A POOL OF RADIATIONS: BECQUEREL AND POINCARÉ'S CONJECTURE

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Abstract: A few weeks after Wilhelm Conrad Röntgen communicated the discovery of X-rays, Henri Poincaré suggested that the emission of those rays could be associated to luminescence phenomena. Following Poincaré's conjecture, many researchers investigated the emission of penetrating radiation by phosphors and other substances. The "discovery" of several new effect was reported – such as the emission of radiation by sugar and glow worms. The paper describes Henri Becquerel's and Silvanus Thompson's study of the radiation of uranium compounds in this context. Both adopted the natural hypothesis that the observed phenomenon was due to a special phosphorescence that violated Stokes' law. Becquerel, Thompson and contemporaneous scientists were unable to distinguish what we now call radioactivity from other spurious reported phenomena. Those researches were made in a highly speculative and uncritical period, when elementary experimental precautions were overlooked.

Keywords: radioactivity; penetrating radiation; X-rays; history of physics; Becquerel, Henri; Thompson, Silvanus

> *My intention in publishing this Budget* [...] *is to enable those who have been puzzled by one or two discoverers to see how they look in the lump.* (Morgan, 1872, p. 5)

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1. INTRODUCTION

The discovery of radioactivity happened in the exciting years following Wilhelm Conrad Röntgen's announcement of X-rays (Röntgen, 1895; Satson, 1945).[1]

It is well known that in the beginning of January 1896 Röntgen sent pre-prints of his first article to the main scientific leaders of that time. A few weeks later, his work was discussed and reproduced all over the world (Jauncay, 1945; Sarton, 1937). Over a thousand papers on X-rays were published during 1896.

In his first paper, Röntgen had already established many physical properties of the X-rays, but for several years the nature of this radiation remained unknown[2]. It was also unknown how they were produced by the electric discharge in the low-pressure Crookes tubes. It was the discussion about the origin of X-rays that led (among other things) to Becquerel's researches on the radiation of uranium compounds.

The aim of this paper is to describe Becquerel's discovery in its proper scientific context, such as contemporaneous researchers regarded it: as one of several instances of emission of penetrating radiation by luminescent bodies.[3] In this perspective, one is able to see why Becquerel's rays were not at first regarded as a revolutionary, outstanding discovery.

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[1] The standard scientific biography of Röntgen was written by Otto Glasser (1933). In this book one can find a translation of Röntgen's relevant papers, together with a discussion of the context of the discovery and early consequences.

[2] At first, there were four main hypotheses concerning the nature of X-rays: (a) they could be short wavelength transversal electromagnetic waves, similar to ultraviolet light; or (b) longitudinal electromagnetic waves (Röntgen's hypothesis); or (c) non-periodic pulses of electromagnetic radiation (Stokes' hypothesis); or (d) modified (neutral) cathode rays (Poincaré, 1897).

[3] This paper was written in 1995-1996, but it was not published. A short version, in Portuguese, was published a few years later (Martins, 2004).

2. X-RAYS AND FLUORESCENCE: POINCARÉ'S CONJECTURE

In the French Academy of Sciences, X-rays were discussed for the first time on the 20th January 1896 – just a few weeks after the publication of Röntgen's work. On this day, the first radiographs produced in Paris were also shown to the Academy. Henri Poincaré had received a pre-print directly from Röntgen, and presented a verbal account of the discovery. He remarked the importance of the new phenomenon and he became deeply interested in it. He conjectured that there could be some correlation between the emission of X-rays and the fluorescence that appeared at the glass wall of the Crookes tubes. Poincaré did not publish his hypothesis in the proceedings of the French Academy, but it appeared in a popular scientific journal (*Revue Générale des Sciences*, 30th January 1896 issue) and became widely known. In this article, Poincaré remarked:

> Therefore it is the glass that emits Röntgen rays, and it becomes fluorescent as it emits them. We may ask ourselves whether all bodies that have a sufficiently intense fluorescence wouldn't emit Röntgen's X rays, besides luminous rays, *whatever be the cause of their fluorescence*. In that case the phenomenon would not be associated to an electric cause. That is not very likely, but it is possible, and it is doubtless easy to verify. (Poincaré, 1896, p. 56)

This hypothesis will be hitherto called in this paper "Poincaré's conjecture". It was soon tested, and led to important findings (to be described below). It was the source of Becquerel's uranium research. Of course, according to our present knowledge, there is no direct relation between X-rays and luminescence, but that mistaken clue was instrumental in the discovery of several new phenomena.

Jean Becquerel, in his account of the discovery of radioactivity, ascribed to his father Henri Becquerel this conjecture:

> The day when Röntgen's first radiographs were presented to the [French] Academy of Sciences by Henri Poincaré (20th January 1896), Henri Becquerel asked his colleague where exactly was the region of emission in the tube that produced those rays. It was answered to him that the radiation came from the part of the glass wall that was stricken by the cathode rays. Henri Becquerel observed to Poincaré that this region of the glass was rendered fluorescent by the cathode rays, and both scholars immediately agreed that one should check whether other bodies besides glass, when rendered fluorescent or phosphorescent by exposure to light and not to cathode rays, would not emit a radiation similar to X-rays. Henri Becquerel soon began the research. (Jean Becquerel, 1924, p. 17)

What was the source of Jean Becquerel's version? His book provided no references. It seems, however, that he was following his father's personal narrative. In 1903 – the year he was accorded the Nobel Prize – Henri Becquerel published his only full length work of radioactivity (Becquerel, 1903a, 1903b). In this account, seven years after the beginning of his first researches on the radiation of uranium, he described the origin of his endeavour in the following words:

> In the meeting of the Academy of Sciences of the 20th January 1896, when Mr. H. Poincaré had just shown the first radiographs sent by Mr. Röntgen, I asked my colleague if it had been ascertained what was the place of emission of those rays, in the vacuum tube that produced X-rays. I was answered that the origin of the radiation was the luminous spot of the wall [of the tube] that received the cathodic flux. I cogitated at once to search whether the new emission was a manifestation of the vibratory motion that gave birth to the phosphorescence and whether all phosphorescent bodies emit similar rays. I communicated this idea and this project to Mr. Poincaré, and on the next day I began, following those ideas, a series of experiments [...]. (Becquerel, 1903a, p. 3)

Therefore, in this late publication, Becquerel ascribed to himself the origin of “Poincaré’s conjecture”. In Becquerel’s Nobel Prize lecture (Becquerel, 1903c; translated in Samuelsson & Sohlman, 1967, pp. 52-70), he did not cite Poincaré’s name:

> At the beginning of 1896, on the very day when the experiments of Röntgen and the extraordinary properties of the rays emitted by the phosphorescent wall of Crookes tubes were known at Paris, I thought of carrying out research to check whether all phosphorescent materials emitted similar rays. (Becquerel, 1903c, p. 1)

If we check Becquerel’s former publications, however, we find a different account. In 1900, during the International Congress of Physics in Paris, he stated:

> The discovery of the spontaneous radiation from uranium was a consequence of the ideas born from the discovery of X-rays; [...]
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> Discarding some hurried publications of Mr. Le Bon and Mr. Ch. Henry, whose conclusions were not verified, and that had as starting point an idea published by Mr. H. Poincaré, the first clear experiment that we find in this order of facts was due to Mr. Niewenglowski who, on the 17th February 1896, showed that some phosphorescent preparations of calcium sulphide exposed to the Sun emitted radiation that traversed black paper. [...]
>
> As to myself, since the day when I became acquainted with professor Röntgen’s discovery, it came also to my mind [*il m’était également venu à l’idée*] to investigate whether the property of emitting very penetrating rays was intimately attached to phosphorescence. (Becquerel, 1900)

From this account, therefore, we could infer that Becquerel’s own ideas were *independent* of Poincaré’s published conjecture. We cannot be sure, however, that this weaker version is the correct one. All French physicists of the time ascribed the conjecture to Poincaré. For instance: at the meeting on 2nd March 1896 of the Academy of Sciences, Arsène d'Arsonval stated: "Fluorescent bodies emit radiation enjoying the properties of X-rays, according to the hypothesis of our colleague Mr. Poincaré" (d'Arsonval, 1896a, p. 501).

In the next meeting (9th March 1896), Louis Joseph Troost, who also detected penetrating radiation emitted by phosphorescent blende (zinc sulphide), stated: "Those results, that confirm the hypothesis of our colleague Mr. H. Poincaré and the experiments recently made by several scholars, and specially by our colleague Mr. H. Becquerel, by Mr. Niewenglowski and by Mr. Charles Henry [...]" (Troost, 1896a, p. 564).

Both d'Arsonval's and Troost's communications were read during meetings of the Academy of Sciences at which Becquerel also presented papers. It is likely that Becquerel accepted, at that time, that Poincaré was the author of this hypothesis, because he didn't claim it as his own.

It is possible to assume that Becquerel progressively changed his account and claimed the authorship of Poincaré's conjecture when he perceived the importance of radioactivity. This is consistent with Henri Becquerel's pattern of behaviour: he usually tried to ascribe to himself the contributions of other researchers (see Martins, 2000).

3. CONFIRMATIONS OF POINCARÉ'S CONJECTURE

In the weeks following the announcement of Röntgen's discovery, several papers related to X-rays were presented to the French Academy of Sciences. There was a search for different ways of producing X-rays. At the meeting on the 3rd February 1896, M. Nordon reported that a voltaic arc does not produce X-rays, but Gustave Moreau (1896) reported that they were emitted by a high voltage discharge from an induction coil, without the use of a vacuum tube (and, therefore, without the intervention of cathode rays). In the same meeting, Louis

Benoist and Dragomir Hurmuzescu reported that X-rays were able to discharge an electroscope (Benoist & Hurmuzescu, 1896) – a phenomenon that would have increasing importance in later researches.

During the following weekly meeting (10th February 1896), Charles Henry reported the first test of Poincaré's conjecture (Henry, 1896a). His paper was presented to the Academy of Sciences by Henri Poincaré himself. Charles Henry first checked whether phosphorescent zinc sulphide was able to increase the effect of X-rays produced by a Crookes tube. He concluded that it was. He covered part of a metallic object with a layer of zinc sulphide, and reported that the radiograph of this object was stronger and sharper bellow the coated region. Then, Henry proceeded to check the emission of X-rays by this phosphorescent substance when excited by light. He reported that it was possible to obtain radiographs without X-ray tubes, by covering the object with a layer of zinc sulphide and by exciting its phosphorescence burning a strip of magnesium in his laboratory. Poincaré's conjecture was confirmed.

In the next weekly meeting (17th February 1896), Gaston Henri Niewenglowski presented a confirmation of Charles Henry's results. He used another phosphorescent substance – calcium sulphide. This is the most relevant part of his report:

> I have packed an ordinary sensitive paper [photographic paper] with several layers of black or red needle paper. I placed two coins over it and covered one of the halves [of the photographic paper] with a glass plate as well as the phosphorescent powder [calcium sulphide]. After four or five hours of exposition to the Sun, the half of the sensitive paper that directly received the solar radiation remained intact and presented no mark of the coin placed upon it, thus showing that the black or red paper had not been traversed by light. The half that received the solar rays only through the phosphorescent plate was completely blackened, except for the part corresponding to one of the coins; its white silhouette was produced on black.

> When I placed only one layer of thin red paper that allowed the passage of the solar rays, I observed that the portion of the sensitive paper that only received the solar radiations after their passage through the phosphorescent layer was blackened much faster than the other. (Niewenglowski, 1896, p. 385)

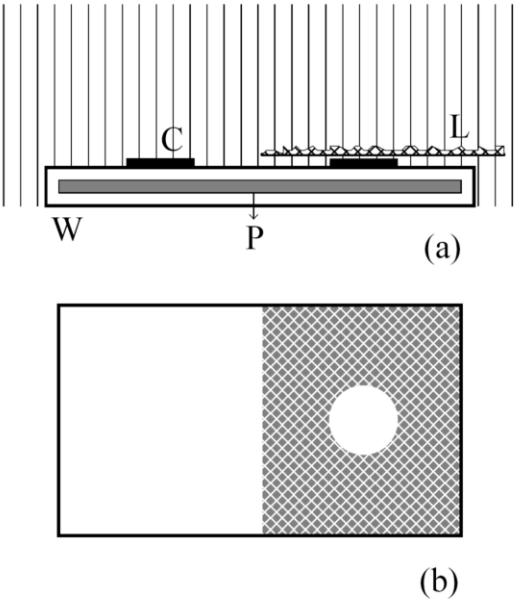

Fig. 1. A reconstruction of Gaston Niewenglowski's experiment. (a) Niewenglowski wrapped a photographic plate (P) with opaque paper (W). He placed two coins (C) over the paper, and a glass plaque with phosphorescent calcium sulphide covered half of the plaque. (b) after exposing the device to sunlight, the part of the photographic plate that was under the phosphorescent powder became dark, with a clearer and well-defined mark corresponding to the coin.

Therefore, according to the observations reported by Henry and Niewenglowski, phosphorescent materials seemed to emit X-rays, when excited by sunlight. But Niewenglowski also checked whether calcium sulphide would continue to emit X-rays when it was put in a dark place, after receiving sunlight. He concluded that this substance continued to emit penetrating radiations in the dark:

> I could also observe that the light emitted in the dark by the phosphorescent powder, previously illuminated by the Sun, was able to pass through several layers of red paper and to darken a sensitive paper that was shielded by those paper layers. (Niewenglowski, 1896, p. 386)

It was natural to check the emission of X-rays in the dark, because a sample of phosphorescent calcium sulphide keeps visibly luminous for a long time after exposition to the Sun. If X-ray emission was associated with luminescence, it was natural to expect that it could be observed also in the dark, for some time, after excitation by light.

After one more week, during the meeting of 24th February 1896, Nikolai Dmitrievich Piltchikoff reported that it was possible to increase the intensity of X-rays by placing a phosphorescent material inside the vacuum tube, at the place where the cathode rays strike the glass wall (Piltchikoff, 1896). With the older kind of vacuum tubes, it was necessary to expose photographic plates for several minutes in order to obtain a radiograph. With Piltchikof's device, the time was reduced to 30 seconds. Of course, this was another confirmation (and technological application) of Poincaré's conjecture.

All those results will strike any contemporary physicist as odd or even impossible. Nowadays we believe that luminescent bodies do not, in general, emit X-rays. Indeed, even in Röntgen's first paper it was clearly stated that X-rays could be generated when cathode rays strike *aluminium*, hence without producing any luminescence[4]. Those experiments should not

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[4] See Röntgen's first paper (Röntgen, 1896, §§ 12-13). This was soon confirmed by Jean Perrin, who therefore denied any relation between luminescence and emission of X-rays (Perrin, 1896).

have yielded the above described results. What happened? We are unable to understand it[5].

At other countries, similar experiments were also performed. J. J. Thomson arrrived independently to Poincaré's conjecture (Thomson, 1896)[6] and tested it, with negative results:

> A very noticeable feature in the bulb producing these Röntgen rays is the phosphorescence of the glass of the bulb. I thought it therefore of interest to try if these rays were generated when the phosphorescence of the glass was produced by other means than the discharge from a negative electrode. To do this, I produced a ring discharge in an electrodeless bulb; this when the pressure of the gas is very low is accompanied by intense phosphorescence of the glass. I exposed a photographic plate protected by thick cardboard for an hour to such a bulb, but without the slightest effect. I next tried filling the bulb with oxygen, a gas which is itself made phosphorescent so as to have both the glass and the gas phosphorescent, but again a photographic plate was not affected after an hour's exposure.
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> I also tried without success to photograph in this way by the phosphorescence excited in a screen powdered over with luminous paint, by the sparks passing between the terminals of a Ruhmkorff coil placed close to the screen.

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[5] The increase of the photographic effect of X-rays by luminescent bodies can be partly explained. At that time, photographic plates were not very sensitive to "hard" (short wave-length) X-rays. Some substances can transform hard X-rays into "soft" (long wave-lenth) ones. Although soft X-rays have a smaller energy (and smaller penetrating power), they produce a stronger photographic effect - exactly because their absorption by matter is stronger. However, this effect cannot account for all the facts described by Charles Henry and Gaston Henri Niewenglowski.

[6] This paper was read on the 27th January 1896 and it is therefore unlikely that Thomson could have received any information about Poincaré's conjecture before he wrote it.

> It would thus appear that we can have vivid phosphorescence without any production of these rays. (Thomson, 1896)

Carey Lea, after reading a description of Charles Henry's experiment and of Poincaré's conjecture, also tested it with new substances:

> It seemed worth while to ascertain if this principle is of general application. A dilute solution of uranin was exposed to sunlight, using a large surface of solution so as to get the best effect. A short distance over the surface was placed a sensitive film protected by aluminium foil 1/10 of a millimetre in thickness and with a lead star interposed. Two hours exposure gave no result. The experiment was repeated with acid solution of quinine, with which five hours exposure gave no result. (Lea, 1896)

It is likely that Lea did not notice any effect of the uranium solution because it was dilute and spread upon a large surface. The exposure time was also too short. Notice, however, that it was *natural*, at this time, to check uranium fluorescent compounds for emission of X-rays.

In Paris, at the same meeting where Piltchikoff's work was presented, Henri Becquerel reported his first research on the emission of X-rays by phosphorescent bodies, as will be described in the next section of this paper.

4. HENRI BECQUEREL'S FIRST PAPER ON "RADIOACTIVITY"

Antoine-Henri Becquerel (1852-1908)[7] belonged to a famous scientific family. His grandfather, Antoine-César Becquerel (1788-1878) is known for his studies on electrochemistry, piezoelectricity, thermoelectricity and voltaic electricity

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[7] He always signed his scientific works (and even his letters) as Henri Becquerel, although his full given name was Antoine-Henri.

(Knight, 1981; Henri Becquerel, 1892). Among many other works, he published a monumental review of electricity and magnetism (*Traité expérimental de l'éléctricité et du magnétisme*, in seven volumes) that remained an obligatory reference work for decades.

One of Antoine-César's sons was Alexandre-Edmond Becquerel (1829-1891), who was also a distinguished physicist (Violle, 1892; Crookes, 1892; Harvey, 1957; Gough, 1981). He initially worked with his father and applied himself to the study of several electromagnetic phenomena (electrochemistry, diamagnetism). His most important work, however, was on luminescence. He was the leading authority on phosphorescence and fluorescence of his time.

Antoine-Henri Becquerel began his scientific career in the footsteps of his father. His initial investigations were on optical phenomena – specially phosphorescence (Romer, 1981). He became familiar with ultraviolet and infrared radiations, and studied the effect of infrared radiation on the release of light by some phosphorescent substances (Becquerel, 1884a; Becquerel, 1884b; Becquerel, 1891). He studied most luminescent substances that had been collected by his father – including some uranium compounds (Becquerel, 1885). At that time, uranium compounds were an interesting subject for luminescence research, for several reasons: there were many different phosphorescent substances containing uranium; and their fluorescence was exceptionally strong. Another deeper reason for checking whether uranium compounds emitted X-rays was discussed elsewhere (Martins, 1997).

Many uranium compounds are phosphorescent or fluorescent. Among them, Edmond Becquerel had studied the nitrate, chloride, double fluoride of uranium and potassium, silicate (uranium glass), phosphate, double sulphate of uranium and potassium, etc. (Edmond Becquerel, 1859b; *idem*, 1872). Most of those uranium compounds have a very short lived phosphorescence (a few milliseconds).

With this background, it was natural that Henri Becquerel would become interested on Poincaré's conjecture and would try to check it.

Henri Becquerel's first works on "radioactivity"[8] are well known and have been translated and published several times (Romer, 1964, chapter I; Boarse & Motz, 1966, chapter 27). Those researches were published as a series of small notes in the *Comptes Rendus* of the Paris Academy of Sciences. As stated above, their starting point was his attempt to test Poincaré's conjecture.

Henri Becquerel's first research on the relation between X-rays and luminescence was presented to the French Academy on the 24th February 1896. In this report, he first acknowledged the previous studies of Charles Henry and Gaston Niewenglowski, without any criticism or reserve:

> In a previous meeting [of the French Academy of Sciences], Charles Henry reported that the intensity of the radiations that penetrate aluminium was increased when phosphorescent zinc sulphide was placed in the path of the rays that came out of a Crookes tube.
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> Besides that, Niewenglowski discovered that commercial phosphorescent calcium sulphide emits radiations that penetrate opaque substances.
>
> This behaviour also belongs to several other phosphorescent substances, and particularly to uranium salts, which have a very short lived phosphorescence. (Becquerel, 1896a, p. 420)

Hence, in his first paper, Henri Becquerel accepted that luminescent bodies emit X-rays (or something similar to X-rays) and reported another instance of the phenomenon

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[8] In 1896, neither the name "radioactivity" nor the corresponding concept existed, but most authors describe Becquerel's publications of that time as his "radioactivity" papers.

previously described by Charles Henry and Gaston Niewenglowski[9].

Becquerel's first experiment is remarkably similar to those of his predecessors:

> I produced the following experiment with double sulphate of uranium and potassium, of which I own some crystals that form a thin, transparent crust.
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> A Lumière photographic plate is wrapped in two very thick black paper sheets, in such a way that the plate is not darkened even when exposed to the Sun for a whole day. A flake of the phosphorescent substance is put over the paper, outside it, and the whole is exposed to the Sun for several hours. When the photographic plate is developed, the silhouette of the phosphorescent substance appears in black in the negative. If a coin or a metallic plate with a hole is placed between the phosphorescent substance and the paper, their images will be visible in the negative.
>
> The same experiments can be repeated placing a thin glass plate between the phosphorescent substance and the paper. This excludes the possibility of any chemical action by vapours that could escape from the substance when it is heated by the rays of the Sun. It is possible to conclude from those experiments that this phosphorescent substance emits radiations that traverse a paper opaque to light and reduce silver salts. (Becquerel, 1896a)

The only relevant new aspect of Becquerel's first paper was the use of a different substance – double sulphate of uranium and potassium. The main result was similar to those of Charles Henry and Gaston Henri Niewenglowski.

5. BECQUEREL'S "DISCOVERY OF RADIOACTIVITY"

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[9] In later works, Becquerel criticized Charles Henry's work and suggested that the observed effects were due to the pressure produced by the coin on the photographic plate (Becquerel, 1903a, pp. 4-5).

During the next meeting of the Academy of Sciences (2nd March 1896), d'Arsonval reported that he had been able to produce radiographs using a fluorescent lamp and placing a fluorescent glass over the objects that were to be radiographed (d'Arsonval, 1896a). Incidentally, the fluorescent glass he used contained an uranium salt. D'Arsonval's conclusion was that all bodies that emit greenish-yellow fluorescent light also emit radiations that are able to produce an impression on photographic plates wrapped in paper opaque to light.

At this same meeting, Henri Becquerel presented a second paper on the subject – the one that is usually described as containing the discovery of radioactivity (Becquerel, 1896b). In this article, Becquerel described new observations of the effects produced by his crystals of double sulphate of uranium and potassium. He compared the radiations of the phosphorescent substance to those produced by X-ray tubes and noticed that they had different penetration powers. He reported that the emission of penetrating radiation occurred when the phosphorescent substance received sunlight directly, or reflected by a mirror, or refracted. The part of the paper that is supposed to report the discovery of radioactivity is the following:

> I will particularly insist upon the following fact, that seem to me very important and foreign to the realm of the phenomena that one would expect to observe. The same crystalline flakes, placed together with photographic plates, in the same conditions, shielded by the same screens, but without receiving excitation by incidence of radiation and kept in the dark, still produce the same photographic impressions. This was the way I was led to make those observations: among the preceding experiments, some were prepared on Wednesday, 26th, and on Friday, 27th February; and since, in those days, the Sun appeared only intermittently, I kept the experiments that I had prepared and put the plates with their wrappings in the darkness of a furniture drawer, leaving the uranium salt flakes in their place. As the Sun did

> not appear again in the following days, on the 1st March I developed the photographic plates, expecting to find very weak images. On the contrary, the silhouettes appeared with a strong intensity. I soon thought that the action should have continued in the darkness [...] (Becquerel, 1896b)

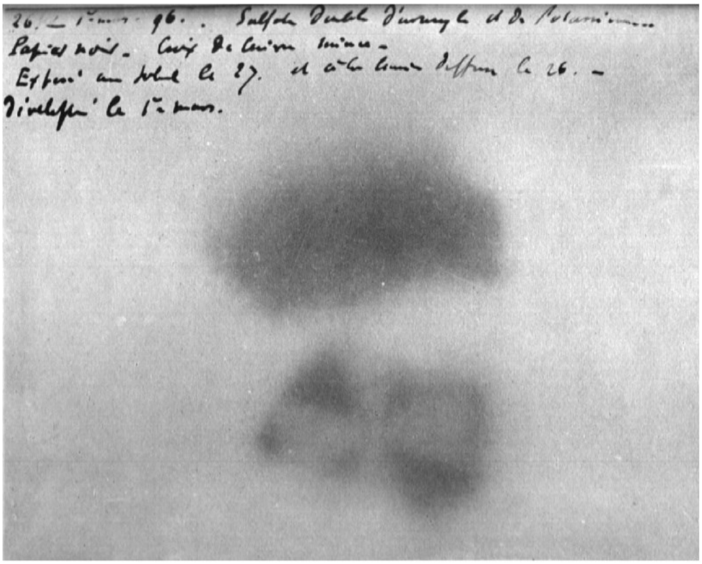

Fig. 2. One of photographs obtained by Henri Becquerel using uranium salt, when the device was kept in a drawer. The lower image was produced through a this copper cross (Becquerel, 1903a, pl. I, fig. 1)

Becquerel's original papers, published in the *Comptes Rendus* of the French Academy of Sciences, are not accompanied by any figure or plate. In much later publications, however, after radioactivity became a really important research subject, Becquerel published his early photographic plates (Becquerel, 1902a; Becquerel, 1902b; Becquerel, 1903a; Becquerel, 1903b; Becquerel, 1903c). One of them (Fig. 2) seems to correspond to Becquerel's second paper.[10]

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[10] In Becquerel's book, this photograph (Becquerel, 1903b, plate I, fig. 1) contains a handwritten statement to the effect that it was prepared on the 26th February and developed on the 1st March 1896.

Why was this new observation unexpected? It was not the existence of penetrating radiations that was odd, but the emission of those radiations in the dark: “It seems that this phenomenon should not be ascribed to luminous radiations emitted by phosphorescence, since after one hundredth of a second those radiations become so week that they are barely perceptible”. Did this show Becquerel that he was facing a completely new phenomenon, foreign to everything that physics had hitherto discovered? Not at all.

Becquerel’s starting point was the (implicit) assumption that luminescent bodies would emit X-rays when they are luminous. In the case of Niewenglowski’s experiment, the emission of X-rays by calcium sulphide in darkness was to be expected, because the phosphorescence of this substance is long lived. Hence, Becquerel expected a very week effect of his crystals.

The strong observed effect was unexpected, but it could be explained *according to existing knowledge about phosphorescence*. Indeed, it is only necessary to read the works of Henri Becquerel’s father to find similar phenomena. The duration of the emissions of different colours of light given out by a given phosphorescent substance can be widely different. In some cases, the longer wavelengths have a longer duration (such is the case for sulphate of quinine and diamond); in other cases, the shorter wavelengths have the longer duration (chalk, Iceland spar) (Edmond Becquerel, 1859a, p. 117). For this reason, the observable colour of a phosphorescent substance, kept in the dark, usually changes with time. It could happen, therefore, that the short lived *visible* phosphorescence of the uranium crystal was accompanied by a long lived *invisible* phosphorescence with emission of penetrating radiation. This was exactly Henri Becquerel’s explanation:

This seems to enhance its documental value and to establish its date. However, the statement was added much later, since in a previous publication there was nothing written on the photograph (Becquerel, 1902a, fig. 1).

> A hypothesis that naturally comes to mind is the assumption that those radiations, which effects have a strong analogy to those produced by the radiations studied by Mr. Lenard and Mr. Röntgen, could be invisible radiations emitted by phosphorescence with a persistence infinitely larger than the persistence of luminous radiations emitted by those bodies. However, the reported experiments, although not contrary to this hypothesis, do not permit us to formulate it. (Becquerel, 1896b, p. 503)

The possibility of an unknown invisible phosphorescence had already been anticipated by Henri Becquerel's father. Edmond Becquerel remarked that even in the case of substances that exhibited no observable phosphoresce in his experiments, there could be some hidden and unknown effect:

> On the other side, even supposing that the bodies are not visible in the apparatus [the phosphoroscope], one cannot state that they have received no modification, because light could excite vibrations with a speed [frequency] different from that of light rays, with a wave length greater than that of the active rays; those vibrations could give rise to heat effects and other still unknown molecular actions. (Becquerel, 1859b, p. 117)

Up to this point, therefore, Becquerel was far from suspecting he had observed anything similar to our concept of radioactivity. In a review paper on X-rays published in March 1896, Camille Raveau described the researches of Henry, Niewenglowski, Piltchikoff, d'Arsonval and Becquerel as special cases of the phenomenon predicted by Poincaré and discovered by Charles Henry (Raveau, 1896).

One week after Becquerel's famous communication of the radiation of uranium salt kept in the dark, the Academy of Sciences heard a new confirmation of Poincaré's conjecture. Louis Joseph Troost confirmed Charles Henry's experiments with phosphorescent zinc sulphide (Troost, 1896a). He obtained strong radiographic effects when its phosphorescence was excited by magnesium light. Troost referred to Niewenglowski's and Becquerel's works as investigations concerning the same phenomenon, predicted by Poincaré.

6. SILVANUS THOMPSON'S SIMULTANEOUS DISCOVERY OF HYPER-PHOSPHORESCENCE

When the scientific conditions for the rise of a discovery are ripe, it usually happens that the discovery is simultaneously made by several independent researchers. This was also the case with the "invisible phosphorescence" of uranium compounds. At the same time as Henri Becquerel, Silvanus Thompson detected this phenomenon – and interpreted it exactly in the same way as Becquerel.

Silvanus Phillips Thompson (1851-1916) is not well known today. His main work was on electricity, but he was also regarded as an authority on luminescence, at the end of the 19th century. In 1899, Lord Kelvin was interested in some aspects of the subject, and wrote a letter to Thompson, asking for help:

> Dear Thompson,
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> I have looked in vain in Encyclopaedias and text-books for something that every one doesn't know regarding the phosphorescence of luminous paint, Canton's phosphorus, &c.; so as you know more than encyclopaedias and text-books put together, I apply to you. [...][11]

In Thompson's biography we find the following account of his discovery:

> During the month of February [1896] Thompson and his assistant, Mr. Miles Walker, were busily engaged in various

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[11] Letter from Lord Kelvin to Silvanus Thompson, 10th October 1899, Cambridge University Library, Manuscripts Department, mss. Add. 7342.T164. Other manuscripts of the same Library will be hereafter be indicated as CUL.

> experiments, using fluorescent substances in contact with the photographic film to hasten chemical action when stimulated by the X-rays. The materials used were finely powdered fluor-spar, sulphide of zinc, fluoride of uranium, and sundry platino-cyanides. While at work Thompson came upon an unexpected effect. He found, on developing a photographic plate, that where uranium nitrate or uranium ammonium fluoride had been used, a distinct action had taken place *through* a sheet of aluminium which is impervious to X-rays [*sic*][12]. He immediately wrote to Sir George Stokes, then President of the Royal Society, on February 26th telling him of this discovery [...] (Thompson & Thompson, 1920, p. 185)[13]

The biography does not reproduce the text of Thompson's letter. It was, however, published in Stokes' correspondence (Larmor, 1907, vol. 2, p. 495):[14]

> Feb 28 1896
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> Dear Sir George Stokes:
>
> I made yesterday an observation of such curious interest that I am minded to bring it before your notice. I find that if a phosphorescent substance such as sulphide of barium is exposed to ordinary white light so as to be well insolated, and brought to the shining condition it emits afterwards (and apparently also during illumination) not only ordinary light that can be cut off with an aluminium sheet, but also something else that is not cut off by aluminium, and is, in this respect at any rate, the same as the X-rays of Röntgen, that it can traverse aluminium and act on a photographic plate. If it is true that there are fluorescent (or phosphorescent) substances that deviate from your law of degradation of

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[12] Of course, X-rays pass easily through thin plates of aluminium.

[13] There are several mistakes in this account, as will become clear afterwards. The date of the letter to Stokes is wrong, as also the content of the letter.

[14] The original letter can be found among Stokes' papers: Letter from Thompson to Stokes, 28th February 1896, CUL Add 7656.T329.

> frequency (or wave-length), this would seem to present an extreme case of such deviation. But if these be Röntgen rays, then I have succeeded in manufacturing them out of common light by a sort of reversal of the process of fluorescence. Do you know of any other instance in which fluorescence or phosphorescence has been found to be reversible in its operation?
>
> I am,
>
> Yours most sincerely,
> Silv. P. Thompson.

Notice that Thompson wrote to Stokes not because the later was the President of the Royal Society, but because he was an expert on luminescence. In this letter, Thompson said nothing about uranium compounds. It seems that the most remarkable effect was observed with sulphide of barium, since this is the only substance named in the letter. Of course, barium sulphide is not radioactive. Joseph Larmor, the editor of Stokes' correspondence, was puzzled by this letter and much time later he asked Thompson about this point.

> [...] in answer to an inquiry he now states that he had been trying various substances, including uranium nitrate, and that he had found, conclusively on Feb. 26-7, the latter was the only one to which the aluminium foil was not opaque, though black paper was transparent to others. (Larmor, 1907, vol. 2, p. 496, second footnote)

It appears from a short note published in Nature on the 12th March 1896 that Thompson was also trying different phosphorescent substances as anti-cathodes (Thompson, 1896a, p. 437)[15]. He reported that calcium sulphide, incorporated in a fusible enamel glass, "appears to form an excellent anti-kathodic [*sic*] surface for generating X-rays".

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[15] Thompson's letter to the Editor of *Nature* was dated March 9, 1896.

According to accounts published a few months later by Thompson (Anonymous, 1896b; Thompson, 1896b; Thompson, 1896c), he tested several materials, including sulphide of calcium, fluorspar, zinc sulphide, fluoride of uranium and ammonium, and several platino-cyanides. He noticed that some of them fogged sensitive films, even when kept in the dark for a long time (fluorspar and the platino-cyanides did not exhibit this power). In the earlier experiments, there was no screen between the phosphorescent bodies and the photographic plate. Afterwards, Thompson put a thin aluminium plate between them and, in this case, only uranium nitrate and uranium ammonium fluoride affected the photographic plate. Thompson arrived at the same results that had been reached by Becquerel: some uranium compounds emitted penetrating radiations that persisted for a long time in darkness. There is no contemporary document, however, to establish the exact date of each kind of experiment.

After receiving Thompson's letter, Stokes immediately replied: "Your discovery is extremely interesting; you will I presume publish it without delay, especially as so many are now working at the X-rays" (Larmor, 1907, vol. 2, p. 495).[16]

In a copy of Stokes' reply to his letter, Thompson added a note:

> This was in reply to a letter of mine to him, telling him of my discovery that rays (which I took to be a species of hyper-phosphorescence) given off by crystals of nitrate of uranium, would pass through black paper and produce photographic effects, an observation which I thought to be discordant with his law that the rays emitted in fluorescence were always of

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[16] A copy of the original letter can be found among Stokes' papers: Letter from Stokes to Thompson, 29th February 1896, CUL Add 7656.T330. The typewritten letter from Stokes to Thompson is kept by the Imperial College Archives, Silvanus P. Thompson's papers, letter 296 (cf. Pingree, 1967).

> longer wave-length than those by which they were stimulated.[17]

A few days later, Stokes wrote again to Thompson, to give him the sad news:

> I fear that you have already been anticipated. See Becquerel, *Comptes Rendus* for Feb. 24, p. 420, and some papers in two or three meetings preceding that. (Larmor, 1907, vol. 2, p. 496)[18]

Stokes accepted that Thompson and Becquerel had discovered the same phenomenon, as may also be inferred from another letter he sent to Thompson a few months later:

> P. S. I may as well mention, in case you should not have seen it, that in the last number of the *Comptes Rendus* is a paper by Becquerel in which he mentioned that the metallic uranium shows the remarkable phenomenon which you and he discovered, independently, about 4 times as strongly as the salts of uranium he had previously used. (Larmor, 1907, vol. 2, p. 498)[19]

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[17] CUL Add 7656.T330. This was a copy of Stokes' letter to Thompson, sent from Thompson to Larmor for publication in Stokes' correspondence. Stokes died in 1903, and shortly after that, Larmor began to collect his letters for publication. We may infer that Thompson's note was written between 1903 and 1906.

[18] A copy of the original letter can be found among Stokes' papers: Letter from Stokes to Thompson, 2nd March 1896, CUL Add 7656.T331. The typewritten letter from Stokes to Thompson is kept by the Imperial College Archives, Silvanus P. Thompson's papers, letter 297.

[19] A copy of the original letter can be found among Stokes' papers: Letter from Stokes to Thompson, 28th May 1896, CUL Add 7656.T332. The original letter from Stokes to Thompson is kept by the Imperial College Archives, Silvanus P. Thompson's papers, letter 298.

At this time, it was, of course, impossible to distinguish Becquerel's work from the researches of Charles Henry, Gaston Niewenglowski, Arsène d'Arsonval and others. Stokes probably referred specifically to Becquerel because he had for five decades been associated with the Becquerel family. On the other hand, Lord Kelvin compared Silvanus Thompson's work to that of d'Arsonval:

> I had noticed that Sylvanus Thompson's very interesting discovery had been anticipated by d'Arsonval in the Comptes Rendus of March 2.[20]

Notice that, in his first letter to Stokes, Thompson interpreted the phenomenon as a special kind of invisible phosphorescence or fluorescence that violated Stokes' law. This was not a strong objection, however, because Stokes informed Thompson that the law was not completely general: "These effects are inconsistent with a law enunciated by Stokes – but which he has since modified" (Anonymous, 1896b). The status of this law and its influence on Becquerel's thought was discussed elsewhere (Martins, 1997).

Silvanus Thompson called the phenomenon "hyper-phosphorescence" and described it in the following way:

> This phenomenon, discovered by the author independently at the same time with M. Henri Becquerel, consists in the persistent emission by certain substances, notably by metallic uranium and its salts, of invisible rays which closely resemble Röntgen rays in their photographic action, and in their power of penetrating aluminium, and of producing diselectrification. (Thompson, 1896b, p. 713)

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[20] Letter from Lord Kelvin to Stokes, 12th March 1896. CUL Add 7656.K313. This letter was published in Wilson, 1990, vol. 2, p. 650 (letter 555).

What was the nature of those radiations? “That their [the uranium rays’] properties are intermediate between those of ultra-violet and of the Röntgen rays furnishes a strong presumption that the latter also differ only in degree, and are an extreme species of ultra-violet light” (Thompson, 1896c, p. 106).

In harmony with this interpretation, Thompson drew the same conclusion as Becquerel:

> The phenomenon of persistent emission of these invisible rays by the uranium compounds long after any electrical or luminous stimulus has ceased to be applied would seem, therefore, to bear the same relation to the transient emission of them in the Crookes tube as the persistent emission of visible light by phosphorescent bodies does to the transient emission of light by fluorescent bodies. Hence the writer ventures to give to the new phenomenon thus independently observed by M. Becquerel and by himself the name of *hyper-phosphoresce*. A hyper-phosphorescent body is one which, after due stimulus, exhibits a persistent emission of invisible rays not included in the hitherto recognized spectrum. (Thompson, 1896c, p. 106)

Henri Becquerel never mentioned Silvanus Thompson’s work. Contemporary physicists ascribed small importance to Thompson’s contribution, perhaps because Becquerel’s results were published a few months before Thompson’s reports. Historians of science seldom refer to his contribution.[21] However, even among French writers, the name “hyperphosphorescence” coined by Thompson was widely accepted and used to describe the phenomenon studied by Henri Becquerel (Guillaume, 1897, pp. 131-135). It was Marie Curie

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[21] One exception is Lawrence Badash, who cited his name (Badash, 1965, p. 63, footnote 29), but provided no information about Thompson’s work.

(not Becquerel) who first criticized the name and the concept underlying it:

> I will call *radioactives* the substances that emit Becquerel rays. The name *hyperphosphorescence* that had been proposed for the phenomenon seems to me to convey a wrong idea about its nature. (Curie, 1899)

7. DO PHOSPHORESCENT ANIMALS EMIT X-RAYS?

Henri Becquerel's researches should be analysed in their historical context. After the discovery of X-rays, scientific periodicals were flooded both by papers concerning the radiation emitted by Crookes' tubes and by communications of new kinds of radiations.

Among the many researches triggered by the discovery of X-rays, one of the most curious was the search for X-ray emitted by animals. The motivation for this search was, once again, Poincaré's conjecture: if the production of X-rays is related to luminescence, then luminescent animals should also emit X-rays.

On 18th April 1896, Raphael Dubois presented to the Biology Society the first evidence of emission of penetrating radiation by a phosphorescent animal (Dubois, 1896a). He studied a bivalve mollusc (*Pholad*) that emitted "a beautiful bluish phosphorescence, that offers to the eye some analogy to that of mineral bodies". Dubois observed that the luminous organ of the mollusc was able to have an effect on a photographic plate, through black paper, after an exposition of 15 hours (without the black paper, it took 12 hours to obtain a photograph). It was also possible to obtain photographic effects through cardboard and thin wood (a few millimetres thick). In this case, it took 18 hours to obtain the effect. He also tried aluminium, but the results were not very clear. His conclusion was:

> Those are, certainly, encouraging endeavors that I will repeat with luminous microbes, but they are not sufficient to demonstrate in a rigorous way the existence of X rays among living bodies, because ordinary radiations could perhaps pass through thin bodies in an amount that cannot be noticed by the eye, but sufficient to impress in a long time a sensible plate, by accumulative action. (Dubois, 1896a, p. 385)

One month later (9th May 1896), Dubois presented the results of his study of luminous microbes. The abstract of his work described positive results:

> I have exposed, above liquid cultures of luminous photobacteria, photographic plates wrapped in two or even in three sheets of the paper used to protect those plates from ordinary light. One coin was placed between the paper sheets. The whole was placed in the most complete darkness. After twenty-four hours of exposition, and after development, the contours of the coin and of the open vessel that contained the culture were clearly distinguished: the space comprised between those two contours was neatly impressed. (Dubois, 1896b, p. 479)

Although this text was careful enough to avoid concluding that those living beings emitted X-rays, the title of his work ("X-rays and luminous microbes") clearly shows Dubois' belief.

Dubois' work had no impact. A few months later, however, there appeared another similar work that was seriously discussed by the scientific community.

On the 5th August 1896, Han'ishi Muraoka[22] sent to the *Annalen der Physik und Chemie* a paper on the light emitted by a kind of firefly (Muraoka, 1896). Muraoka had studied Becquerel's work on the penetrating radiation emitted by fluorescent compounds of uranium, and he conjectured that light emitting insects could also produce penetrating rays similar to X-rays.

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[22] Han'ichi Muraoka (1853-1929) was a physics professor at Kyoto.

Muraoka used photographic plates upon which he placed a card with a cross-shaped hole. Upon the card he placed thin plates of different metals (aluminium, copper, zinc, etc.) and the whole was wrapped in three or four folds of black paper. The prepared plate was then exposed during two or three days to the radiation emitted by about 300 fireflies[23]. The card between the metal and the photographic plate was intended to avoid contact effects that had already been studied by MacIntyre and that were observed to produce effects on the photographic plates[24]. Muraoka reported a positive effect, and he studied the penetration of the rays through different metals and substances. The rays did not affect fluorescent screens, and produced no electric discharge. Muraoka described evidence that the rays could be reflected, but he has found no definite evidence of refraction or polarisation.

Those rays had some strange properties. The effect was stronger directly under a cardboard than at the places where the cardboard had a hole. The cardboard seemed to produce some kind of "suction effect" upon the rays, analogous to the effect of iron for magnetic lines of force. It also seemed that only upon filtration by cardboard, paper or metal, the radiation emitted by the fire-flies was able to produce effect upon photographic plates.

Muraoka concluded that the rays emitted by his insects was similar to Becquerel's rays, that he called "Becquerel's fluorescent rays" [*Becquerel'schen Fluorescenzstrahlen*].

Muraoka's work called the attention of several researchers[25]. Among them, Silvanus Thompson was specially interested in

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[23] The insects used by Muraoka appeared in Kyoto around the middle of June and were named by him (in German) as "Johanniskäfer", that means *St. John's beetle*. The name was not adequate, and the fireflies used by Muraoka were later identified as *Luciola vitlicollis* and *Luciola picticollis* (see Lungo, 1897, p. 130).

[24] MacIntyre's work is described in Anonymous (1896a, p. 379).

[25] See, for instance, the abstract published in *The Electrician* **38**: 238, 1896, where Muraoka's paper is described as "the sensation of the

the phenomenon, and he reported that Dawson Turner had also observed that glow-worms emit rays that can pass through aluminium (Thompson, 1897, p. 126).[26]

Independently of Muraoka, Charles Henry had described a related phenomenon (Henry, 1896b). He put a few glow-worms over photographic plates wrapped in black paper. When the plates were developed, he observed dark tracks reproducing the tracks of the worms upon the plates. However, Charles Henry did not give much attention to this effect.

Muraoka sent a copy of his paper on "Das Johanniskärferlicht" to Stokes, who replied to him[27] on the 18th March, 1897. Stokes found Muraoka's work "extremely interesting" and suggested to him some new experiments.

Stokes had once observed fireflies and had a hypothesis concerning the production of light by those insects: "I could not help supposing that the light arose in some way from an electric discharge, made at the will of the animal, as in the case of electric fishes, though how the discharge, if there were one, produced the light, I could not tell". Therefore, Stokes was led to think that at least part of the effect observed by Muraoka could be due to an electric discharge. But he also accepted the possibility of "beetle rays", that is, radiation emitted by the insects and that could traverse black paper.

Stokes supposed that "beetle rays" could not traverse metal plates, but that they could produce a slight electric charge upon the surface of the metal (such as happens with X-rays or Becquerel rays). This electric charge could flow through the photographic plate and produce the observed effects. For this reason, the effect was stronger directly under a metal plate, as Muraoka had described. Accordingly, Stokes suggested that

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current number of Wiedemann's *Annalen*". Abstracts were also published in the *American Journal of Science* IV, **3**: 151-152, 1897, and in several other scientific journals.

[26] It seems that Turner never published those observations.

[27] Letter from Stokes to Muraoka, 18 March 1897, CUL Add. 7656.M759.

Muraoka connected the metal plates to the Earth, or placed a thin mica foil between the metal plates and the photographic plate.

Muraoka replied to Stokes[28] in a letter dated 12th October 1897. He tried to analyse the light emitted by the fireflies, but could obtain no result since he used a glass prism (that is opaque to ultraviolet rays). He tried to detect electric currents in the beetles, and connected to the Earth the metal plates, with no positive effect.

He reported that the use of mica produced an inversion of the darker and lighter parts of the image on the photographic plate. He was led to think that besides the direct effect of the penetrating beetle rays there should be a second cause. In this letter, Muraoka stated: "Several experiments I made led me to assume vapours of bodies used in the experiments as the second cause". In some experiments with wood, he believed that the resin also produced photographic effects: "When the action of the beetle rays surpasses that of the resin vapour then is the action at the softer part stronger and in the other case the denser part appears darker".

Muraoka still believed that the fireflies emitted penetrating rays, but he could not find new effects, and for this reason he sent for publication in the *Annalen der Physik und Chemie* only a discussion of the effect of vapours upon photographic plates.

Muraoka's second paper (Muraoka & Kasuya, 1898) was received for publication in the *Annalen der Physik und Chemie* on the 24th November 1897. In this paper, Muraoka and Kasuya recall that several researchers had also described penetrating rays from luminous insects[29]. Stokes' letter to Muraoka was acknowledged and part of it was translated.

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[28] Letter from Muraoka to Stokes, 12 October 1897, CUL Add. 7656.M760.

[29] They cite the works of Charles Henry, R. Dubois, K. Shimada and D. Turner (*apud* Silvanus Thompson).

The main influence studied in the second paper was the effect of water. In the first paper, Muraoka had already described that it was necessary to keep the insects slightly wet so that they could live for several days. In the second paper, Muraoka reported that the darkening of the photographic paper was different according as the insects were more or less dry. This observation led him to investigate the effect of damp and vapours upon photographic plates. He noticed that the presence of several substances (such as coffee) would darken the photographic plates. Some metals, such as zinc, cadmium and magnesium also affected photographic plates.

Although there is no final conclusion in this paper concerning the previous researches on the radiation of fireflies, most readers must have concluded that the former results were spurious and that the observed effects were all due to vapour emitted by several substances. In a review of experiments related to "Becquerel rays", Stewart (1898) commented Muraoka's researches:

> Much interest was excited but a short time ago over a supposed invisible radiation from glow worms. The discoverer [Muraoka] has lately announced that the effect was in some way due to moisture, it being necessary to keep the glow worms wet. Moistened paper gave the same effect that the glow worms had.

Notice, however, that this was not, Muraoka's belief. In his second letter to Stokes, he still maintained that the action of vapours was a "second cause", that could be weaker or stronger than the direct effect of the beetle rays.

8. DOES SUGAR EMIT PENETRATING RAYS?

Of course, the early search for bodies emitting X-rays or other radiations was not limited to phosphorescent animals. One of the most famous claims of 1896 was Gustave le Bon's discovery of "black light" – a radiation emitted by common flames, that could traverse thick opaque bodies and thin metal plates[30]. In this case, as in several other episodes of the time, there was an intricate mixture of interesting new phenomena and mistakes.

In a letter to Gustave le Bon, written on the 6th June 1896, Auguste Lumière complained about the multitude of "new radiations" discovered after the X-rays:

> Everyday someone submits to us some cases of this kind; we have by the hundreds cases of a partial or total clouding of photographic plates, of impressions produced in extraordinary circumstances, without intervention of light, or without apparent intervention. In most of these cases which are submitted to us constantly, we have almost always been able to find the cause of these phenomena, after a study – albeit sometimes very lengthy – of each of them.[31]

The Lumière brothers, who produced most of the photographic plates used in those researches, carefully checked and dismissed many early claims – such as the supposed emission of penetrating radiations by electric arcs and flames – as due to heat or penetration of common light (Lumière & Lumière, 1896a). On the 24th February, the same day when Henri Becquerel presented his first "radioactivity" paper, the Lumière brothers warned again that many different agents could affect photographic plates: mechanical pressure, contact with several substances, heat, penetration of light through the boxes or wrappings that contained the plates, etc. (Lumière & Lumière, 1896b). Similar warnings were published by René Colson, who added to the Lumières' list the action of water vapour, and infrared and ultraviolet radiations that can sometimes pass through considerably opaque bodies (Colson, 1896).

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[30] This interesting episode will not be discussed here; see Nye (1974).

[31] Letter from Auguste Lumière to Gustave le Bon, 6 June 1896, cited by Nye (1974).

Several researchers have looked for materials that emitted penetrating radiations. RenéColson and Henri Pellat described the action of some metals (zinc, magnesium, cadmium, steel) on photographic plates (Colson, 1896; Pellat, 1896). Colson ascribed the effect to metal vapour, but Pellat suggested that the observed effects could be due to penetrating radiations similar to those of uranium.

F. McKissick (1897), inspired by Becquerel's work, reported that the following substances produced photographic effects through the cover of a plate holder: lithium chloride, barium sulphide, calcium sulphate, quinine chloride, quinine sulphate, calcium nitrate, sugar, chalk, glucose, sodium tungstate, sterein, uranium acetate, and ammonium phospho-molybdate. Both glass and metal were opaque to the radiation emitted by those substances, while cardboard and wood were "very transparent". The most active of all substances tried by McKissick was sugar: "I have succeeded in taking a fairly clear negative through 2½ in. of wood with sugar".

There were some unbelievable aspects in McKissick report: "Generally more than one image of an object was produced, although the object was in direct contact with the sensitive plate. In one negative there are four images of one half-dollar, in another two images of a key, the images being at right angles to each other". Of course, this is only possible if the object moved over the photographic plate during the exposition.

In 1897, Russell Russell began his researches repeating some of Becquerel's experiments but soon obtained anomalous results: when a perforated zinc screen was put between the active substance and the photographic plate, the part of the photographic place below the hole was less effected than the part under the metal plate (Russell, 1897). Repeating the experiment without uranium compounds, Russell noticed that zinc alone would darken the photographic plate. The action of zinc was observable even when paper, parchment or rubber screens were interposed between the metal and the photographic plate.

Other metals were observed to produce similar effects: mercury, magnesium, cadmium, zinc, nickel, aluminium, pewter, fusible metal (an alloy of lead, bismuth and tin), lead, bismuth, tin, cobalt, antimony. Other metals, such as iron, gold and platinum, produced no observable effect. He reported that wood was active, as also charcoal, straw and silk. The ink used in some newspapers was also very active.

In some cases, Russell conjectured that vapours emitted by the active substance could be the cause of the observed effect. However, it was difficult to accept that this could be the case with metals. Further experiments (Russell, 1898), however, confirmed that the active metals had the property of giving off (even at ordinary temperature) some kind of vapour which could affect photographic plates. This vapour was able to pass through thin sheets of paper, gelatine, celluloid, etc., and could be carried by a current of air. A last series of experiments (Russell, 1898) led to the conclusion that the effect was not due to metallic vapour, but to hydrogen peroxide produced at the surface of metals by reaction with air and moisture.

All those instances show how difficult it was, in 1896-97, to understand what meaning should be ascribed to spots on photographic plates. In some of his experiments, Becquerel had only wrapped his photographic plates in black paper – and the observed effect could be due to anything, from X-rays to heat and hydrogen peroxide. Only from 1898 those pitfalls were avoided by the use of electrical methods.

Gerhard Schmidt was led to discover that thorium and its compounds emit radiations similar to those of uranium when he studied the several substances that seemed able to darken photographic plates (Schmidt, 1898). Schmidt was aware of the works of Muraoka, Henry, Russell and others. He observed that the uranium radiations were different from the “radiations” of all other substances, because only uranium radiations rendered the air an electric conductor. He investigated several other substances, and was lucky enough to find out that thorium compounds also darken photographic plates *and* produce electric conduction in the air. Marie Curie was also led to the simultaneous discovery of the radiation of thorium by the same method (Curie, 1898).

The discovery of a second metal that produced radiations similar to those of uranium led, as is well known, a new impulse to the research of what we call radioactivity. But the fundamental finding was not the discovery of the radioactivity of thorium: it was the new electrical research method. It was only after Schmidt and Curie began to use electrical conduction as the criterion for recognition of radiations, in 1898, that it was possible to conclusively dismiss the supposed emission of penetrating radiations by metals, glow worms and sugar.

9. FINAL COMMENTS

Viewed "in the lump" among other researches concerning penetrating radiation emitted by several bodies, in the period 1896-1897, Becquerel's work was just one among several strange reported phenomena. Most of this early research was guided by Poincaré's conjecture. During all this period, Becquerel himself made no effort to draw a distinction between his own research and that of other people who had verified Poincaré's conjecture. Except for the case of Gustave le Bon's "black light" – that was violently attacked by Becquerel – he never criticised the works that described other penetrating radiations.

The discovery of X-rays excited the imagination of scientists and laymen alike, and it was followed by a large amount of speculative activity[32]. Among the several suggestions about the nature of X-rays, Poincaré's conjecture was particularly fertile. It was easy expose photographic plates to luminescent bodies and to look for something similar to X-rays. On the other hand, hypotheses such as Röntgen's suggestion of longitudinal ether

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[32] According to Oliver Lodge, general doubts about accepted knowledge and speculative activity are usually produced by new discoveries (Lodge, 1912).

waves were much more difficult to test and led to a limited number of publications (Thomson, 1896; Kelvin, 1896).

The nature and the process of production of X-rays was unknown, and even the empirical recognition of X-rays did not follow clear rules. That explains the widespread confusion between X-rays and many other effects that nowadays we would classify as spurious or as representing different phenomena. In this period the scientific community was, as a whole, highly uncritical and scientific periodicals accepted for publication reports that nowadays we would describe as ridiculous.

Among other issues, this episode raises the problem of evaluation of experimental research: was it possible, in 1896-1897, to distinguish Becquerel's work from other reported findings, and to assess their relative scientific values? In principle, yes. Any old-fashioned manual of scientific method would tell us that one should test the reliability of the experimental techniques themselves[33]. In practice, however, there was no systematic precaution concerning replicability, control of confounding factors, variation of conditions and observation techniques, etc. The lack of rigour must have been perceived by skilled scientists – but they probably did not pay much attention to the many claims of new radiations and effects following Röntgen's discovery.

Before 1898 – when the emission of radiations from thorium was found – not much attention was paid to Becquerel's research. He also must have thought that it was not a very interesting subject – just a new kind of invisible phosphorescence – and turned his attention to another subject: the Zeeman effect.

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[33] See, for instance, Mario Bunge (1967). In the recent literature, the possibility of establishing criteria for acceptance of empirical knowledge has been usually denied. Some authors, however, maintain the existence of objective experimental criteria. See Franklin (1986), Woodward & Bogen (1988), Culp (1995).

It was not Becquerel who called the attention of the world to a new, strange phenomenon. It was due to Schmidt's and Curie's works that the radiations emitted by uranium (and thorium) were clearly distinguished from other reported effects.

It was Marie Curie and not Becquerel who rejected the name "hyperphosphorescence" and coined the word "radioactivity", dismissing Poincaré's hypothesis and calling the attention of the scientific world to a new class of phenomena. Marie Curie was responsible not only for the word "radioactivity", but also for the establishment of radioactivity as a new research field. It was mainly due to Marie Curie's work, after the discovery of the radioactivity of thorium, polonium, and radium, that the subject became widely known and discussed, and the research of radioactivity became fruitful and was detached from the swarm of strange effects that arose around X rays.

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