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The discovery of the electron: II. The Zeeman effect

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Abstract. The paper gives an account of the discovery, in the fall of 1896, of the Zeeman effect and of the developments in the months that followed. It is to a large extent based on previously unknown archival material.

1. Introduction

In the fall of 1896, the Leyden physicist Pieter Zeeman discovered a new phenomenon that would soon be known as the Zeeman effect. He observed a clear widening of the sodium D-lines under the influence of a magnetic field. Not long after the discovery, his colleague Hendrik Antoon Lorentz developed a theory predicting that the observed widening actually was a splitting of the lines in three components when observed in a direction perpendicular to the field. In a direction parallel to the field, two lines, with opposite circular polarizations, would be visible. Both predictions were confirmed by Zeeman: the polarization was observed in Leyden, the splitting in Amsterdam, early in 1897, where, in the meantime, Zeeman had been appointed lecturer.

Lorentz’s theory was based on the assumption of the existence of charged vibrating particles inside atoms. Zeeman’s discovery, together with Lorentz’s theory, were the first indications of the existence of a new charged particle, later known as the electron. In this paper I will give an account of the discovery of the Zeeman effect, supplemented with a short biographical sketch of Zeeman (see the appendix). The paper is to a large extent based on material from the Zeeman archive, which was discovered only a few years ago [1].

2. The Leyden tradition

At the physics laboratory in Leyden, two lines of research were pursued during the last decades of the nineteenth century. One dealt with the equation of state and the behaviour of matter at low temperatures, and would eventually lead to successes such as the liquefaction of helium and the discovery of superconductivity. The other one was the ‘Lorentz-series’ of magneto-optical experiments. The name Lorentz-series indicates part of the background to this work: it was intimately connected to Lorentz’s work in electromagnetism, the work that would ultimately be known as the electron theory. The collaboration between Lorentz and his assistants and the experimenters led by Heike Kamerlingh Onnes was fruitful and provided important support for Lorentz’s theoretical work [2].

Pieter Zeeman obtained his doctorate under Kamerlingh Onnes with a dissertation in magneto-optics. It dealt with the Kerr effect, which has to do with the change in degree of polarization of light reflected by a magnetized mirror. This background is important, because it gave Zeeman a feel for the field of magneto-optics and made him aware of the unexplored areas in this field. His search for an influence of a magnetic field on spectral lines must be seen in this light.

3. The discovery

In some later reminiscences [3] Kamerlingh Onnes mentions an early attempt by Zeeman to establish the possible influence of a magnetic field on spectral lines. The thought had occurred to Zeeman when he wondered if a magnetic field would not only modify the way light is propagated and reflected, but also its frequency. Onnes’s account is corroborated by a remark by Zeeman in his first paper on the Zeeman effect [4]. He mentions an earlier inconclusive experiment, involving the spectrum of sodium. Of this particular
work no notes are preserved. But there is an intriguing letter to Onnes from 1891, in which Zeeman reports having looked at the spectrum of iron in a magnetic field and having been ‘unable to observe a displacement of the lines’ [5]. It is possible that this is a reference to the earlier experiment.

The Zeeman archive also provides more background to the motivation behind Zeeman’s experiment. In his first paper on the Zeeman effect [4] Zeeman mentions why he had returned to the experiment, in spite of its initial failure. The reason was a passage in an article on Michael Faraday, written by Maxwell, in which Faraday’s unsuccessful attempts are mentioned to ‘detect any change in the lines of the spectrum of a flame when the flame was acted on by a powerful magnet’ [6]. After reading this passage, Zeeman decided to repeat the experiment, because, as he put it: ‘If a Faraday thought of the possibility of the above-mentioned relation, perhaps it might be yet worth while to try the experiment again with the excellent auxiliaries of spectroscopy equipment of the present time, as I am not aware that it has been done by others.’

This kind of inspiration fits in with what we can learn from material in the Zeeman archive. In a notebook, started in 1890 as a record of his intellectual development, Zeeman jotted down all kinds of thoughts and ideas, as well as passages from his readings. One of these is Faraday’s account of his experiment on the possible influence of a magnetic field on the spectrum of sodium. It is accompanied by Zeeman’s observation that ‘experiments, with negative outcome, performed by great scientists from the past, using worse instruments than are currently available, are worth being repeated’ [7]. To this remark a cautionary observation is added: ‘One should not communicate to others ideas that have not been worked out yet, plans that have not been carried out yet, experiments that have not been performed yet.’ The notebook contains many such observations and passages copied from the works of great scientists. At least during the early part of his career, Zeeman clearly derived much inspiration from the work of famous predecessors.

One of the items in the Zeeman archive is a laboratory notebook that contains the first recorded observation of the Zeeman effect [8]. The entry is dated 2 September 1896 and is preceded by many pages of notes on totally unrelated experimental work. It opens with the words: ‘Influence of magnetization on flame.’ The notes that follow describe a very simple experiment: a piece of asbestos, soaked in a solution of kitchen salt, is put in a flame placed between the poles of a magnet. With the help of a grating, a spectrum is created. The yellow sodium D-lines appear as narrow and sharp lines. ‘When the magnet is switched on’, the description continues, ‘the lines become wider until they are two to three times as wide’. This simple sentence describes the discovery...
of the Zeeman effect. Everything that follows is just an elaboration of this brief statement.

As we see, no actual splitting of the spectral lines was observed initially, owing to the insufficient strength of the magnet: although Zeeman used an excellent original Rowland grating with a radius of 10 ft and 14,938 lines per inch, the 10 kG produced by the magnet was insufficient to make the splitting visible. It would take several more months before an actual splitting of spectral lines could be established. This event took place in Amsterdam in 1897 and the line in question was the blue cadmium line [9].

Since only a widening of the spectral lines was observed, it was by no means certain that a new effect had been found. No one was more aware of this than Zeeman himself. The two days following the discovery were spent in further observations. Zeeman concluded that quite possibly the broadening was caused by pressure differences owing to temperature or density gradients produced by the magnetic field. The third day after the discovery Zeeman returned to the experiment he had been working on before 2 September.

4. The follow-up

It was not until more than a month later, on 9 October, that Zeeman returned to his magneto-optical work. Now he started a systematic series of experiments, in which the true nature of the discovered effect had to be established. I will not go into much detail here; let me just mention that Zeeman investigated the influence of the form of the flame on the broadening and the effect for absorption lines instead of emission lines, trying to eliminate complicating factors such as temperature and density gradients in his samples. The picture of Zeeman that emerges here is that of a painstakingly careful experimenter, who is his own most severe critic. As J D van der Waals Jr observed much later:

Whoever reads the publications gets the impression that not the experimenter himself is reporting, but a somewhat unfriendly critic, whose goal is not to evaluate the experiments and investigate their consequences, but to be suspicious of all that he is told. [10]

Towards the end of the month, Zeeman finally became convinced that he had really discovered
something new. A publication describing his experiments was presented by Kamerlingh Onnes at the monthly meeting of Saturday 31 October of the Section of Sciences of the Dutch Academy of Sciences. In it Zeeman concluded:

The experiments have made it increasingly probable that absorption and thus also emission lines of a gaseous substance are widened by magnetic forces. [4]

We now know that the experiments had continued until right before the paper was submitted and new experimental results had been added at the last minute. One of these was in response to a remark by Onnes, who had suggested, when he saw the experiment for the first time the day before the Academy meeting, that convection currents might be responsible for the observed phenomena.

According to Zeeman’s reminiscences [11], the Monday following the Saturday on which Zeeman’s paper was submitted, a theoretical explanation of the effect was proposed by Lorentz, who had been present at the Academy meeting. The explanation is based on the following model. Atoms contain charged particles, harmonically bound to a centre. They are called ‘ions’. The frequencies of their vibrations correspond to the frequencies of the spectral lines of the substance in question. When a magnetic field is applied, the vibrating particles will experience a Lorentz force, in addition to the harmonic force. For a field in the z-direction the equations of motion take the following form:

\[
\begin{align*}
    m \frac{d^2x}{dt^2} &= -kx + \frac{eH}{c} \frac{dy}{dt} \\
    m \frac{d^2y}{dt^2} &= -ky - \frac{eH}{c} \frac{dx}{dt} \\
    m \frac{d^2z}{dt^2} &= -kz.
\end{align*}
\]

The general solution of the last equation is:

\[
z = a \cos(\omega_0 t + p)
\]

with \(a\) and \(p\) constants and \(\omega_0 = 2\pi\sqrt{k/m}\). For the \(x\) and \(y\) motions two sets of solutions are found:

\[
\begin{align*}
    x &= a_1 \cos(\omega_0 t + p_1) \\
    y &= -a_1 \sin(\omega_0 t + p_1)
\end{align*}
\]

and

\[
\begin{align*}
    x &= a_2 \cos(\omega_2 t + p_2) \\
    y &= a_2 \sin(\omega_2 t + p_2)
\end{align*}
\]

The new frequencies \(\omega_2\) and \(\omega_2\) are found from:

\[
\begin{align*}
    \omega_2^2 &= \frac{eH}{mc} \omega_0 = \omega_0^2 \\
    \omega_2^2 + \omega_2 &= \omega_0^2.
\end{align*}
\]

Instead of the one frequency \(\omega_0\) that occurs in the absence of a magnetic field, three frequencies appear. One of the new frequencies is smaller than \(\omega_0\), the other is larger. For the case that the relative frequency change is very small the frequency difference \(\Delta\omega\) is found as

\[
\Delta\omega = \frac{eH}{2mc}.
\]

The ‘new’ \(x\) and \(y\) vibrations can be combined to two circular motions in the \(x-y\) plane: one with a higher and one with a lower frequency. This implies that, parallel to the magnetic field, the original spectral line is split into two lines (the vibrations in the \(z\)-direction are invisible in that case, because no radiation is emitted parallel to the axis of vibration). Moreover, these components are circularly polarized. Perpendicular to the field, three lines appear: one in the original location, one with a higher and one with a lower frequency. All three components are linearly polarized.

These consequences were immediately clear to Lorentz and he discussed them with Zeeman. On 10 November, Zeeman began to investigate the polarization of the edges of the broadened lines. Initially without success, until he discovered why ten days later: he had been looking perpendicular to the field instead of parallel to it. As he wrote: ‘The experiment should be done with lines of force in the direction of the grating!’ [8]. Observing along the field lines is not a straightforward operation since it involves drilling holes in the poles of the magnet. Finally, on 23 November Lorentz’s prediction was confirmed, the edges were circularly polarized. It was a moment of great triumph for Zeeman and Lorentz and Zeeman noted in a diary:

23 November 1896. Finally confirmed that an action of magnetization on light vibrations does indeed exist. With the help of Lorentz shown that the explanation through a modified motion of ‘ions’ is correct or at least highly probable. Shown Lorentz the experiment in the morning of the 24th. He calls it a ‘lucky break’ and a direct proof for the existence of ions, together with the Faraday rotation and the Kerr effect. [12]

On 28 November, a second paper by Zeeman was submitted to the Academy of Sciences, in which the confirming results are presented [13].

5. The value of \(e/m\)

Equation (11) implies that from the magnitude of the splitting of the lines the ratio of the charge and the mass of the intra-atomic ‘ions’ can be determined. Even though Zeeman had only observed a widening, he succeeded in calculating \(e/m\). He found a value of approximately \(10^7\) emu g\(^{-1}\). From Zeeman’s later reminiscences it appears that Lorentz and Zeeman were surprised and puzzled by this value, which is much larger than would have been expected if Lorentz’s ‘ions’ were the same as electrolytic ions. According to Zeeman, Lorentz even called it ‘a bad thing’ initially [11]. Curiously, in the paper of 28 November, in which this value is first published, Zeeman does not comment on this anomaly. In a letter to Oliver Lodge, who had
expressed his surprise at the large value in a letter of 28 February 1897 [14]. Zeeman even argued that his value was not strange at all because it agreed well with the value derived from the magnetic deflection of cathode rays [15]. Zeeman simply concluded that different kinds of ‘ions’ existed and that the ‘ions’ introduced by Lorentz were different from the electrolytic ions.

In addition to determining the value of $e/m$, Zeeman also succeeded in establishing that the intra-atomic ‘ions’ were negatively charged (although initially, as reported in his paper of 28 November, an experimental error had led him to the conclusion of a positive charge).

6. Later developments

Soon after Zeeman had moved to Amsterdam it became clear that conditions in the Amsterdam laboratory were unfavourable for further work on the Zeeman effect. The building was plagued so much by disturbing vibrations that only a fraction of the photographic exposures could be used. Thus, Zeeman missed the discovery of the anomalous effect [16] and had to turn to less sensitive experiments. He worked on related problems, such as magnetic double refraction and rotation of the plane of polarization, as well as the occurrence of asymmetries in intensity and position of the shifted lines. Only after 1923, when he had his own laboratory, built especially for precision experiments, did Zeeman return to spectroscopic precision work.

In order to establish the historical importance of the discovery of the Zeeman effect two aspects should be mentioned. First, of course, is its role in the confirmation of the existence of the electron. But secondly, and more importantly in the long run, the fact that the Zeeman effect, in combination with Lorentz’s theory, provided a tool to probe the interior of atoms. (Since spectral lines have to do with an atom’s interior, a change of frequency reflects a change of this internal structure.)

In the following decades, the importance of the Zeeman effect for theories of atomic structure was made clear time and again. In particular a satisfactory explanation of the anomalous effect was a crucial test for any quantum theory of atomic structure. The importance attached to the Zeeman effect in those years was summarized by Lorentz in 1923, when he said, speaking of the Zeeman effect and its theoretical difficulties:

Still, here too, gradually order was achieved, and as this succeeded it became clear, clearer even than ever before, that the study of the Zeeman effect is one of the most beautiful ways to explore the constitution of matter. [17]
Two years later, and almost thirty years after Zeeman’s discovery, all forms of the Zeeman effect were finally explained through the introduction of the electron spin.

Appendix

Pieter Zeeman was born in 1865, in a small village in the Dutch province of Zeeland. He was the son of a protestant minister. After finishing secondary school, he continued his studies at the University of Leyden, where he specialized in physics and served as an assistant to the theoretician Hendrik Antoon Lorentz and to the experimenter Heike Kamerlingh Onnes. Zeeman wrote his dissertation under the guidance of Kamerlingh Onnes; it dealt with the experimental investigation of the Kerr effect. This work marks the start of Zeeman’s interest in magneto-optical phenomena and fitted in an already-existing line of research in Leyden.

Not very long after the discovery of the Zeeman effect in the fall of 1896, Zeeman was appointed lecturer at the University of Amsterdam. He remained there until his retirement in 1935, rising from the position of lecturer to that of extraordinary, and later ordinary professor, and subsequently becoming director of the physics laboratory and then head of his own, specially created and designed laboratory. Zeeman received many honors, the most important of which was the Nobel Prize in 1902. He shared the prize with Lorentz for their work in magneto-optics. Zeeman died in 1943, in the middle of the Second World War.

Zeeman was an experimenter par excellence, whose work is in the first place characterized by extraordinary precision. He had a unique talent for designing precision experiments and performing them with great persistence. After his initial work on the Zeeman effect, he had to shift to different fields of research, because of the unfavourable conditions in the Amsterdam laboratory. After having worked on related topics, such as magnetic double refraction and the rotation of the plane of polarization in a magnetic field, he applied his talents to experimental relativity: first he repeated Fizeau’s experiment with unprecedented accuracy, confirming the prediction of special relativity for the speed of light in moving media (in particular the occurrence of a dispersion term in the expression for the speed of light). A few years later, he investigated the equality of gravitational and inertial mass for anisotropic and radioactive materials, using a very sensitive torsion-balance. Toward the end of his career, he tried to observe the transverse Doppler effect and became involved in nuclear physics through his investigation of the hyperfine structure of spectral lines.

The Zeeman archive, discovered in 1989, provides much new material on all of Zeeman’s work, in correspondence, scientific notes and laboratory notebooks. In addition, it gives much background information on Zeeman’s personality. He emerges as a dedicated scientist, who was constantly looking for ways to apply his skills to new problems and kept a lively interest in current developments in physics. The wealth of archival material makes it possible to develop a detailed and balanced view of Zeeman’s work and of his personality.

References

[1] The Zeeman Archive is kept in the Rijksarchief in Noord-Holland (Haarlem). Items from the archive are referred to with the abbreviation ZA, followed by a number and, if necessary, a page number. See also the appendix for more information on the archive.
[5] Zeeman P 1897 Phil. Mag. 43 226 (Engl. transl.)
[6] Zeeman P to Kamerlingh Onnes H, 31 July 1891 (ZA 82)
[8] ZA 313, p 63
[9] ZA 506
[12] Zeeman P to Lodge O 1 March 1897 (ZA 101)
[13] Lodge O to Zeeman P 26 February 1897 (ZA 101)
[14] Zeeman P to Lodge O 1 March 1897 (ZA 101)
[15] In the anomalous Zeeman effect, discovered in 1898, a splitting in more than three components is observed.
[16] Lorentz H A 1925 Physica 5 73