THE GUIDING HYPOTHESIS OF THE CURIES' RADIOACTIVITY RESEARCH: SECONDARY X-RAYS AND THE SAGNAC CONNECTION

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Abstract: Pierre and Marie Curie's main discoveries on radioactivity are usually regarded as empirical investigations that were developed without any theoretical guidance. Their papers avoid indeed theoretical discussion, but it is possible to identify the main hypothesis that directed their work. They thought that the radiation emitted by uranium compounds (and, later, by other similar substances) was similar to the secondary radiation emitted by heavy metals when they are hit by X-rays. This hypothesis, together with other relevant assumptions, was suggested by Georges Sagnac's investigation on X-rays. This paper describes Sagnac's studies and how the acceptance of the secondary radiation hypothesis guided the study of radioactivity by the Curies. For the Curies, this hypothesis explained one of the anomalous characteristics of radioactivity – the continuous emission of energy without any noticeable change of the emitting bodies. When the magnetic deviation of the beta-rays of radioactive bodies was discovered, in 1899, this presented a challenge to their hypothesis. They carefully checked that discovery, and attempted to produce a magnetic deflection of X-rays, with negative results. However, in 1900 Pierre Curie and Georges Sagnac investigated secondary X-rays and concluded that they contained both "soft" X-rays and a negatively charged radiation (similar to beta-rays). Because of those results, they still kept their faith in the secondary radiation hypothesis at the time when Rutherford and Soddy began to develop the disintegration theory of radioactivity.
Keywords: radioactivity; X-rays; history of physics; Curie, Marie; Curie, Pierre; Sagnac, Georges

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1. INTRODUCTION

Pierre and Marie Sklodowska Curie's main discoveries on radioactivity are usually regarded as empirical investigations that were developed without any theoretical guidance. Their approach has been contrasted to Ernest Rutherford's, and it has been suggested that the use of concrete models and hypotheses by the later contributed to his success, where the Curies failed.

Up to 1900, the French were the leaders in the study of radioactivity (Jauncey, 1946). However, the understanding of radioactivity as a phenomenon of atomic transmutation came from abroad. How did they loose their leadership?

In 1899 the Curies discovered that an object placed near to a strongly radioactive source became radioactive. Ernest Rutherford also noticed that bodies near thorium became radioactive. In both cases, it was noticed that the radioactivity of those bodies was short-lived. The Curies described the phenomenon as an "induced activity", and they initially rejected Rutherford's proposal that it could be produced by a material emanation coming from the radioactive substances. Rutherford's approach led to the discovery of radon and of atomic transmutation. The Curies' approach to induced radioactivity led to a mere accumulation of facts and attempts to discuss them in a more general, abstract way.

According to some historians, the Curies systematically adhered to an abstract and timid approach to radioactivity, attempting to produce generalisations from observed facts and following a thermodynamic perspective. Rutherford, on the other hand, is described as a bold researcher who framed concrete, risky hypotheses and allowed them to guide his research.

The difference between the attitudes of Rutherford and the Curies has been sometimes described as due to contrasting personalities; or to national differences (see Malley, 1979; Nye, 1993, for a discussion of the French and English national styles)[1]; or to the distinct research schools to which they belonged (Davis, 1995).

However, before attempting to *explain* a fact, it is wise to check whether the fact is true, or an artefact produced by the historian's analysis.

I maintain in this paper that the attitudes of the Curies and Rutherford respecting the use of hypotheses were not widely different as has been claimed.

2. HYPOTHESES IN THE RESEARCHES OF BECQUEREL AND THE CURIES

It is usually assumed that Henri Becquerel's research was also purely empirical. In a former paper I have argued that Becquerel's work was guided by a hidden hypothesis concerning the violation of Stokes' law in uranium and its compounds (Martins, 1997). I contend that, in a similar way, the Curies' researches on radioactivity were strongly directed by a hypothesis – one that was not as concealed or secret as in the case of Becquerel's work. Indeed, the Curies' papers usually averted theoretical discussion and presented no hint of a guiding hypothesis. However, in other papers it is possible to identify plain clues of the main hypothesis that directed their work.

The hypothesis that will be discussed here appeared in print, for the first time, in Marie Sklodowska Curie's paper announcing that thorium emitted a penetrating radiation, just like uranium. She suggested that the radiation emitted by uranium and thorium compounds (and, later, by other similar substances) was produced by an unknown radiation coming from space, that was transformed inside those substances, in the same way as X-rays can be transformed into secondary rays. This hypothesis, together with other relevant assumptions, was suggested by Georges Sagnac's investigation on X-rays.

[1] Of course, national differences between England and France are difficult to apply in this specific case, because Rutherford was from New Zealand and Marie Sklodowska Curie was Polish.

> *Analogy with the secondary rays of the Röntgen rays*. – The properties of the rays emitted by uranium and thorium are very similar to those of the secondary rays of the Röntgen rays, recently studied by Mr. Sagnac. Besides that, I have noticed that under the action of the Röntgen rays, uranium, pitchblende and thorium oxide emit secondary rays which, from the point of view of the discharge of electrified bodies, often produce stronger effects than the secondary rays of lead. Among the metals studied by Mr. Sagnac, uranium and thorium would be placed in the neighbourhood of lead, and beyond it.
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> To elucidate the spontaneous radiation of uranium and thorium we could imagine that the entire space is always crossed by rays analogous to the Röntgen rays, but much more penetrating and that could only be absorbed by certain elements with a large atomic weight, such as uranium and thorium. (Sklodowska-Curie, 1898a, p. 1103)

Let us first make clear the meaning of Marie Sklodowska Curie's hypothesis. The starting point of her research was, of course, Henri Becquerel's investigation of the rays emitted by uranium and its compounds, in 1896-1897. Becquerel believed that those rays were similar to X-rays (or Röntgen rays). Although the nature of X-rays was not established at that time, Becquerel believed that they were high-frequency electromagnetic waves (beyond the ultraviolet). He supposed that uranium and its compounds could transform visible light into X-rays by a special phenomenon of phosphorescence violating Stokes's law. Led by his belief, [2] Becquerel reported observations to the effect that the radiation emitted by uranium compounds decreased slowly in the darkness, and increased after they were strongly illuminated; that the radiation of uranium compounds could be reflected by a metallic mirror, could be refracted by glass and polarised by a tourmaline

[2] See MARTINS, Roberto de Andrade. Becquerel's experimental mistakes, in this volume.

crystal. All his experiments seemed to confirm that uranium radiation was a high-frequency electromagnetic radiation.

Becquerel's early investigations on uranium radiation lasted from 1896 to 1897. During this period, there were very few other scientists who published any paper on the subject. The limited literature on this theme was one of the reasons that led Marie Sklodowska Curie to choose it as a research object for her PhD thesis. The decision was made towards the end of 1897. Her experimental researches started on the 16th of December, 1897 (Joliot-Curie, 1955, p. 106).

Georges Sagnac (1869-1928), a close friend of the Curies at that time, was one of the very few people who had carefully studied Becquerel's work before 1898 and he published a review paper on that phenomenon (Sagnac, 1896). It is possible that Sagnac influenced Marie Sklodowska Curie's choice of uranium radiation as a subject of research.

When Marie Curie started her work on uranium, both Georges Sagnac and Jean Perrin (1870-1942) – another friend of the Curies – were working on their PhD theses on X-rays. Perrin studied the discharge of electricity produced by X-rays. Sagnac studied the secondary radiation emitted by metals hit by X-rays. It is likely that Perrin and Sagnac discussed their researches with the Curies.

Becquerel had shown that the uranium rays were also able to discharge electrified bodies, as X-rays did. Marie Sklodowska Curie's first experiments, as shown in her laboratory notebook, were aimed at the study of the conductivity of air produced by uranium radiation. It is likely that she initially accepted all the conclusions published by Becquerel, and that she intended to develop a research similar to that of Jean Perrin, making a detailed study of all circumstances involved in the production of electric conduction by the uranium rays. Indeed, if the uranium rays were similar to X-rays, it was natural to use the researches on X-ray of her friends as a model for her own investigation. This circumstance could be the motivation for the specific choice made by Marie Curie at the beginning of her research.

Some early experiments led Marie Sklodowska Curie to conclude (as Becquerel had already noticed) that chemical reactions or temperature changes do not modify the intensity of the radiation emitted by uranium compounds (Joliot-Curie, 1955, pp. 106-108). The emission of the radiation only depended on the amount of uranium in a sample. Subsequently Curie noticed that all thorium compounds also emitted a similar radiation. As the emission was not influenced by external changes, it seemed an *atomic property* – and, of course, at that time, it was customary to regard atoms as unchangeable particles[3].

This was one of the explicit hypotheses presented by the Curies. It is well known that this hypothesis – that the emission of radiation was an atomic property – guided their successful search for new elements in pitchblende. The *atomic property hypothesis* was also confirmed when Marie Sklodowska Curie noticed that the amount of radiation emitted by uranium compounds is approximately proportional to their uranium contents, independently of the presence of other non-active elements in the substance.

Those facts did not conflict with Becquerel's initial conclusions. However, one of her early findings was that the radiation emitted by uranium and its compounds, carefully measured with an ionisation chamber, did not decrease in darkness and did not increase under strong illumination (Joliot-Curie, 1955, p. 106). Therefore, it did not behave as a phosphorescence phenomenon, as was supposed by Becquerel.

This discovery commanded a reflection on the source of energy behind the radiation phenomenon. Of course, for Becquerel the problem did not exist – the uranium radiation was

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[3] Some years later, Frederick Soddy remarked: "The view that radioactivity is an atomic property necessitates, on the older view of the unchangeability of the atom, that the activity should be in all cases a permanent property of the matter exhibiting it." (Soddy, 1905, p. 256)

just a form of energy that had been absorbed by the uranium compounds from light, and was slowly released under the form of penetrating radiation. However, since that interpretation was not correct, it became imperative to find out the energy source behind the emission of radiation by uranium and thorium. This was probably the motive that led the Curies to formulate their second hypothesis (the penetrating radiation hypothesis), that has already been pointed out.

On April 12, Marie Sklodowska Curie's first paper on the radiation of thorium was read by Gabriel Lippman at the French Academy of Science. In a period of less than 4 months, besides obtaining several relevant experimental results, the Curies had also framed the hypotheses that would guide their future research, abandoning Becquerel's perspective concerning the uranium phenomenon[4].

3. SAGNAC'S INFLUENCE

Marie Sklodowska Curie's initial experiments were probably guided by Becquerel's ideas and by her own experimental results. When did Georges Sagnac's influence start?

This happened probably in the second half of March. The laboratory notebooks of Marie and Pierre Curie show that on the 16th of March most of the measurements required by the thorium paper had already been completed (Joliot-Curie, 1955, p. 109). Pierre was beginning to help Marie, and on that day they both wrote a summary of the previous work, probably as a draft for a future paper. They were probably excited with the new results, and it is likely that they would discuss their research with Jean Perrin and Georges Sagnac.

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[4] One may wonder why it was Gabriel Lippman, not Henri Becquerel, who was asked by the Curies to report Marie's first paper to the Paris Academy of Science. Perhaps the reason was just that Marie had already worked with Lippman for some time, while studying the magnetism of several alloys. However, there might be another reason: the disagreement between Marie's results and Becquerel's ideas.

Sagnac was studying the secondary radiation produced by X-rays when they strike metals. Several researchers had attempted to detect the reflection of X-rays by metals and had failed. However, in some cases a dispersed radiation was observed coming from metals hit by X-rays. The initial interpretation was that the X-rays had been diffused or scattered by the metal; however, the diffuse radiation was less penetrating than the original one. Therefore, the metal had *transformed* the incident radiation. The phenomenon was similar to visible light fluorescence: the light emitted by a fluorescent substance has a smaller frequency than the incident radiation, according to Stokes' law. If the penetration of X-rays was related to their high frequency, then a secondary radiation of lower frequency was expected to be less penetrating.

In a paper where he described several properties of X-rays, including the production of secondary radiation, Sagnac remarked the similarity between the Röntgen rays and Becquerel's rays:

> It is appropriate to remind here the discovery due to H. Becquerel of new invisible radiations emitted during several months, without noticeable weakening, by uranium salts and especially by uranium, that have always been kept in darkness. Up to the present day it seems that there is no limit for the duration of those phenomena, for which S.-P. Thompson proposed the name *hyperphosphorescence*. We ignore if here there is really a transformation of radiations or simply a spontaneous radiation due to a new mechanism. Anyhow, those remarkable *uranium rays* are very close to the X-rays by their electrical properties. (Sagnac, 1898, p. 314)

The production of secondary radiation (or S-rays, as Sagnac called them) was especially strong when X-rays stroke metals of high atomic weight, such as lead. In the case of low atomic weight metals, such as aluminium, the incident rays traversed the metal without producing noticeable secondary radiation.

The secondary radiation was less penetrating than the original X-rays. For that reason, it was strongly absorbed and produced stronger effects (ionisation and photographic effects). The most penetrating X-rays passed by matter without noticeable energy loss, and therefore produced weak effects. The secondary radiation produced stronger effects, because its energy was easily absorbed by matter.

It is likely that Sagnac and the Curies discussed their mutual researches in the early months of 1898. Sagnac had been studying the secondary rays for some months, and several of his results had already been published, but he was continuing his researches during this period. The comparison between the two lines of research exhibited remarkable similarities. Marie Curie noticed that the rays emitted by uranium and thorium were similar to Sagnac's secondary rays:

1. Both the secondary rays and the uranium radiation were less penetrating than X-rays.
2. Only high atomic weight elements produced a large amount of easily absorbed secondary rays. The two elements that were known to emit Becquerel rays (uranium and thorium) were the elements with the highest atomic weight known at that time.

In her search for other substances that could emit penetrating rays, Marie Sklodowska Curie had noticed that some other elements (cerium, niobium, and tantalum) also seemed slightly active, but only uranium and thorium were very active. She commented:

> It is remarkable that the two more active elements, uranium and thorium, are those that have the highest atomic weights. (Sklodowska-Curie, 1898a, p. 1102)

This striking similarity suggested either to Sagnac or to the Curies the hypothesis of a penetrating radiation that could account for the energy emitted by uranium and thorium. Inasmuch as Marie Sklodowska Curie had already concluded that the emission of radiation by uranium was not similar to phosphorescence, and since the energy output seemed constant, the energy source could not be in the active material itself. It should come from outside, and the active substances just *transformed* some other form of energy existing in the environment into the Becquerel rays. The phenomenon could be analogous to the production of Sagnac's secondary rays by X-rays.

4. THE HYPOTHESIS OF A PENETRATING RADIATION

Marie Curie conjectured that a very penetrating unknown radiation existed everywhere. It produced no observable effects in ordinary matter but its transformation by heavy atomic weight elements could produce a detectable secondary radiation – the Becquerel rays.

This trend of ideas is not explicit in the early papers published by Marie Sklodowska Curie, but that seems a plausible reconstruction of the reasoning that led to the hypothesis of the penetrating radiation.

It seems that the hypothesis was not due to Sagnac. Indeed, in a paper on X-rays and secondary rays he published in 1898, Sagnac referred to the similarity between X-rays and the Becquerel rays, but did not compare them to the secondary rays. Also, as will be seen later, in 1901 this hypothesis was clearly ascribed to Marie Curie.

On the 1st April, the laboratory notebook shows that the Curies had already began to study the penetrating radiation conjecture. A series of experiments begun on this day, having the title "Effect of X-rays", attempted to detect changes in the amount of radiation emitted by uranium and other active materials when they were submitted to X-rays. The content of the notebook was described by Irène Joliot-Curie in the following way:

> The experimental conditions are not precisely described. It seems that the idea was the following: the active matter was irradiated through the support, that absorbed little; the active matter was covered by a plate that could absorb only part of its radiation, but almost completely the X rays (this plate could be made of lead). They searched whether the X-rays excited or not a radiation analogous to the normal activity of the active substances. The active materials used were uranium, uranium oxide, orangite and pitchblende. (Joliot-Curie, 1955, p. 111)

It is obvious that, at this point, the relation between the secondary radiation produced by X-rays and the emission of Becquerel rays by uranium and other active substances was already at work, guiding the experiments of the Curies.

On the same day, the Curies compared the penetrating powers of the rays emitted by thorium and uranium. They observed that the radiation emitted by uranium was less penetrating than that emitted by thorium. In the case of secondary rays, those emitted by elements with higher atomic weight were also less penetrating. Therefore, this experiment disclosed another important similarity between the radiation of uranium and thorium and Sagnac's S-rays.

As was already described, a few days later Marie Sklodowska Curie's first paper was read by Gabriel Lippman. It contained a clear presentation of the penetrating radiation hypothesis. No alternative hypothesis was discussed in that paper. This circumstance strongly suggests that the Curies were immediately convinced that this was a correct assumption.

The atomic property hypothesis and the penetrating radiation hypothesis were in mutual agreement and reinforced each other. If the Becquerel rays were the outcome of the transformation of a penetrating radiation by elements of high atomic weight, this should be a property that depended on the properties of the *atoms* (not molecules), and the total amount of radiation produced in uranium compounds should only depend on the amount of the active element in the substance.

5. A RESEARCH GUIDED BY HYPOTHESES

However, there were two empirical exceptions to the atomic property hypothesis: pitchblende and chalcolite, two uranium minerals, were more active than metallic uranium. If the atomic property hypothesis were a mere empirical generalisation, it should have been rejected because of those exceptions. However, the Curies chose to retain this hypothesis and added another supposition: that there was another, unknown active element, in pitchblende. This risky supposition was already presented in Marie Sklodowska Curie's first paper:

> Two uranium minerals, pitchblende (uranium oxide) and chalcolite (phosphate of copper and uranium) are much more active than uranium itself. This is a very remarkable fact and it leads to the belief that those minerals can contain an element that is much more active than uranium. (Sklodowska-Curie, 1898a, p. 1102)

The strong confidence shown by the Curies in the atomic property hypothesis at this early stage of their researches is a strong evidence that this hypothesis was not just an empirical generalisation. It was part of a broader theoretical interpretation of the phenomenon, reinforced by Sagnac's work on the secondary radiation. Everything seemed to fit those hypotheses, and guided by those hypotheses the Curies embarked into a strenuous search for the unknown active element in pitchblende. The hypothesis of the penetrating radiation, and the hypothesis that radioactivity was an atomic phenomenon (but without any assumption of atomic change) guided those investigations of the Curies from April 1898 onwards.

The two hypotheses led them to the discovery, in 1898, of two new radioactive elements: polonium and radium. In their following papers describing the discovery of polonium and radium, the Curies did not mention the penetrating radiation hypothesis, but they did refer to the atomic property hypothesis.

6. TESTING THE HYPOTHESIS OF THE PENETRATING RADIATION

It seems that the search for the new active elements absorbed most of their time, and they did not attempt to check the penetrating radiation hypothesis. Meanwhile, other researchers did it. In September 1898 Johann Elster and Hans Geitel submitted to the journal *Annalen der Physik und Chemie* a paper where they discussed several contrasting explanations of the Becquerel rays – including Marie Sklodowska Curie's penetrating radiation hypothesis.

After a theoretical discussion of the several suggestions, Elster and Geitel described an experimental test of Marie Sklodowska Curie's conjecture (Elster & Geitel, 1898). The hypothetical penetrating radiation should be able to penetrate the whole atmosphere (equivalent to about 10 meters of water), the walls of laboratory buildings and metallic apparatus used in radiation experiments, without noticeable absorption. However it would be extravagant to suppose that it could penetrate any thickness of matter without suffering absorption. If radioactivity was produced by a penetrating radiation coming from space, it should be weaker in deep pits. Hence, they were led to test whether the emission of radiation by uranium suffered any change when it was observed in a very profound pit, about 850 metres deep. The experiment showed, however, that the activity of the radioactive sample was the same at the depth of 850 metres and at the ground level. The authors concluded:

> From those researches it seems to us that the hypothesis of production of Becquerel rays by other rays pre-existent in space is improbable to the highest degree. (Elster & Geitel, 1898, p. 740)

Marie Sklodowska Curie became aware of this paper soon after it publication, in December 1898, and referred to its negative result in a long review article she published in January 1899 (Sklodowska-Curie, 1899a, p. 50). In that paper, Marie presented for the first time *several* explanations that had been suggested for radioactivity – including the penetrating radiation hypothesis.

The Curies acknowledged that the result of the experiment made by Elster and Geitel presented a difficulty for the penetrating radiation conjecture. However, they did not give up their hypothesis. They possibly thought that the radiation was not noticeably absorbed by the materials constituting the crust of the Earth, for depths of a few hundred metres, because the minerals that build up that crust do not contain a strong proportion of high atomic weight elements. They devised another test, which was shortly described in Marie Sklodowska Curie's thesis. The date of this experiment is unknown:

> We have measured the radioactivity of uranium at noon and at midnight, thinking that if the Sun were the source of the hypothetical primary radiation, this could be partially absorbed in passing across the Earth. Experience did not provide any difference between the two measurements. (7, 1903, p. 140)

Although 850 metres of rock did not produce any change, the whole Earth should produce a noticeable absorption. If the penetrating radiation came from the Sun, the activity of uranium should be greater at noon than at midnight. No difference was observed, however.

Notice that the Curies did not gave up the penetrating radiation hypothesis after Elster and Geitel's results. Notice also that their own experiment could only possibly *confirm* the penetrating radiation hypothesis, because the negative outcome could be interpreted in a very simple way: the penetrating radiation did not come from the Sun.

7. INDUCED RADIOACTIVITY

The penetrating radiation hypothesis had a strong influence on the interpretation of the Curies concerning "induced radioactivity". They described their discovery of the phenomenon in the following manner:

> While studying the properties of strongly radioactive matter, prepared by us (polonium and radium), we have noticed that the rays emitted by those substances, acting upon inert substances, can communicate radioactivity to them, and that this radioactivity remains during a very long time. (Curie & Sklodowska-Curie, 1899, p. 714)

Notice that in the very description of the discovery, the Curies assumed that *the rays* had induced radioactivity in other materials. A "neutral" description of the phenomenon would only specify that an inert body put close to a strongly radioactive source would become radioactive.

After describing the experiments that they made concerning the phenomenon, the Curies concluded:

> The phenomenon of induced radioactivity is a type of secondary radiation due to the Becquerel rays. However, this phenomenon is different from the one that is known for Röntgen rays. Indeed, the secondary rays of the Röntgen rays that have been studies up to now are born immediately when the bodies that emit them are hit by the Röntgen rays and cease immediately with the suppression of the later. (Curie & Sklodowska-Curie, 1899, pp. 715-716)

Therefore, the hypothesis of the penetrating radiation and secondary rays was the basis of their initial interpretation of "induced radioactivity".

8. NON-ELECTROMAGNETIC RADIATIONS

In 1899, new advances brought fresh difficulties for the interpretation of radioactivity. When the Curies began their studies on uranium and its radiation, nobody suspected that those rays could be classified into several different types. They seemed very similar to soft X-rays. The situation changed in

1899. Ernest Rutherford studied the absorption of radiation by thin metallic foils and distinguished the α and β rays. In the same year, Fritz Giesel, Stefan Meyer and Egon von Schweidler noticed that some of those rays could be deviated by a magnetic field. Now, the similarity between the Becquerel rays and X-rays began to dwindle, and this was a challenge to the views embraced by the Curies.

The possibility of diverting the rays was first confirmed by Becquerel, and Pierre Curie himself soon confirmed that some of the rays produced by radium and polonium could also be deviated by a magnetic field. Was this a clear proof that they were charged particles? Perhaps it was not. The Curies decided to check this point. They soon described an experiment where they separated and collected the magnetically deflected rays (Rutherford's β rays). They were able to detect that those rays carried a negative electric charge (Curie & Sklodowska-Curie, 1900b). They seemed of the same nature as cathode rays. This finding threatened all their theoretical assumptions, because now the Becquerel rays could not be anymore assumed to be similar to the secondary radiation of X-rays.

The analogy could be maintained, however, if the X-rays also carried an electrical charge. The Curies tested this possibility, and did not find any clear evidence that X-rays conveyed electrical charges (Curie & Sklodowska-Curie, 1900b, p. 650).

Of course, they must have discussed the uncomfortable situation with Sagnac, and their old friend came to their rescue. Indeed, in 1898 Sagnac had noticed that the secondary rays contained, besides neutral radiation, some electrically charged particles. The evidence he obtained in 1898 was not altogether clear and he decided not to publish his discovery. However, in order to be able to claim priority afterwards, he placed a description of his research in a sealed envelope ("pli cacheté"), that was delivered to the French Academy of Sciences on July 18, 1898. In February 1900 he asked the Academy to open the envelope. Its content was then read and published (Sagnac, 1900).

That was a very important point. Pierre Curie and Georges Sagnac soon began a detailed joint investigation of this topic[5]. On April 9, 1900, they presented to the Paris Academy of Sciences the result of their research (Curie & Sagnac, 1900). They confirmed the previous result of the Curies that Röntgen rays do not carry a noticeable electric charge; however, "on the contrary, *the secondary rays* originating from the transformation of Röntgen rays *do convey electrical charges with them*, similar to cathode rays, as do the rays from radium" (Curie & Sagnac, 1900, p. 1013; emphasis of the authors).

The paper published by Curie and Sagnac did not mention the penetrating radiation hypothesis of radioactivity. However, the connection between the experiments and the hypothesis was made clear in another work on the same subject that they presented on the 3rd of May 1901 to the French Physical Society.

> The weak penetration power of the secondary rays of heavy metals reminds us Lenard's cathode rays: they can only reach a few centimetres in the atmospheric air, where they are strongly diffused. This analogy led us to search whether the secondary rays, which are strongly absorbed by the air, carry with them negative electric charges, since this is the fundamental characteristic of the cathode rays. The deviation of the rays by a magnetic or electric field will be the probable consequence of their electrification. *There is no contradiction between this hypothesis and those that have been developed by one of us*, since the beam spontaneously emitted by the *radium* of Mr. and Mrs. Curie is a mixture of rays with negative electricity, analogous to the cathode rays, that can be deviated by the magnetic field and by the electric field, together with rays that cannot be deflected, analogous to X-rays, which seem devoid of electrical charges. (Curie & Sagnac, 1902, p. 13; my emphasis)

[5] Let us remark that this was the only joint research ever done by Curie and Sagnac.

The paper did not elucidate what the authors meant by the hypothesis that had been developed by one of them. Was that hypothesis proposed by Sagnac, or by Pierre Curie? An anonymous account of the meeting of the French Physical Society where they presented this paper leaves no doubt concerning this point: "The existence of electrified secondary rays producing a deflectable beam is in accordance with the analogy between the secondary rays and the spontaneous rays of radioactive bodies pointed out by Mrs. Curie" (Anonymous, 1901, p. 499). Therefore, it is unlikely that Sagnac had suggested the penetrating radiation hypothesis. The two previous citations imply that it had been proposed by one of the Curies.

Pierre Curie and Georges Sagnac concluded from their experiments that the penetrating radiation hypothesis could be maintained in face of the new discovered properties of radiation. They noticed that the emission of negative charges together with the secondary rays was especially noticed in heavy metals – a circumstance that enhanced the similarity between this phenomenon and radioactivity (Curie & Sagnac, 1900; Curie & Sagnac, 1902).

9. THE FATE OF THE HYPOTHESIS OF SECONDARY RAYS

In 1900 the Curies presented a report on radioactivity to the International Congress of Physics that occurred in Paris. At the end of that report they discussed the nature of the Becquerel rays. They reported that those rays contain both charged rays, similar to the cathodic rays, and others that were similar to X-rays. The occurrence of both kinds of rays seemed easy to explain:

> This mixture should not amaze us. In the vacuum tubes the X-rays are born at the walls hit by cathodic rays. On the other side, when X-rays hit the bodies they produce the birth of the secondary rays studied by Mr. Sagnac, and those secondary

> rays seem also to be formed by a mixture of non-deflectable rays and rays charged with electricity, analogous to cathode rays. There is therefore a strong analogy between the spontaneous emission of the radioactive bodies and the secondary rays of the Röntgen rays. This analogy had hit us since the beginning of this study, and afterwards it always became stronger.
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> [...]
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> According to what has just been said, it is possible to regard the Becquerel rays as a secondary emission due to some rays analogous to X-rays that traverse all space and every body.
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> If the emission in its totality is not a secondary emission, this could however be true for one of the two groups of rays; one could consider as primary rays either the non-deflectable rays, of the deflectable rays. (Curie & Sklodowska-Curie, 1900a, pp. 113-114).

The Curies also mentioned, at the end of their paper, the idea of a changing atom, but ascribed this idea to William Crookes and J. J. Thomson – not to themselves. It is plain that at that time the Curies had a strong confidence in the penetrating radiation hypothesis, and thought that it would remain acceptable at least for one of the types of radiation emitted by radioactive bodies.

It is possible to find other evidences that from 1900 to 1903 the Curies still accepted this hypothesis, notwithstanding the new facts that were being discovered. In 1903, for instance, Pierre Curie and André Laborde published the first measurement of the energy released by a radium salt. They concluded that 1 g of radium liberates about 100 calories per hour. The authors discussed the hypothesis that the energy liberation was due to an atomic change, and then they remarked: “The hypothesis of a continuous change of the atom is not the only one compatible with the release of heat by radium. This heat release can also be explained by supposing that the uranium makes use of an external energy of unknown nature.” (Curie & Laborde, 1903, p. 675)

This suggests that Pierre Curie had not given up the penetrating radiation hypothesis, at this time. It is also relevant to notice that when Becquerel and the Curies received the Nobel Prize for their researches, in 1903, the former researcher maintained that the penetrating radiation hypothesis was still acceptable – although he preferred the idea of atomic transformation:

> Among the hypotheses which suggest themselves to fill the gaps left by current experiments, one of the most likely lies in supposing that the emission of energy is the result of a slow transformation of the atoms of the radioactive substances. [...]
>
> In this scheme, there would still be scope to wonder whether the transformation of the atom comprises a slow, spontaneous evolution, or whether it is the result of the absorption of external radiation beyond the range of our senses. If such a radiation were to exist, one could still picture the radioactive substances transforming it without themselves being altered. So far no experiment has confirmed or invalidated these hypotheses. (Becquerel, 1903, p. 15)

On the same occasion, Pierre Curie discussed the existing explanations of radioactivity. He presented a description of the earlier views of the Curies that is at variance with existing evidence:

> Since the beginning of our researchers we have noticed, Mrs. Curie and I, that to explain the phenomena it is possible to frame two distinct very general hypotheses that were presented by Mrs. Curie in 1899 and 1900. (Curie, 1903, p. 5)

The two hypotheses are then presented by Curie: the penetrating radiation hypothesis and the hypothesis of atomic disintegration. As has been shown above, the only hypothesis described in Marie Curie's early research papers is the first one. The second hypothesis does appear, *among several others* (for instance, a violation of the second law of thermodynamics) in the papers published in 1899 and 1900 by Marie Curie; but his only occurred after the penetrating radiation hypothesis had been challenged by the experiment of Elster and Geitel[6]. Now, in 1903, Pierre Curie seemed convinced that the atomic transformation hypothesis was the best explanation; and so he was careful enough to *conceal* that their initial assumption was the penetrating radiation hypothesis.

10. CONCLUSIONS

The penetrating radiation hypothesis had been very fruitful, in 1898, since it provided an explanation for the atomic property hypothesis that guided the discovery of polonium and radium. When the hypothesis encountered strong difficulties – such as Elster and Geitel's negative experiment in the late 1898 – the Curies maintained their hypothesis. When the conjecture was threatened by the discovery of the nature of the β radiation, in 1899, Pierre Curie and Georges Sagnac were able to sustain the hypothesis by showing that the secondary rays also contained particles with negative charge.

However, it is likely that this loyalty to the old hypothesis acted as a barrier to the understanding of radioactivity, in the next years. The Curies still kept their faith in this hypothesis at the time when Rutherford and Soddy began to develop the disintegration theory of radioactivity. They resisted the new theory, not because of their aversion to concrete, material hypotheses (as has been claimed) but because the new theory was incompatible with their own cherished explanation of radioactivity. In a few years, nonetheless, they had to give up their explanation because only Rutherford's theory of atomic disintegration and change could account for the wealth of evidence amassed by himself, by Frederick Soddy and by several other researchers.

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[6] In her 1899 paper, Marie Curie described *five* (not two) groups of hypotheses for explaining the emission of energy by radioactive bodies (Sklodowska-Curie, 1899).

Although the traditional accounts of the work of the Curies do not emphasise their use of conjectures (see Weill, 1970; Wyart, 1970), I claim that their radioactivity researches were guided by some definite hypotheses, in the same way as Becquerel's research. In both cases, their scientific papers convey the feeling that their research was purely empirical and that they avoided any specific hypothesis, but that was not the case. Rutherford's hypotheses were perhaps more detailed and they were explicitly presented by him, in his paper. But that is just a difference of degree, not a qualitative difference between the attitudes of Rutherford and the Curies.

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BIBLIOGRAPHIC REFERENCES

[ANONYMOUS]. Société Française de Physique. Séance du 3 Mai 1901. *Revue Générale des Sciences* **12**: 498-499, 1901.

BADASH, Lawrence. Radioactivity before the Curies. *American Journal of Physics* **33**: 128-135, 1965.

BECQUEREL, Henri. Sur les radiations émises par phosphorescence. *Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences de Paris* **122**: 420-421, 1896 (a).

BECQUEREL, Henri. Sur les radiations invisibles émises par les corps phosphorescents. *Comptes Rendus*

Hebdomadaires des Séances de l'Académie des Sciences de Paris **122**: 501-503, 1896 (b).

BECQUEREL, Henri. Sur quelquer propriétés nouvelles des radiations invisibles émises par divers corps phosphorescents. *Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences de Paris* **122**: 559-564, 1896 (c).

BECQUEREL, Henri. Sur une propriété nouvelle de la matière, la radio-activité. *Les Prix Nobel* **3**: 1-15, 1903.

CROOKES, William. *La genèse des éléments*. Translated by Gustave Richard. Paris: Gauthier-Villars, 1887.

CURIE, Ève. *Madame Curie*. Paris, Gallimard, 1939.

CURIE, Pierre. L'état actuel des recherches sur les substances radioactives. *Archive des Sciences Physiques et Natureles* [4] **10**: 388-389, 1900.

CURIE, Pierre. Conférence Nobel faite a Stockholm devant l'Académie des Sciences. *Les Prix Nobel* **3**: 1-7, 1903.

CURIE, Pierre & LABORDE, A. Sur la chaleur dégagée spontanément par les sels de radium. *Comptes Rendus de l'Académie des Sciences de Paris* **136**: 673-675,1903.

CURIE, Pierre & SAGNAC, Georges. Électrisation négative des rayons secondaires produits au moyen des rayons Röntgen. *Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences de Paris* **130**: 1013-1016, 1900.

CURIE, Pierre & SAGNAC, Georges. Électrisation négative des rayons secondaires issus de la transformation des rayons X. *Journal de Physique* [series 4] **1**: 13-21, 1902.

CURIE, Pierre & SKLODOWSKA-CURIE, Marie. Sur une substance nouvelle radioactive, contenue dans la pechblende. *Comptes Rendus de l'Académie des Sciences de Paris* **127**: 175-178, 1898.

CURIE, Pierre & SKLODOWSKA-CURIE, Marie. Sur la radioactivité provoquée par les rayons de Becquerel. *Comptes Rendus de l'Académie des Sciences de Paris* **129**: 714-716, 1899.

CURIE, Pierre & SKLODOWSKA-CURIE, Marie. Sur la charge électrique des rayons déviables du radium. *Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences de Paris* **130**: 647-650, 1900 (a).

CURIE, Pierre & SKLODOWSKA-CURIE, Marie. Les nouvelles substances radioactives et les rayons qu'elles émettent. Vol. 3, pp. 79-113, *in*: GUILLAUME, Charles-Édouard & POINCARÉ, Lucien (eds.). *Rapports Présentés au Congrès International de Physique réuni a Paris en 1900.* 3 vols. Paris: Gauthier-Villars, 1900 (b).

CURIE, Pierre, SKLODOWSKA-CURIE, Marie & BÉMONT, G. Sur une nouvelle substance fortement radioactive, contenue dans la pechblende. *Comptes Rendus de l'Académie des Sciences de Paris* **127**: 1215-1217, 1898.

DAVIS, J. L. The research school of Marie Curie in the Paris Faculty, 1907-14. *Annals of Science* **52**: 321-355, 1995.

ELSTER, Johann & GEITEL, Hans. Versuche an Becquerelstrahlen. *Annalen der Physik und Chemie* [2] **66**: 735-740, 1898.

JAUNCEY, G. E. M. The early years of radioactivity. *American Journal of Physics* **14**: 226-241, 1946.

JOLIOT-CURIE, Irène (ed.). *Oeuvres de Marie Sklodowska Curie / Prace Marii Sklodowskiej-Curie.* Varsovie / Warsawa: Panstwowe Wydawnictwo Naukowe, 1954.

JOLIOT-CURIE, Irène. Les carnets de laboratoire de la découverte du polonium et du radium. Pp. 103-124, *in*: SKLODOWSKA-CURIE, Marie. *Pierre Curie*. Paris: Denoël, 1955.

MALLEY, Marjorie. The discovery of atomic transmutation: scientific styles and philosophies in France and Britain. *Isis* **70**: 213-223, 1979.

MARTINS, Roberto de Andrade. Becquerel and the choice of uranium compounds. *Archive for History of Exact Sciences* **51** (1): 67-81, 1997.

NYE, Mary Jo. National styles? French and English chemistry in the nineteenth and early twentieth centuries. *Osiris* **8**: 30-49, 1993.

PERRIN, Jean. Rayons cathodiques et rayons de Röntgen. Étude expérimentale. *Annales de Chimie et de Physique*, [série 7], **11**: 496-554, 1897.[7]

RUTHERFORD, Ernest. Uranium radiation and the electrical conduction produced by it. *Philosophical Magazine* **47**: 109-163, 1899.

SAGNAC, Georges. Les expériences de M. H. Becquerel sur les radiations invisibles émises par les corps phosphorescents et par les sels d'uranium. *Journal de Physique Théorique et Appliquée* [3] **5**: 193-202, 1896.

SAGNAC, Georges. Luminescence et rayons X. *Révue Générale des Sciences* **9**: 314-320, 1898.

SAGNAC, Georges. Rayons X et décharge: généralisation de la notion de rayons cathodiques. *Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences de Paris* **130**: 320-323, 1900.

SAGNAC, Georges. Propagation des rayons X de Röntgen. *Annales de Chimie et de Physique* [série 7] **22**: 394-432, 1901 (a).

SAGNAC, Georges. Rayons secondaires dérivés des rayons de Röntgen. *Annales de Chimie et de Physique* [série 7] **22**: 493-563, 1901 (b).

SAGNAC, Georges. Relation des rayons X et de leurs rayons secondaires avec la matière et l'électricité. *Annales de Chimie et de Physique* [série 7] **23**: 145-198, 1901 (c).

SKLODOWSKA-CURIE, Marie. Rayons émis par les composés de l'uranium et du thorium. *Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences de Paris* **126**: 1101-1103, 1898 (a).

SKLODOWSKA-CURIE, Marie. Poszukiwania nowego metalu w pechblendzie. *Swiatlo* **1**, 1898 (b). Reproduced in

[7] This paper reproduces Perrin's PhD thesis.

pp. 49-56, JOLIOT-CURIE, *Oeuvres de Marie Sklodowska Curie*.

SKLODOWSKA-CURIE, Marie. Les rayons de Becquerel et le polonium. *Révue Générale des Sciences* **10**: 41-50, 1899.

SKLODOWSKA-CURIE, Marie. Sur le poids atomique du baryum radifère. *Comptes Rendus de l'Académie des Sciences de Paris* **131**: 382-384, 1900.

SKLODOWSKA-CURIE, Marie. Sur le poids atomique du radium. *Comptes Rendus de l'Académie des Sciences de Paris* **135**: 161-163, 1902.

SKLODOWSKA-CURIE, Marie. *Recherches sur les substances radioactives*. Paris: Gauthier-Villars, 1903.[8]

SKLODOWSKA-CURIE, Marie. *Pierre Curie.* Trad. Charlotte and Vernon Kellogg. With an introduction by Mrs. William Brown Meloney and autobiographical notes by Marie Curie. New York: MacMillan, 1923.

SODDY, Frederick. Radioactivity. *Annual Reports on the Progress of Chemistry for 1904 Issued by the Chemical Society* **1**: 244-280, 1905.

WEILL, Adrienne R. Curie, Marie (Maria Sklodowska). Vol. 3, pp. 497-503, *in*: GILLIESPIE, Charles Coulston (ed.). *Dictionary of Scientific Biography*. 16 vols. New York: Charles Scribner's Sons, 1970.

WYART, Jean. Curie, Pierre. Vol. 3, pp. 503-508, *in*: GILLIESPIE, Charles Coulston (ed.). *Dictionary of Scientific Biography*. 16 vols. New York: Charles Scribner's Sons, 1970.

[8] This was Marie Curie´s PhD thesis.

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