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Becquerel and the Choice of Uranium Compounds

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Introduction

HENRI BECQUEREL's early researches on the radiation emitted by uranium compounds were part of a collective attempt to check HENRI POINCARÉ's conjecture concerning the relationship between X rays and luminescence (JAUNCEY *1946*; BADASH *1965*b; MARTINS *1996*a). He was neither the first nor the last to search for penetrating radiations emitted by luminescent bodies. BECQUEREL's early results were similar to those obtained by CHARLES HENRY and GASTON HENRI NIEWENGLOWSKI. There was, however, a new (and lucky) feature in BECQUEREL's early papers: the use of a new substance — the double sulphate of uranium and potassium.

BECQUEREL's choice of uranium compounds for investigation usually has been ascribed to chance: "He placed photographic plates wrapped in thick black paper against a luminescent material he had on hand, potassium uranyl-sulphate (a uranium salt) and exposed the assembly to sunlight for several hours . . . " (WASSON *1987*, 70). But was BECQUEREL's choice of uranium compounds due to chance? Did BECQUEREL randomly choose any luminescent substance "he had on hand" in his laboratory to test POINCARÉ's conjecture?

The answer is "no". BECQUEREL had in his laboratory dozens of luminescent substances, but he consciously chose uranium compounds. He was guided by his previous knowledge of luminescent substances: uranium compounds had some peculiar properties that led him to believe the emission of penetrating radiation was to be expected in their case. In this paper I propose a reconstruction of BECQUEREL's thought that elucidates this and several other aspects of his research.

Becquerel's Early Experiments

BECQUEREL's first paper on the radiation emitted by uranium salts was presented five weeks after the meeting at which POINCARÉ presented WILHELM CONRAD RONTGEN's discovery of X rays. Meanwhile, CHARLES HENRY and GASTON NIEWENGLOWSKY already had communicated the results of their experiments on POINCARÉ's conjecture. Why did BECQUEREL take five weeks to produce his first results? His experiment was simple (it took him only a few days), and it seems that everything he needed for it was already in his laboratory: photographic plates and phosphorescent bodies.[1]

According to BECQUEREL's account of his work, written in 1903, he began the search for X rays emitted by phosphorescent substances on 21 January 1896 — the day after POINCARÉ's presentation of RÖNTGEN's paper at a meeting of the Academy of Sciences. BECQUEREL's first experiments, with several different phosphorescent bodies (blende, fluorspar, etc.), produced no results. He did not publish these null results, because he believed that he could obtain positive results with uranium compounds. He had loaned his preparations of double sulphate of uranium and potassium to GABRIEL LIPPMANN; immediately after their return, he began his well-known successful experiments (BECQUEREL *1903*a, 3, 7–8).

Why did BECQUEREL believe that he would succeed with uranium compounds? In several of his accounts of his experiments, we find a passing mention of his motivation:

> The trend of ideas raised by RÖNTGEN's experiments led to a search for whether matter was able to emit similar radiations, and the phenomenon of phosphorescence, which produced a known transformation and emission of energy, was initially considered. This idea was not to be applied to the phenomenon we consider, but it was nevertheless fruitful. It led to a choice, among phosphorescent bodies, of the uranium salts, which have a remarkable optical constitution with a series of harmonic bands in their spectra of absorption and phosphorescence (BECQUEREL *1902*, 85)

> Among phosphorescent bodies, uranium salts were particularly recommended for those investigations because of the exceptional constitution that the harmonic series of bands comprising their absorption and phosphorescence spectra seems to disclose. (BECQUEREL *1903*b, 1)

> . . . notwithstanding the negative experiments with other bodies, I placed great hopes in experimentation with uranium salts, whose phosphorescence I had formerly studied, following the works of my father. Those bodies, which emit and absorb a whole series of harmonic luminous radiations, seem to have a particularly remarkable molecular constitution, at least from the point of view of absorption and phosphorescence. (BECQUEREL *1903*a, 8)

In all of these accounts, BECQUEREL stresses the peculiar harmonic bands in the spectra of uranium salts. It seems that this remark has never before attracted the attention of historians of science, although it provides an essential hint to BECQUEREL's motivation in selecting uranium salts for study.

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[1] LAWRENCE BADASH described BECQUEREL's previous acquaintance with luminescence, uranium compounds and photography as conditions for the discovery of radioactivity (BADASH *1965*a).

The "Peculiar Harmonic Series of Bands"

The spectra of several luminescent bodies had been studied and described for the first time by BECQUEREL's father EDMOND. Among other substances, EDMOND BECQUEREL had studied several uranium compounds: uranium nitrate, uranium glass (silicate), double fluoride of uranium and potassium, uranium percloride, natural uranite, double sulphate of uranium and potassium. In all cases, the fluorescence spectra displayed series of bright, thin bands, with roughly equal spacing between them (BECQUEREL *1867–68*, v. 1, 378–81). No other luminescent substance exhibited a similar spectrum and for this reason he stated that "the composition of the emitted light is very remarkable." However, he made no attempt to explain this peculiar type of spectrum.

Stimulated by his father's researches, HENRI BECQUEREL had turned his attention to the spectra of uranium compounds as early as 1885 (BECQUEREL *1885*). He believed that their study would elucidate the processes of selective absorption and emission of fluorescent and phosphorescent radiation. They had a special property: the emission and absorption spectral bands of all uranium compounds obeyed a simple relationship: There were common emission and absorption bands, so that absorption seemed to be some type of resonance phenomenon. He also noticed that the difference between the mean frequencies of successive bands was nearly constant. He interpreted this property in the following way:

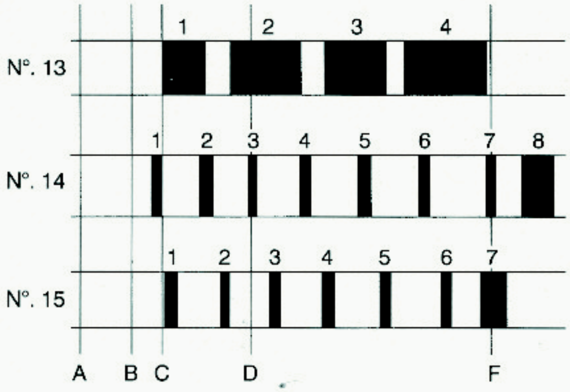

Fig. 1. Fluorescence emission spectra of two uranium compounds, according to the observations of EDMOND BECQUEREL (adapted from BECQUEREL *1867–68*, vol. 1, plate 39, numbers 13–15). The upper spectrum (N°.13), given here for comparison, corresponds to carbon hydride. The middle spectrum (N°. 14) represents the fluorescence emission of uranium nitrate (uranium glass has a similar spectrum). The lower spectrum (N°.15) shows the emission bands of uranium perchloride. The spectra of natural uranite and of the double fluoride of uranium and potassium are similar. The spectrum of the double sulphate of uranyl and potassium is described by EDMOND BECQUEREL as intermediate between those of uranium nitrate and the double fluoride of uranium and potassium.

> Therefore, the radiations absorbed by uranium compounds, which satisfy a common law, excite in all of these bodies the same luminous vibratory motions, of different periods, which seem to be lower harmonics of the exciting radiations (BECQUEREL *1885*, 1253).

Here we find for the first time a reference to the "harmonic series" of the bands of uranium compounds. This theoretical interpretation of absorption and emission as due to resonance between the incident light and natural molecular vibration frequencies was based upon the special behavior of uranium compounds, but BECQUEREL thought that similar considerations could be applied to other substances as well (BECQUEREL *1885*, 1255). In a subsequent paper, he returned to this point:

> I formerly have demonstrated that in some bodies, such as the uranium compounds, the absorbed radiations corresponded to vibratory motions that were harmonics of those of the radiations emitted by phosphorescence. One could suppose that inside the bodies some vibratory motions are produced, either permanent, or born under the influence of the incident radiations and stopping at the same time as these; by an extension of Kirchhoff's law, the absorbed radiations would be those with vibrations either synchronous or harmonic to those of the intermolecular vibrations (BECQUEREL 1891, 623)

This hypothesis was not original to BECQUEREL. He acknowledged the priority of EUGEN LOMMEL:

> A similar hypothesis has been developed by Mr. E. Lommel, in a very interesting memoir, *Theorie der Absorption und Fluorescenz* [LOMMEL *1878*]; however the conclusions of the author, relative to several fluorescent fluids, do not touch any of the points dealt with in the present communication; their principal aim is to explain his experiments adverse to STOKES's law, and that could not be verified afterwards by other physicists. (BECQUEREL *1886*, 107, footnote 1)

In these early papers, therefore, we find the root of BECQUEREL's later remarks on the harmonic series of bands in the spectra of uranium compounds. However, this does not seem to shed any light on the relationship of this property to the emission of penetrating radiation by uranium compounds. We must probe deeper to find some important clues here.

Stokes' Law and Its Validity

As indicated above, BECQUEREL refers to LOMMEL's work and to STOKES's law in his discussion of the peculiar spectra of uranium compounds. Let us explore these hints further.[2]

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[2] MARJORIE MALLEY (*1991*) published a detailed historical account of the development of fluorescence research and discussion of STOKES's law.

We recall that in 1896 BECQUEREL was searching for penetrating radiations (similar to X rays) emitted by phosphorescent or fluorescent bodies,[3] following POINCARÉ's conjecture. If the emission of X rays were linked to fluorescence, then X rays should be a type of penetrating electromagnetic radiation. Thus one of the hypotheses on their nature at that time was that they were an extreme form of ultraviolet light. Could fluorescent bodies emit that type of radiation?

According to STOKES's law, luminescent substances can emit radiation only of a wavelength greater than that of the exciting radiation — or, as STOKES expressed it, "The refrangibility of the incident light is a superior limit to the refrangibility of the component parts of the dispersed light" (STOKES *1852*, 556). Therefore, it could not be expected that a fluorescent (or phosphorescent) substance could emit more penetrating electromagnetic radiation — unless it was an exception to STOKES's law.

Anyone in 1896 having a reasonable knowledge of luminescent phenomena might have arrived at this conclusion. Thus, when SILVANUS P. THOMPSON, independently of BECQUEREL, observed the emission of penetrating radiation by luminescent bodies, he was worried immediately because this seemed to conflict with STOKES's law — and for this reason he consulted STOKES himself on this issue (MARTINS *1996*a). What, then, was the status of STOKES's law in the late nineteenth century?

In the middle of the nineteenth century, STOKES's law had been widely confirmed both by STOKES himself and by HENRI BECQUEREL's father. But in his early publications EDMOND BECQUEREL did not accept the generality of STOKES's law: "In most cases, but not in all of them, phosphoresce is the result of the emission of rays of weaker refrangibility [greater wavelength] and consequently of smaller speed of vibration [smaller frequency] than the rays that, by their influence, gave rise to this phenomenon" (BECQUEREL *1859*a, 13). He soon dismissed these exceptions, however, and accepted STOKES's law as a general one:

> The same body can be influenced by rays of different refrangibility and can emit, under the action of each of them, rays that differ in their duration and their refrangibility. In this case, this body only gives rise to rays with a refrangibility smaller than, or at most equal to, that of the active ray. . . .

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[3] Nowadays, textbooks present a clear distinction between phosphorescence and fluorescence. Phosphorescence is the emission of radiation *after* a substance has been excited by light; fluorescence is the emission of radiation that occurs only *during* excitation by light. In the nineteenth century, however, there was no clear-cut distinction between these concepts. EDMOND BECQUEREL had shown that many bodies that were called "fluorescent" were really short-lived phosphorescent bodies. He therefore suggested that the difference between fluorescence and phosphorescence was only quantitative, not qualitative. HENRI BECQUEREL also drew no clear-cut distinction between those concepts, and for this reason I will treat "fluorescence" and "phosphorescence" as equivalent terms in this paper.

> In some cases in which I had observed the emission of rays with a wavelength smaller than that of the exciting rays, I have noticed that the luminous phenomenon was complicated by effects of phosphorescence by elevation of temperature that do not obey the same laws, the heat action being able to excite light rays of any wavelength (BECQUEREL *1859*b, 121–2).

Exceptions to STOKES's law were found later by other researchers, however, LOMMEL observed that a solution of naphthalene red (*Magdala pink*) in alcohol could emit greenish yellow light under the influence of red and yellow light (LOMMEL *1871*, *1872*). EDMOND BECQUEREL, however, denied this claim (BECQUEREL *1872*, 547–8). Later, LOMMEL stated that chlorophyll and eosin also produced anomalous fluorescence (LOMMEL *1878–80*). His results were confirmed by BOHUSLAV BRAUNER (*1877*) and OSCAR LUBARSCH (*1874–79*), but denied by EDUARD HAGENBACH (*1872*, *1879*) and SERGEI LAMANSKY (*1879*a, *1879*b, *1879*c, *1880*).

A few years later, GEORGES SALET suggested that any violation of STOKES's law would conflict with the second law of thermodynamics because it would amount to the transformation of lower-temperature radiation into higher-temperature radiation (SALET *1892*). This is not a correct application of the second law of thermodynamics, however, as was pointed out by CHARLES-ÉDOUARD GUILLAUME. Such a transformation would be forbidden only if *no other simultaneous effect* occurred. If part of the exciting radiation were transformed into higher-frequency radiation, with the simultaneous emission of an adequate amount of lower-frequency radiation, this would not conflict with the second law of thermodynamics (GUILLAUME *1897*, 135).

Although not decided clearly by theory or by experiments, LOMMEL's exceptions came to be accepted towards the end of the nineteenth century (MALLEY *1991*). SILVANUS THOMPSON informed LORD KELVIN in a letter that STOKES himself had changed his mind on this question:

> In the case of fluorescence STOKES — as you say — found the fluorescent light of longer period than that of the originating light. That was in his first researches. I had occasion some months ago to ask him whether he still held that this was always the case; and his reply was that he no longer considered it to be exclusively so. For instance, the late Prof v. LOMMEL found a fluorescence of contrary kind (the Germans call this "fluorescence of the second species") in the case of some of the coloured bodies that have strongly marked absorption bands. (THOMPSON *1899*)

Thus, at the end of the nineteenth century, the assumption of an anomalous fluorescence, contrary to STOKES's law, was not incompatible with established knowledge. This opened the possibility of interpreting POINCARÉ's conjecture by the hypothesis that there could exist a fluorescence of the second species that produced X rays. This was THOMPSON's interpretation of the phenomenon of "hyperphosphorescence": "These effects are inconsistent with a law enunciated by STOKES — but which he has since modified" (ANONYMOUS 1896)[4].

Did HENRI BECQUEREL share this view? It seems so. Let us return to his explanation of the "peculiar harmonic series of bands" of the uranium compounds.

Lommel's Vibratory Theory of Fluorescence

LOMMEL's theory of fluorescence (LOMMEL *1871*, *1878*) assumed that vibratory motions of material intramolecular particles are damped oscillations (with a resistance proportional to the velocity of the particle) and that the interaction between light and those particles is of the same type as the interaction between mechanical waves and mechanical oscillators. For full generality, LOMMEL supposed that the restoring force that attracts the oscillating particle to its equilibrium position is not simply proportional to the distance: he represented it as a power series. He then studied the forced oscillations stimulated by an external periodic force — the stimulating radiation.

LOMMEL obtained several well-known results concerning resonance (BRADBURY *1968*, 142–89; RAYLEIGH *1894*, v. 1, 76–85). In the case of gases, assuming harmonic oscillations, he found that the maximum absorption of energy occurs when the frequency of the stimulating external force is equal to the frequency of the oscillations of the particles. In the case of solid and liquid substances, however, the introduction of special resistances led to the conclusion that the maximum absorption of energy occurs when the frequency of the stimulating force is different (larger) than the fundamental frequency of the particles. This would explain STOKES's law. However, LOMMEL proved that an oscillating particle also would oscillate with twice its fundamental frequency, when stimulated by an external force close to the ground frequency (second harmonic, or first overtone). The amplitude of the second harmonic, of course, is smaller than that of the first harmonic, but not zero. This second type of excited oscillation would produce emission of radiation with a higher frequency and therefore would not obey STOKES's law.

It is easy to see how this theory can be applied to substances that exhibit a periodic series of absorption bands. Suppose that the fundamental frequency ν_0 of the particles of a given substance is very low (corresponding to the far infrared). Its overtones, $\nu_1, \nu_2, \nu_3, \ldots$, will be separated by a constant difference ($\nu_{n+1} - \nu_n = \nu_0$). As shown above, HENRI BECQUEREL noticed that this was the

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[4] STOKES's change of opinion is documented in some of his letters to KELVIN, where he refers to THOMPSON's and BECQUEREL's researches and states that in some cases (*e.g.*, in the so-called *calorescence*) low-frequency vibrations can excite shorter-period vibrations (WILSON *1990*, vol. 2, 649 [letter 554, STOKES to KELVIN, 12 March 1896]; 652 [letter 557, STOKES to KELVIN, 13 and 14 March 1896]; 661-2 [letter 564, STOKES to KELVIN, 26 March 1896]; and 664 [letter 567, STOKES to KELVIN, 27 March 1896]).

case for uranium compounds. One then should expect that when a uranium compound is excited by a suitable radiation of frequency slightly larger than some of its natural frequencies ν_n, it should emit radiation corresponding both to lower and higher harmonics.

HENRI BECQUEREL was not a theoretical physicist. He tried to justify, by qualititative reasoning, that incident light of a given frequency could excite vibrations only of a lower frequency — a conclusion that was at variance with classical mechanics. The main reason why he could not accept LOMMEL's conclusion was his father's opinion (based upon his own experiments) that STOKES's law seemed to be valid. However, since BECQUEREL accepted the main hypotheses of LOMMEL's theory, it is natural to infer that he would be willing to accept violations of STOKES's law, if they were observed. It is also natural to predict *that such violations would be especially likely in substances that exhibit a series of harmonic emission and absorption bands, such as uranium compounds.*

Suppose, now, that someone with BECQUEREL's background wanted to look for a luminescent phenomenon of emission of very high-frequency (low-wavelength) radiation, in violation of STOKES's law. What kind of substances would he try? Of course, uranium compounds. Or, invert the question: Why should phosphorescent and fluorescent uranium salts be expected to emit penetrating radiation similar to short-wavelength ultraviolet light? Because it could happen that visible (long-wavelength) light excited higher harmonic frequencies in those compounds.

This seems to be a likely reconstruction of the trend of thought that led BECQUEREL to his choice of uranium compounds for his research. It is difficult to imagine any other interpretation of BECQUEREL's remarks on the relevance of the spectra of uranium compounds in his early radioactivity experiments.[5]

According to the interpretation proposed here, it is also easy to understand why BECQUEREL studied many uranium compounds that were not luminescent, and even metallic uranium, without giving up his "invisible-phosphorescence" interpretation of radioactivity, as I now will discuss.

Emission of Radiation by Uranium Compounds and Metallic Uranium

In his two earliest radioactivity papers, HENRI BECQUEREL studied a single substance: the double sulphate of uranyl and potassium. In his third paper, he described his first attempts to find new substances that emit penetrating rays. He reported that some other luminescent compounds of uranium and two calcium sulphides[6] also emitted the invisible radiation (BECQUEREL *1896*a). The

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[5] The same theoretical basis seems to have played an important role in BECQUEREL's unfortunate involvement with N-rays (MARTINS *1996*b).

[6] HENRI BECQUEREL's calcium sulphide experiments led him to several wrong conclusions, including his belief in reflection and refraction of the penetrating radiation (MARTINS *1996*b).

title of this paper ("On some new properties of the invisible radiations emitted by several phosphorescent bodies") shows that he still thought that the phenomenon was related to visible phosphorescence.

Not every uranium compound is luminescent. Uranium(VI) — that is, uranic — compounds exhibit fluorescence (and phosphorescence), but uranium(IV) — that is, uranous — compounds are neither phosphorescent nor fluorescent. However, BECQUEREL soon observed that uranous as well as uranic sulphate emits invisible radiations (BECQUEREL *1896*b). He also observed that uranium nitrate in solution lost its fluorescence, but still emitted penetrating radiations.

The title of BECQUEREL's fourth communication of 23 March 1896 was, "On the invisible radiations emitted by uranium salts." At this time, he began to distinguish between effects obtained with uranium compounds and those with other luminescent substances.

It might seem that when BECQUEREL noticed the emission of penetrating radiation by non-luminescent compounds of uranium, he should have dismissed POINCARÉ's conjecture and concluded that he was facing a completely new phenomenon. However, the situation was more complex at that time. It seems that BECQUEREL still believed in POINCARÉ's conjecture, because one week later he suggested that X-ray tubes produced *two different radiations*. X-rays were produced by the direct effect of cathode rays, independently of any fluorescence, as had been shown by JEAN PERRIN (*1896*). However, BECQUEREL remarked:

> As to the phosphorescence of the glass of Crookes tubes, it is possible that they are accompanied by radiations analogous to those emitted by uranium salts, but it is probable that a very long exposition would be needed to exhibit their evidence (BECQUEREL *1896*c, 767)

One month later, BECQUEREL presented to the Academy of Sciences a communication by F.-P. LE ROUX (*1896*) that confirmed this suggestion. LE ROUX reported that in his first experiments with RÖNTGEN's radiation, metals were very easily traversed by the rays, but that in later experiments his former observations could not be reproduced. He noticed that the glass of the older tubes exhibited strong luminescence, while with newer tubes the cathode rays were projected onto a metal electrode and the luminescence was very weak. He remarked that metals were more transparent to BECQUEREL's rays than to X rays. His interpretation was straightforward: the old (luminescent) tubes emitted a radiation similar to that of uranium compounds and a small amount of X rays, while the new (non-luminescent) tubes emitted few radiations similar to uranium rays and a large amount of X rays.

It also seemed to LE ROUX that metals traversed by the radiations emitted in phosphorescence produced secondary penetrating rays, because the darkening of a photographic plate below a piece of metal could be stronger than elsewhere: "Metals seem therefore to enjoy some kind of fluorescence."[7]

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[7] The effects observed by LE ROUX can be interpreted in another way. According to our knowledge, shorter wavelength X rays ("hard" X rays) have a greater penetrating

Shortly after the presentation of LE ROUX's paper, BECQUEREL presented a new communication to the Academy of Sciences on 18 May 1896 (BECQUEREL *1896*d). This paper contains but a single new piece of new information: he reported that pure metallic uranium also emits the penetrating radiation and that it is about four times more active than the double sulphate of uranyl and potassium.

It might seem that BECQUEREL clearly perceived at this time that he was studying a completely new phenomenon.[8] Some historians describe his discovery of the emission of radiation by metallic uranium as the culminating point of his contribution: "With this last announcement, on 18 May, BECQUEREL's discovery of radioactivity was complete . . . " (ROMER *1981*, 559). Earlier ROMER had reached a similar conclusion:

> Seven weeks more went by and the discovery was complete. Uranium always gave out the penetrating rays, whether it was in fluorescent or non-fluorescent crystals, whether in the light or in the dark, whether dissolved in water or isolated in Moissan's pure and uncombined metal. (ROMER *1964*, 18)

WHITTAKER noted similarly that:

> It was soon found that those salts of uranium which do not phosphoresce — that is, the uranous series of salts — and the metal itself, all emit the rays; and it became evident that what BECQUEREL had discovered was a radically new property, possessed by the element uranium in all its chemical compounds. (WHITTAKER *1987*, v. 2, 1)

Let us, however, consider HENRI BECQUEREL's own conclusion:

> While continuing the study of those new phenomena, I thought that it was not devoid of interest to point out the emission produced by uranium,

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power and produce a smaller photographic effect than longer wavelength ("soft") X rays. When X rays were discovered, it was usual to use the highest possible voltage to excite the CROOKES tubes, and high-voltage apparatuses produce hard X rays. When hard X rays strike different substances, they produce the emission of secondary, softer X rays, which produce a stronger photographic effect. Therefore, with high-voltage X rays, it might happen that the darkening of a photographic plate below a metal coin would be stronger than at other places. Thus, the difference between LE ROUX's early and later experiments could be explained by the difference between the *induction coils* used, instead of a difference between the *phosphorescences* of the tubes.

[8] According to BADASH (*1966*) the discovery of radioactivity had happened as early as 1 March 1896, when BECQUEREL found that a phosphorescent uranium salt kept away from direct sunlight had affected photographic plates. BADASH stated that BECQUEREL "recognized the significance of his surprising observation" (BADASH *1966*, p. 269) and thus discovered radioactivity. However, as shown below, even after that experiment he maintained his early belief that the phenomenon he was studying was an invisible luminescence.

> which, I believe, is the first instance of a metal presenting a phenomenon of the kind of an invisible phosphorescence. (BECQUEREL *1896*d, 1088)

Was it conceivable, at this time, to ascribe an invisible phosphorescence to metallic uranium and to non-luminescent uranium compounds? This seemed to conflict with established knowledge. According to the observations of EDMOND BECQUEREL, metals are never phosphorescent (BECQUEREL *1859*b, 116). Why should uranium be an exception? In fact, there was a reason it might be one. Recall that BECQUEREL's choice of uranium compounds for his experiments was not due to chance, but to the harmonic structure of their series of spectral bands. In 1885, he had noticed that non-luminous uranium compounds also had well-defined and regularly spaced *absorption* bands. There was even a similarity between the wavelength of a strong green absorption band of those compounds and the wavelengths of the strongest emission lines of metallic uranium vapour (BECQUEREL *1885*). Therefore, *all* uranium compounds (and even metallic uranium) seemed to have the same inner vibratory structure. Hence, both non-luminescent compounds and metallic uranium could, in principle, be excited by the same radiations as luminescent compounds, and perhaps they also could emit penetrating radiation by the same process.

I note that SILVANUS P. THOMPSON also thought that metallic uranium could emit penetrating radiation — when stimulated by cathode rays. Shortly after the publication of BECQUEREL's article on metallic uranium, STOKES wrote a letter to THOMPSON telling him about the new discovery. THOMPSON replied to STOKES that he had not yet seen BECQUEREL's paper ("I don't see the *Comptes Rendus* usually until they are 10 days old"), but that he himself had planned to study the properties of metallic uranium:

> I had been — a month ago — applying to Crookes for some metallic uranium for experiments. In particular, I wanted to put a specimen into a "focus" tube in place of the usual platinum piece, to see if it would be more active in transmuting the kathode rays into "x"-rays. . . . I wanted to try uranium in place of platinum because its greater atomic weight, and presumably greater opacity to "x" rays seemed to suggest that it would be a better radiator of them. (THOMPSON *1896*a)

Shortly after writing this letter, SILVANUS THOMPSON used uranium as a target for cathode rays and observed that "uranium, as a target, appeared to be more active than platinum in evoking emission of RÖNTGEN rays" (THOMPSON *1896*b). RÖNTGEN tubes with metallic uranium anticathodes became widely used afterwards.

From BECQUEREL's first paper on radioactivity to the discovery of the emission of radiations from metallic uranium, less than three months had elapsed. Subsequently, he published three papers (BECQUEREL *1896*e, *1897*a, *1897*b) that did not add anything significant to his earlier ones. He then seemed to lose interest in these phenomena. For more than a year, he turned to the study of the recently discovered ZEEMAN effect.

Why did not BECQUEREL look for other substances similar to uranium? MARIE CURIE's systematic search for other radioactive elements seems so natural that it is difficult to understand why BECQUEREL himself did not carry out such a search. The reason may be this: if to him the peculiar properties of uranium compounds were related to their peculiar spectra, then there was no basis to look for other similar substances.

Conclusion

The common assumption that BECQUEREL had no special reason to study uranium compounds in his search for substances emitting penetrating radiation cannot explain (a) BECQUEREL's own accounts, which refer to his choice as due to "the peculiar harmonic series of bands"; (b) BECQUEREL's systematic test of all uranium compounds (and metallic uranium), in contrast to his neglect of other substances; and (c) BECQUEREL's belief in invisible phosphorescence as an explanation of the radiation emitted by uranium compounds, even after his discovery that non-luminescent and metallic uranium also emit penetrating radiation.

By comparing BECQUEREL's older studies of uranium to his radioactivity research, this paper has presented a reconstruction that can explain all of these points above. According to the historical evidence presented here, it is likely that BECQUEREL concentrated his attention on uranium and its compounds because the mechanical theory of luminescence opened up the possibility that, precisely in the case of uranium and its compounds, a violation of STOKES's law could occur, and penetrating short-wavelength radiation could be emitted through a special type of phosphorescence.

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