entertaining to nineteenth-century science students. Neon gas, discovered in 1898, was instilled within the Geissler tube to create brilliant red signs for commercial advertising after about 1910. Different gases, usually from the inert (noble) gases, were used to produce different colors: such as argon (green), xenon (blue), and krypton (white). Regardless of the color, the signs were all called Neon [1]. In 1923, Georges Claude (1870–1960) and his French company Claude Neon, introduced neon gas signs to the USA, when he sold two in Los Angeles. The legendary Packard dealership of E. C. Anthony bought two “Packard” signs for US\$1250 each [13].

By 1901, a fluorescent lamp was invented that used the cathode electrons to excite atoms of mercury vapor. However, the emitted photons from the mercury atoms were mostly in the ultraviolet range and invisible. General Electric solved that problem by filling the tube with both mercury and argon and a “phosphor.” Electrons strike the mercury vapor atoms and produce an invisible ultraviolet light. The ultraviolet light impinges upon a fluorescent and/or phosphorescent coating on the inside of the tube to produce visible light. The coatings are called phosphors, which emit photons that are visible to the human eye. The phosphor chemicals are of various metallic and REE salts, such as elements # 39 and # 57–71. The same phosphors were being studied by General Electric and Radio Corporation of America (RCA) for use in the screens for commercial television, which began in Germany in 1935, in the UK in 1936, and in the USA in 1939 [1, 14].

By 1934, General Electric was able to produce a prototype fluorescent lamp. General Electric started sales of fluorescent lights in 1938 and promoted them at the 1939 World’s Fair, where they accounted for one third of all the exterior lighting. They gained acceptance in department stores, factories, and large office buildings during World War II. Eventually, they were marketed for kitchens, bathrooms and work areas, garages, and cellars. By 1951, more light was produced in the USA by fluorescent tube lamps than by the incandescent lightbulb. The fluorescent or “cold light” is reported to use one fourth the energy and emit one fourth the heat of an incandescent light of the same strength [1].

2.3 Discovery

W. C. Röntgen (1845–1923) was an only child, who was born in Germany but attended no schools there. His father was a textile merchant who had married his Dutch first cousin and then moved to Holland, where they all became Dutch citizens. After undergraduate education in Apeldoorn, Holland, Röntgen earned an engineering degree in Zurich in 1868, without much in the way of instruction in physics. However, he decided to pursue a career in experimental physics after he was befriended by the noted experimentalist Arnold Kundt. Röntgen earned his physics Ph.D. at Zurich in 1869 [15–20].

While in Zurich, he became enamored of (Anna) Bertha Ludwig (1839–1919), and it was not difficult to see why: Fig. 2.2. She was some 6 years his senior and had been a patient for several months in 1899 at a local Zurich sanatorium, presumably for tuberculosis. She was the daughter of a Zurich innkeeper, who was a German political activist in exile. They married in January of 1872 and remained childless. They later adopted a niece of Berthas, named Josephine, later, Mrs. B. Donges. Röntgen’s uncle Ferdinand and his cousin Louise immigrated to America during 1872–1879. Louise married an Indianapolis, Indiana, minister J. G. Grauel. Another cousin was Johann Heinrich Röntgen, who in 1893 was a minister of the First Reformed Church of Cleveland and superintendent of the Bethesda German Hospital. Other relatives were A. E. Röntgen of Cleveland and Mrs. H. Grabhorn in Indianapolis [15, 16].

Fig. 2.2 Bertha Ludwig Röntgen (<1923). (Public domain)



Röntgen became an assistant to Professor Kundt and accompanied him to Würzburg, Germany, in 1870 and then to Strasburg in 1872. Röntgen became an associate professor of physics there from 1876 to 1879. Then, after an essentially 10-year apprenticeship from 1869 to 1879, he was able to obtain a position as professor of physics. This was at Ludwigs University in Giessen from 1879 to 1888. The Institute of Physics at Julius Maximilians University in Würzburg called him to chair their Physics Department in 1888. By the end of 1894, he had published 50 papers in experimental physics and his excellent work was well known both inside and outside Germany. Twenty-nine of his papers were published in international journals and 21 in regional publications, such as in Munich and in Würzburg [17].

In 1892, German physicist H. R. Hertz reported that the cathode rays could penetrate thin metal, gold, and aluminum foil windows at the opposite end of the tube. His pupil, Paul Lenard, studied this penetration by the cathode rays. Lenard published three papers during 1893-94 concerning the behavior of cathode rays (electrons) penetrating outside the tube and their absorption in matter. He found irradiation that was absorbed only after traveling about 3–5 cm, 1 or 2 in., through matter [17]. It is possible that Lenard was indeed measuring cathode rays, but cathode rays (electrons) can be blocked by as little as 5 mm of aluminum foil. More likely is that Hertz and Lenard were unknowingly creating X-rays at the point of impact of the cathode rays upon the metal window (target) (Fig. 2.1, Tube II).

In the spring of 1894, Röntgen became interested in the experiments of Paul Lenard and the study of the cathode rays (electrons) which reportedly penetrated outside the tube. He wrote Lenard in Breslau for advice in May of 1894. Lenard obliged him with details of his tubes and furnished him with small thin metal windows for the tubes. After studying Lenard's publications, Röntgen sought to first

duplicate Lenard's findings and then to explore his own ideas. Unlike many other significant discoveries, Röntgen kept no historical record of the actual discovery, and he had all his notes burned upon his death [17–20]. We do know that Röntgen was using a Crookes–Hittorf glass tube, pear shaped, with the cathode (negative) at the small end and the anode (positive) at the side (Fig. 2.1, Tube III).

The electricity was provided by the standard Ruhmkorff induction coil energized by batteries. The negative rays exited from the cathode and were attracted by the anode onto a path towards the opposite end of the tube. It had been noted by all investigators that as the cathode rays struck the opposite glass wall of the tube, it caused a greenish glow or fluorescence. In order to mask this tube fluorescence, Röntgen covered the tube with lightproof black cardboard [19]. This made it easier to detect any induced fluorescence outside the tube. To better observe any fluorescence *outside* the tube, observers had to become dark-adapted in a completely darkened room before turning on the tube. Lenard had been studying the range of the apparent penetration of the cathode rays by observing this fluorescence outside the tube. He detected it by creating a thin paper screen soaked with an organic chemical, penta-decylparatoly-keton, which was relatively insensitive to everything but cathode rays. Using these screens as detectors, Lenard had estimated the penetration of apparent cathode rays (electrons) outside the tube at 3–5 cm [19].

After repeating Lenard's work, Röntgen decided to use tubes with thick walls and without the thin metal windows used by Lenard. Presumably, he wished to see if the cathode rays could really penetrate a thick glass wall. And Röntgen used a cardboard screen coated with inorganic barium platinocyanide, which was highly sensitive to any light. Specifically, he was not using the relatively insensitive organic ketone chemical detector used by Lenard [19]. Lenard wanted to measure only cathode rays not any extraneous fluorescence.

Röntgen, after a childhood illness, was partially blind in one eye. And he was color blind. In spite of this, he enjoyed hunting and was allegedly a good shot [15, 16]. He probably had the deuteranomaly type of color blindness, which results in a mild deficiency in perception of the green spectrum. This is the most common type of color vision deficiency and affects about 5% of white males [21]. His choice of screen detector may have been influenced by his color blindness. Certainly, there was a large discrepancy in screen sensitivity between his barium platinocyanide and the penta-decylparatoly-keton of Lenard (Fig. 2.3).

With the tube on, Röntgen noted fluorescence of one of his screens which was estimated to be 100 cm or 39 in. away. This screen was too far away to be affected by the cathode rays and there was no light in the room. No matter how far he moved the screen away from the tube, it still fluoresced. He even observed the glow when he placed the detector screen behind a thick wooden door. He had embraced photography as a hobby and was pleasantly surprised to find that the invisible rays served to expose photographic glass plates and/or photographic film. He reported that this took 3–10 min/exposure. He had discovered a new invisible light presumably produced by the cathode rays as they impinged on the glass wall. Since their identity was unknown, he called them X-rays [15–20].

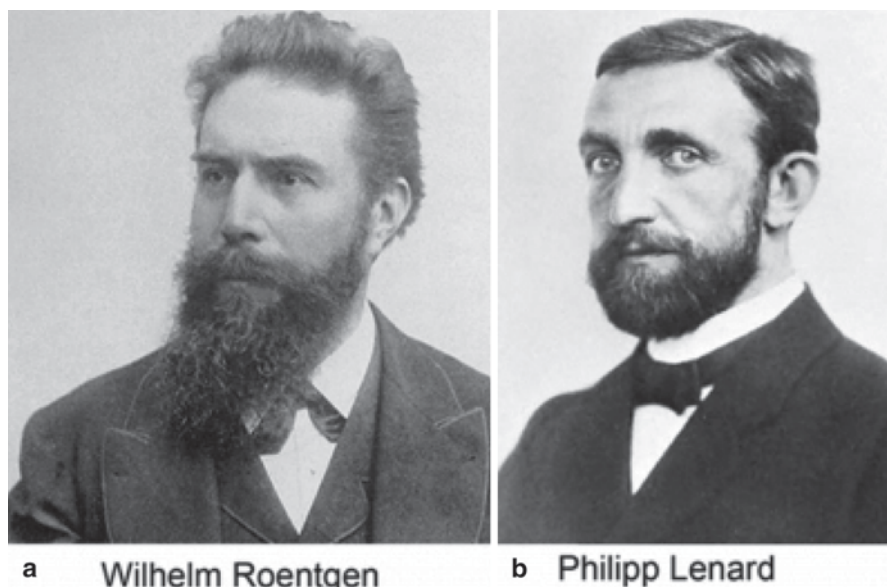


Fig. 2.3 W. C. Röntgen and Phillip Lenard (<1923). (Public domain)

During November and December, Röntgen was able to characterize the new unknown rays as (a) causing fluorescence and exposing photographic plates in the absence of visible light; (b) traveling in a straight line, unaffected by a magnet (neutral charge); (c) affected by the geometric inverse square law: intensity inversely proportional to the square of the distance between tube and screen; and (d) penetration of most solid matter but attenuated by the density and thickness of metals. A thickness of 1.5 cm of lead served to stop the rays.

While working on this penetration of the rays and holding attenuating objects in front of the screen, he must have been startled to see the bones of his hand appear on the screen. He documented this effect by placing Frau Röntgen's hand on a photographic plate for a 15-min exposure to the X-rays. He used the rays to expose several other objects on photographic plates. He also found that the output of X-rays could be increased by directing the cathode rays onto a heavy metal *target* at the anode instead of onto the opposite glass wall (Fig. 2.1, Tube IV) [17].

2.4 Post-discovery Reports

He submitted his paper on 28 December to the local Würzburg science journal which was already in press for the end of year edition. He had not presented the paper at the December meeting, but it was added as the last article in the December Proceedings. He instructed the printer to place it at the end, before the 1895 annual

report [17]. The Proceedings of the Physical-Medicine Society of Würzburg did not have the international reputation and prestige of the journals at the major academic centers in Vienna, Berlin, and Paris. However, Röntgen was undoubtedly in a hurry to submit his priority because physicists all over Europe had been working with the cathode ray tubes and had undoubtedly been producing X-rays for years without knowing it. By submitting his phenomenal paper locally, he was assured of immediate publication. However, it was at the risk of it being overlooked by prominent physicists.

Röntgen was a mature academic, age 50, with 50 prior publications [15, 16]. He knew what would be academically correct in reporting his phenomenal discovery. Since the local Proceedings would not be published and distributed until the first week of January 1896, or later, Röntgen arranged with the publisher, Stahel's Royal and University Book and Art Merchants, to immediately run off about 90 reprints of his article. Thus, the reprints were available before the Proceedings were published. Within the next 2 months, there would be five different printings of these reprints (*Auflage*), which Stahel would sell for 60 pfennigs each. Collectors are able to differentiate the five printings by changes on the yellow wrapper cover pages [17, 22]. The original reprints of Röntgen's first two papers were available in 2011 to collectors for US\$19,500.00 [23].

On January 1, a Wednesday, Röntgen mailed out these 90 reprints [24]. Seventy were sent to friends and colleagues in Germany, Austria, and Switzerland and another 20 to other European countries. None crossed the Atlantic Ocean. Röntgen's paper consisted of ten pages from the Proceedings, pages 132–141, and contained no illustrations, nor photographs. However, he included a sample of some of the nine X-ray photographs, which he had taken, in the mailing to at least ten prominent European physicists [17, 20, 24]. The most astounding image, which was not even mentioned in the article, was of Bertha Röntgen's hand; the single-ring photograph. This startling picture of bony anatomy instantly demonstrated, to both scientific and laypersons, the practical medical value of the discovery (Fig. 2.4a). This image was among those sent out with the reprints to a select group:

F. S. Exner in Vienna
 Voller in Hamburg
 O. Warburg in Berlin
 O. Lummer in Berlin
 L. Zehnder in Freiberg
 F. W. G. Kohrausch in Gottingen
 H. H. Lorentz in Leiden
 Lord Kelvin (Wm. Thompson) in Glasgow
 Schuster (German born) in Manchester
 H. Poincare in Paris

Physicist Franz Serafin Exner (1849–1926) in Vienna, the medical capital of the Western world at that time, received the reprint along with several photographs including that of the hand. Röntgen had worked with Exner in Professor Kundt's departments during the 1870s. At a Saturday night social engagement on January 4, he showed them to Dr. Ernst Lecher, the son of the publisher of the newspaper *Wiener Neue Freie Presse*. The story and the X-ray photo of the hand were then published

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