

# Who discovered the magnetocaloric effect?

## Warburg, Weiss, and the connection between magnetism and heat

Anders Smith<sup>a</sup>

Department of Energy Conversion and Storage, Technical University of Denmark,  
Frederiksborgvej 399, 4000 Roskilde, Denmark

Received 8 January 2013 / Received in final form 3rd April 2013

Published online 3rd June 2013

© EDP Sciences, Springer-Verlag 2013

**Abstract.** A magnetic body changes its thermal state when subjected to a changing magnetic field. In particular, if done under adiabatic conditions, its temperature changes. For the past 15 years the magnetocaloric effect has been the focus of significant research due to its possible application for efficient refrigeration near room temperature. At the same time, it has become common knowledge within the magnetic refrigeration research community that the magnetocaloric effect was discovered by the German physicist E. Warburg in 1881. We re-examine the original literature and show that this is a misleading reading of what Warburg did, and we argue that the discovery of the effect should instead be attributed to P. Weiss and A. Piccard in 1917.

## 1 Introduction

Ferromagnetic materials have a remarkable response to an external magnetic field at temperatures near their Curie temperature, i.e. the temperature above which their intrinsic magnetisation disappears: they heat up when put into a magnetic field and cool reversibly again when removed from the field. This magnetocaloric effect has been used since the beginning of the 1920s as a means to investigate the internal magnetic structure of iron and other ferromagnets. However, for the past 15 years the magnetocaloric effect has also been the focus of significant research in its own right, due to its possible application for efficient refrigeration near room temperature. During the same period it has also become common knowledge within the magnetic refrigeration research community that the magnetocaloric effect was discovered by the German physicist E. Warburg in 1881 [Warburg 1881].

Recently, we argued that for purely physical reasons Warburg could not have observed the magnetocaloric effect in iron at room temperature [Smith 2012]. In the present paper we expand on that conclusion by examining the original literature before and after Warburg. The viewpoint will be that of the working physicist. Thus, we will not touch directly on the large body of work on the concept of ‘discovery’ in

---

<sup>a</sup> e-mail: [ansm@dtu.dk](mailto:ansm@dtu.dk)

the natural sciences and the extent to which a discovery has to be considered not as a historical event but as “a retrospective social judgment” [Gross 1998]. For a useful recent overview of this discussion, which goes back at least to [Merton 1957] and [Kuhn 1962], see [Caneva 2005]. In any case, the interpretation of the historical facts connected with the discovery of the magnetocaloric effect turns out to be relatively uncontroversial, as we will argue below.

The paper is organised as follows: first we discuss the early work on magnetism and heat, in particular the contribution of Thomson who first identified the thermodynamics underlying the magnetocaloric effect. Then we turn to the contribution of Warburg and consider in some detail what he set out to accomplish and what he indeed accomplished. Some early ‘thermomagnetic’ heat engines and their relation to the magnetocaloric effect are discussed before turning to the work of Langevin and Weiss and Piccard. The latter two, as we shall see, discovered the magnetocaloric effect in nickel. A brief treatment of the early work on magnetic cooling and a discussion of how Warburg came to be associated with the magnetocaloric effect follow. Finally, we sum up and consider the implications of our findings.

## 2 Early work on the connection between magnetism and ‘calorific’ effects

Interest in the connection between magnetism and heat goes back well over 150 years. In 1831 Faraday discovered that a time-varying magnetic flux will induce an electrical current, thus showing that currents can be generated by other means than batteries. It was natural to ask whether such currents had the same properties as currents from different sources. As part of his extended investigations on the mechanical value of heat, Joule considered the effects of induction currents. Joule’s 1843 paper ‘On the Calorific Effects of Magneto-Electricity, and on the Mechanical Value of Heat’ [Joule 1843] made clear that the heat evolved by the electromagnetically induced current is indeed equal to that evolved by any other kind of electrical current. Following Joule’s work it was generally accepted that repeated magnetisations and demagnetisations of a ferromagnetic material give rise to a temperature increase due to the heat dissipated by induction currents. There was some discussion in the literature as to whether additional heat is evolved during magnetisation and demagnetisation due to the friction associated with the movement or rotation of the molecular magnets, presumed to be the origin of the magnetism. This was investigated experimentally in the 1870s by, among others, [Cazin 1875] and [Herwig 1878].

However, early on it was also realised that there are other ways in which a magnetic field can cause a temperature change. In an 1860 contribution to Nichol’s *Cyclopedia of the Physical Sciences* [Thomson 1860] (later incorporated into [Thomson 1878]), William Thomson (the later Lord Kelvin) deduced from general thermodynamic considerations that a temperature dependence of the magnetisation of a body will manifest itself in its temperature response to an external magnetic field. Thomson knew that ferromagnetic materials abruptly lose their magnetisation when heated sufficiently. This led him to make the correct prediction that iron “at a moderate or low red heat” (i.e. close to the temperature at which iron loses its intrinsic magnetisation) will experience a cooling effect when drawn gently away from a magnet and conversely a heating effect when allowed to approach the magnet, and that nickel “at ordinary temperatures” and cobalt at high temperatures (“below that of melting copper”) will exhibit the same effect. Thomson clearly understood that the effect will be largest in the temperature range where the material loses its magnetic properties (i.e. near what later came to be called the Curie temperature). He also explicitly states that the effect is reversible. On the other hand, it is not clear whether he appreciated

that there actually will be a significant magnetocaloric effect closely *above* the Curie temperature as well. Furthermore, he makes no estimate of the size of the effect or whether it will be feasible to observe the effect experimentally. In fact, in iron, its magnitude of a few degrees for a field of 1 tesla at  $\sim 770^\circ\text{C}$  makes it challenging to measure. The first reliable measurement of the magnetocaloric effect of iron was only done more than 70 years later by [Potter 1934].

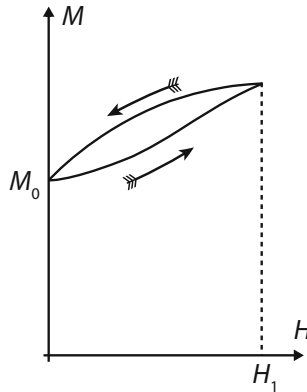
It is perhaps worth mentioning that Thomson predicted the reverse effect for cobalt “at ordinary atmospheric temperatures”: a cooling when magnetised and a heating when demagnetised. This he based on Faraday’s observation that in this temperature range the magnetisation of cobalt actually increases as a function of temperature [Faraday 1856]. This observation is most likely due to the fact that Faraday’s samples were not single-phase. It turns out that precise measurements of the magnetisation curve of cobalt are rather difficult, partly owing to the fact that polycrystalline cobalt often is of mixed phase at ordinary temperatures. However, careful measurements on single crystals have shown that the magnetisation of cobalt indeed monotonously decreases up to  $431^\circ\text{C}$  where there is a phase change to a face-centred cubic structure [Myers 1951]. Nevertheless, the fact that Thomson based on Faraday’s results predicts the opposite sign of the effect in cobalt clearly shows that his thermodynamic understanding of the effect was basically correct.

### 3 The contribution of Warburg

Warburg’s now-famous 1881 paper is entitled ‘Ueber einige Wirkungen der Coërcitivkraft’ (*On some effects of the coercive force*). He defines the coercive force as that force which causes a part of the magnetisation of an iron body to remain even after the magnetising force has ceased. He then sets out by explaining a consequence of the coercive force: when an iron wire is subjected to an increasing magnetic field from 0 to  $H_1$  which then subsequently decreases from  $H_1$  to 0, the magnetic moment (magnetisation,  $M$ ) of the wire is (for the same magnetic field) larger when the field is decreasing than when it is increasing. If the magnetisation cycle is repeated a few times, the magnetic moment will end up tracing out a closed curve in an  $(M, H)$ -diagram, see Fig. 1. Warburg expresses some slight puzzlement that this observation has never been published and speculates that it must have been known to other researchers. In fact, independently of Warburg, J.A. Ewing discovered the same phenomenon and gave it its name, *hysteresis* [Ewing 1882].

Warburg then turns to a consideration of the work performed on the iron wire in such a magnetisation cycle. He shows, by direct calculation of the force on the wire, that the work is equal to the negative of the line integral around the closed magnetisation curve  $C$ :  $A = - \int_C M dH$  (in cgs units; in SI units the integral needs to be multiplied by the vacuum permeability,  $\mu_0$ ) which in turn equals the area enclosed by the curve. After each cycle, the iron wire and the (permanent) magnet ends up in the same magnetic state. The work must therefore be dissipated as heat in the body, a conclusion which holds even if the magnetic field is not generated by a permanent magnet. Thus, hysteresis is a source of loss and for each hysteresis loop an amount of heat equal to the area enclosed by the loop is dissipated in the ferromagnetic body. This became known as *Warburg’s law*.

Turning now to experiment, Warburg determines  $M$  as a function of  $H$  by using a solenoid, through which the current can be varied, as the field source, and measuring  $M$  by the deflection of the iron wire which is suspended by a torsion thread. From this he calculates the area enclosed by the magnetisation curves, and in this way obtains the work. He gives his results in a (to the modern reader) slightly unfamiliar way, namely as the equivalent temperature rise the iron body would have experienced



**Fig. 1.** The closed magnetisation-demagnetisation loop considered by Warburg. Redrawn from [Warburg 1881].

due to the heat dissipated *if the body were made of water*. This quantity is then reported for several different experiments. Typical values obtained are of the order of  $10^{-6}$  °C. It should be emphasised that in this paper Warburg neither measured quantities of heat nor temperatures, although his way of reporting his results may give that impression on a cursory read. Finally, Warburg compared his results with those of [Cazin 1875] and [Herwig 1878] and found qualitative agreement, even though he states that a large fraction of the heat observed by Cazin must be attributed to induction heating.

In a subsequent paper with L. Hönig [Warburg 1882], Warburg clearly distinguished between the three different contributions to the thermal response of a magnetic body subject to a time-varying magnetic field: (1) hysteresis heat (‘magnetic friction heat’ in Warburg’s terms), i.e. the heat considered in [Warburg 1881]; (2) a heating (‘electromagnetic heat’) due to the eddy currents induced in the body by the magnetic field; (3) the reversible heat production owing to a temperature dependent magnetisation. The latter, which Warburg states he was not aware of when writing his 1881 paper but only discovered from [Ewing 1882], is clearly attributed to Thomson. Warburg and Hönig tried to measure the heat evolved in a piece of iron directly, not only through a calculation of the work as in the 1881 paper. They had to take great pains to insulate the sample from the heat developed by the magnet coil, and to determine the small changes in temperature was challenging. After trying different calorimeters they ended up constructing their own, basically an ether thermometer consisting of a 50 cm<sup>3</sup> vessel continued in a capillary tube with a radius of 0.0673 mm. The height of the ether meniscus was observed against a backlighted scale using a loupe. The iron piece was placed in a glass container to avoid corrosion from the ether and then placed inside the calorimeter. Each time the sample was changed, the calorimeter had to be emptied and opened. Due to the small temperature changes involved, the measurements were close to the instrumental limits of the equipment. Warburg felt compelled to state that he could only look at the results as ‘provisional’, in part due to doubts about the physical parameters of the ether used. However, he felt that the orders of magnitude obtained were trustworthy. Ewing comments later that the difficulty of direct calorimetric measurements “is well illustrated by the poor agreement [Warburg] finds between the two classes of observations” [Ewing 1885].

Warburg and Hönig explicitly consider the magnitude of the ‘Thomson heat’ and derive an upper limit of  $\sim 10^{-5}$  °C, concluding that in the present case it is several orders of magnitude smaller than the hysteresis heat and cannot be observed in their experiments. Some years later H. Delere takes up this question

again and claims that the Thomson heat actually constitutes up to 15% of the total heat [Delere 1905]. However, as Warburg is quick to point out in a rejoinder [Warburg 1906], Delere bases his claim on the false assumption that the closed hysteresis loop of magnetisation-demagnetisation is a reversible process. Now Delere's doctoral supervisor, A. Heydweiller, felt compelled to reply [Heydweiller 1906]. He points out that Delere's 'mistake' rests on an authority whom Warburg also will recognise, namely Warburg himself: Warburg used the same equation for the reversible temperature change when estimating the Thomson heat in [Warburg 1882]. The main point for the present paper is that the exchange demonstrates that Warburg certainly did not think that he either discovered or measured this heat. Later measurements, in fact, made clear that Warburg's estimate of the heat was more correct than Delere's, but this seems to reflect the limited precision of Delere's measurements more than anything else. Only in the late 1920s and early 1930s does it in fact become possible to measure the heat evolved along the individual parts of the hysteresis loop (see [Bates 1951] for a review), and the question of how to separate the reversible and irreversible parts of this heat experimentally was still an active area of research in the 1950s [Bates 1955].

## 4 Early thermomagnetic devices: Stefan, Edison, Tesla

The fact that a ferromagnetic material loses its magnetisation when heated above its Curie temperature, not only has implications for its temperature response, it also means that the force experienced by it due to an external field will change drastically. Although this effect is unrelated to the magnetocaloric effect, in later literature the two are often conflated. We will therefore briefly summarise the early development of 'pyromagnetic' or 'thermomagnetic' devices.

An iron body below its Curie temperature is strongly attracted to a magnet. By letting it approach the magnet, useful work can be extracted. Heating the body while in the vicinity of the magnet makes it lose its magnetism, and it can be removed from the magnet with little expenditure of work; finally the body can be cooled to make it magnetic again. This basic insight makes it possible to build a motor or a generator which takes heat as its input and which generates mechanical or electrical power. The concept of a 'thermomagnetic motor' was first suggested by J. Stefan ([Stefan 1871], [Stefan 1889]) who gave the above simple explanation of the principle, and both Edison [Edison 1888] and Tesla [Tesla 1889] patented versions of such a motor. They also both patented similar generators in the 1890s ([Tesla 1890], [Edison 1892]), where the basic idea is to have a coil surrounding an iron core close to a permanent magnet. When the iron core is periodically heated and cooled above and below its Curie point, the magnetisation will disappear and appear accordingly, and the resulting time-varying magnetic field will induce a current in the coil. However, the operation frequency is limited by the time needed to cool the iron core, and although both Edison and others apparently demonstrated working prototypes [Stefan 1889], neither the motor nor the generator was able to compete with more conventional motors and generators.

## 5 The molecular field: Langevin and Weiss

A significant step forward in the understanding of ferromagnets came with the concept of the molecular field, introduced by P. Weiss [Weiss 1907]. In 1905 Langevin had investigated paramagnetic gases theoretically, on the assumption that each gas molecule carried an independent magnetic moment resulting from the movement of its electrons. He showed that this hypothesis could explain the so-called Curie law, i.e.

that the susceptibility of a paramagnetic gas varies inversely proportional to the absolute temperature. He also considered the temperature rise experienced by such a gas when magnetised, and he calculated that at ordinary temperatures the temperature change in oxygen would amount to  $1/1000$  °C in a field of 1 tesla.

Weiss extended Langevin's theory to ferromagnets by introducing the concept of an internal field which is present even in the absence of an external field. This molecular field acts on the molecular moments and is in turn generated by the molecular magnetic moments themselves; the moments are no longer independent as in the case of a paramagnet, but point in the same direction as their neighbours. Weiss derived a number of consequences from this concept, in particular the abrupt disappearance of the magnetisation at the Curie temperature  $T_C$ , and the Curie-Weiss law according to which the susceptibility of a ferromagnet above  $T_C$  is inversely proportional to  $T - T_C$  ( $T$  is the temperature). In the following years he continued to explore the thermodynamic consequences of his theory. For example, he could show that the specific heat must have a discontinuity at the Curie temperature which fact he then proceeded to verify experimentally [Weiss 1908].

Crucial to Weiss' studies of ferromagnetism was the need to map the magnetisation precisely as a function of field and temperature. In 1917 Weiss and his long-time collaborator A. Piccard returned to this question again (here we follow the account given by Weiss himself in [Weiss 1921]), and during their researches on the magnetisation of nickel they made – as a 'by-product' – an interesting discovery [Weiss 1917]<sup>1</sup>: A reversible heating of nickel in the vicinity of its Curie temperature (354 °C) when a magnetic field is applied. They found a temperature rise of 0.7 °C in a field of 1.5 tesla. As they state in their paper, the reversibility of the effect alone is sufficient to distinguish it from the hysteresis heat. The order of magnitude is also very different: even in hard steel the temperature rise due to hysteresis is only  $1/200$  of a degree per cycle. Thus, Weiss and Piccard felt justified in calling their discovery for a 'novel magnetocaloric phenomenon' [Weiss 1918], incidentally coining the word 'magnetocaloric' at the same time [Oxford English Dictionary]. It is unknown to the present author whether Weiss was aware of Thomson's work, but he must have known of the possibility of magnetic materials changing their temperature in response to a magnetic field from [Langevin 1905]. In their paper, Weiss and Piccard derive a simple thermodynamic relation (closely related to that derived by Langevin) for the temperature change and go on to show that the magnetocaloric effect, like the discontinuity of the specific heat, is a consequence of the molecular field. Weiss later comments in [Weiss 1921] that he and Piccard had all the elements at hand to predict the effect and blames himself for not seeing "*cette chose si simple*". Like many discoveries, it seemed obvious in retrospect. In any case, Weiss and Piccard were the first to identify and observe unequivocally the two key features of the magnetocaloric effect – its reversibility and the fact that it peaks around the Curie temperature.

The uncontroversial nature of this discovery in subsequent decades is nicely illustrated by the fact that in the standard historical survey of solid state physics *Out of the Crystal Maze*, S.T. Keith and P. Quedec can write in connection with the magnetocaloric effect that "[w]e may again observe that the inventor of the molecular field indeed had no competitors" [Keith 1992]. It should be noted that the authors only trace the pre-history of the effect back to Langevin.

## 6 Magnetic refrigeration

By the middle of the 1920s P. Debye [Debye 1926] and W.F. Giauque [Giauque 1927] had independently of each other realised that very low temperatures can be attained

<sup>1</sup> The more cited [Weiss 1918] is a condensed version of this paper.



by using adiabatic demagnetisation of paramagnetic salts. The physics behind it is similar to that of the magnetocaloric effect for ferromagnets. By magnetising the salt while it is in thermal contact with a liquid helium bath, insulating the magnetised salt thermally, and removing the magnetic field, temperatures considerably below 1 kelvin can be achieved. This was first experimentally demonstrated by Giauque and MacDougall in 1933 [Giauque 1933].

Since the work of Debye and Giauque comes relatively close in time after Weiss and Piccard's discovery of the magnetocaloric effect, it is tempting for a present-day physicist to assume that their work builds on this discovery. However, the field of magnetic refrigeration using adiabatic demagnetisation seems to have developed entirely separate from the magnetocaloric effect. Neither Debye nor Giauque quote Weiss but rely on general thermodynamic considerations and Langevin's work to show that paramagnetic substances which follow the Curie law will cool significantly if demagnetised at low temperatures, where the heat capacity is very low.

The magnetocaloric effect, on the other hand, attracted attention mainly as a tool for estimating the equilibrium value of the intrinsic magnetisation of ferromagnets. When Weiss introduced the concept of the molecular field or spontaneous magnetisation for ferromagnets, he realised that for zero external field, the total equilibrium magnetisation of a sample will be zero even when the spontaneous magnetisation is non-zero. This is due to the domain structure of the sample: the individual domains will arrange the direction of their magnetisation so as to minimise the total magnetic energy. This makes it impossible to measure the spontaneous magnetisation directly. However, Weiss showed that the adiabatic temperature change below the Curie temperature is approximately given by

$$\Delta T = A(M^2 - M_0^2), \quad (1)$$

where  $A$  is a positive constant,  $M$  is the magnetisation in a given field  $H$ , while  $M_0$  is the spontaneous magnetisation in the absence of an external field. Thus, measurements of  $\Delta T$  and  $M$  for a range of fields allow  $M_0$  to be deduced [Weiss 1924]. This Weiss and Forrer did for nickel [Weiss 1926], and measurements of the magnetocaloric effect continue to be used for this purpose.

One reason for the separate development was presumably the lack of any reasonable applications of the magnetocaloric effect in ferromagnets like nickel, iron, and cobalt with their high Curie temperatures. The standard material for cooling by adiabatic demagnetisation at low temperatures was gadolinium sulphate,  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ . Little was known of the properties of pure gadolinium. However, in the beginning of the 1930s, it became possible to produce reasonably pure samples of the light lanthanides by electrolysis [Gschneidner 1984], and in 1935 Urbain, Weiss, and Trombe announced the discovery of a new ferromagnetic element, gadolinium, with a Curie temperature close to room temperature [Urbain 1935]. Even though Weiss was a co-discoverer, he does not seem to have investigated the magnetocaloric effect of gadolinium. This was only done in the 1950s, as discussed in our recent review [Smith 2012].

## 7 How did the misconception arise?

The field of near-room temperature magnetic refrigeration can be said to date from the 1976 paper by G. Brown, in which he demonstrates a device using gadolinium which could attain a temperature span of 47 °C (−1 °C to 46 °C) [Brown 1976]. Brown does not cite Weiss and Piccard (or Warburg, for that matter). He merely states in the introduction that “the application of a field under adiabatic conditions

gives a temperature change which is sharply peaked near  $T_c$ ” and adds that “Edison and Tesla held early patents (1887 and 1890) for a heat engine based on the inverse of this effect.” As we have seen, the latter statement is not quite correct.

Other pioneering efforts, including that of [Steyert 1978], also do not cite either Weiss or Warburg; Steyert simply takes the work of Debye and Giauque as his starting point. In 1979 an article entitled ‘Magnetic refrigerator–heat pump’ in *Physics Today* helped draw attention to Brown’s and Steyert’s work in the wider physics community [Schwarzschild 1979]. Here it is stated that the magnetocaloric effect “has been known for a long time” and, following Brown’s original paper closely, that Edison’s and Tesla’s patents were based on the inverse of this effect.

Only J.A. Barclay and coworkers seem to be aware of Weiss and Piccard whom they correctly credit in their papers [Barclay 1979] and [Barclay 1982]; the former is focused on application at 2–4 K, thus perhaps escaping the attention of the near-room temperature community, but the latter – which has a succinct and precise description of the contribution of Weiss and Piccard – continues to be cited (though perhaps not read).

Apart from this, there is little discussion of the history of the magnetocaloric effect in the papers on magnetic refrigeration published before the discovery of the giant magnetocaloric materials in the second half of the 1990s, the majority of papers simply quoting [Brown 1976].

It is notable that, with a single exception, until 1999 Warburg was never mentioned in connection with the magnetocaloric effect or magnetic refrigeration (according to the citation data available in ISI Web of Science). The exception is a paper from 1992 by M.D. Kuz'min and A.M. Tishin claiming merely, if imprecisely, that Warburg was “the first to observe heat evolution in iron under the application of a magnetic field” before going on to mention Weiss and Piccard as the discoverers of the magnetocaloric effect in nickel [Kuz'min 1992]. The first time Warburg is unequivocally cited as the discoverer of the magnetocaloric effect seems to be in a paper by A.M. Tishin, K.A. Gschneidner and V.K. Pecharsky [Tishin 1999], possibly due to a misremembering of (or by inadvertently strengthening the wording of) the 1992 paper with which they shared a joint author. The way in which Warburg stated his results, i.e. as an equivalent temperature change of water, has probably contributed to the misunderstanding.

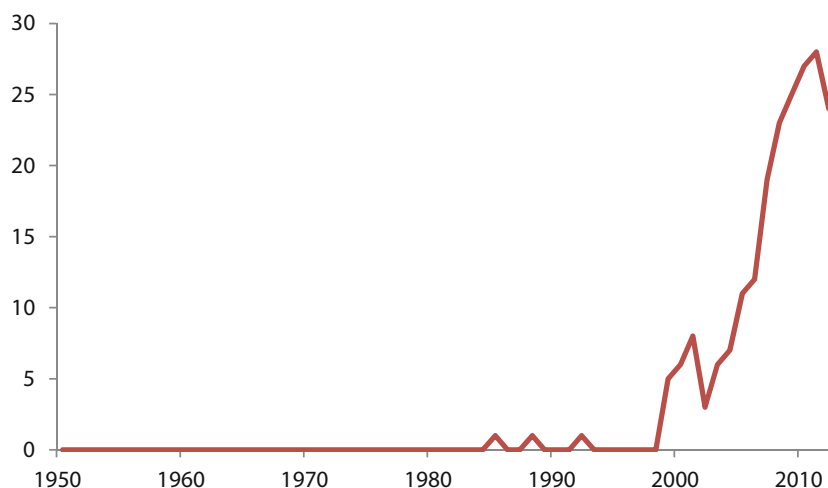
Several other papers from 1999 co-authored by K.A. Gschneidner and V.K. Pecharsky repeat the same information, including a very influential early review on near-room temperature magnetic cooling [Gschneidner 1999]. Due to the authors’ (deservedly) great reputation in the field, the notion that Warburg discovered the magnetocaloric effect spread rapidly in the magnetic refrigeration research community. From 1999 to the present Warburg’s 1881 paper has been cited more than 200 times, almost exclusively in connection with the magnetocaloric effect (see Fig. 2). In comparison, Weiss and Piccard have only been cited five times in the same period of time.

## 8 Conclusion

Warburg did not discover the magnetocaloric effect, nor was he the first to observe that heat is generated in iron under repeated magnetisations and demagnetisations. As we have seen, several 19th century researchers, starting with Joule in 1843, observed that heat is evolved in iron samples subject to a changing magnetic field. By the 1880s this was widely known and accepted.

William Thomson was the first to realise that if the magnetisation of a sample decreases (increases) as a function of temperature, the sample will reversibly heat (cool) slightly when introduced into a magnetic field and cool (heat) slightly when withdrawn from the field again. This he demonstrated on thermodynamic grounds





**Fig. 2.** Yearly citations 1950–2012 of Warburg's 1881 paper; data from ISI Web of Science.

in 1860. However, he did not estimate the magnitude of the effect and did not attempt to observe it experimentally.

In 1881 Warburg discovered the hysteresis of ferromagnets (or was at least the first to publish the observation) and he stated Warburg's law, according to which the heat dissipated during a hysteresis loop is equal to the area enclosed by the loop in an  $M$ - $H$ -diagram. Warburg and Hönig tried to measure the hysteresis heat directly in 1882. They explicitly considered the reversible 'Thomson heat' and concluded that it was unobservably small under their experimental conditions.

Weiss and Piccard discovered the magnetocaloric effect experimentally in 1917 by observing a sizable and reversible temperature change in nickel near its Curie temperature. They clearly distinguished it from the hysteresis heat and gave a satisfactory thermodynamic treatment of the effect. Their discovery was well known and uncontroversial in the physics community for much of the 20th century.

The attribution of the discovery of the magnetocaloric effect to Warburg only took place in 1999. After that it spread widely in the magnetic refrigeration community and beyond.

In closing, we briefly consider the wider significance of the present case. It is a common experience that cited references, when tracked down, do not always support what is being claimed for them in the citing paper. This can be based on either a faulty reading of the original paper or, more troubling, on the fact that the paper being cited has not been read. Indeed, some studies claim – based on an analysis of the propagation of misprints in citations – that it is only a small fraction of cited papers that are actually read ([Simkin 2003], [Simkin 2012]). Whether one is willing to accept such a far-reaching claim (after all, misprints may be propagated by the use of electronic citation lists, irrespective of whether the article in question has been read) or not, the widespread attribution of the discovery of the magnetocaloric effect to Warburg is certainly a striking example of a paper which is correctly cited, but for a finding which does not appear in it. This should highlight the need for careful reading of a paper before citing it. In particular, this is necessary when the paper in question is not recent, since the theoretical framework or use of wording may be significantly different than that prevailing today.

*Acknowledgements.* Useful discussions with Dr. C.R.H. Bahl are gratefully acknowledged.

## References

- Barclay, J.A., O. Moze and L. Paterson. 1979. A reciprocating magnetic refrigerator for 2-4 K operation: Initial results. *J. Appl. Phys.* **50**: 5870-5877
- Barclay, J.A. 1982. Use of a ferrofluid as the heat-exchange fluid in a magnetic refrigerator. *J. Appl. Phys.* **53**: 2887-2894
- Bates, L.F. 1951. The Thermal Effects Associated with Magnetization Processes. *J. Phys. Radium* **12**: 459-470
- Bates, L.F. and N.P.R. Sherry. 1955. The Direct Separation of the Reversible and Irreversible Components of the Magnetothermal Effect. *Proc. Roy. Soc. B* **68**: 642-648
- Brown, G.V. 1976. Magnetic heat pumping near room temperature. *J. Appl. Phys.* **47**: 3673-3680
- Caneva, Kenneth L. 2005. 'Discovery' as a site for the collective construction of scientific knowledge. *Hist. Stud. Phys. Biol.* **35**: 175-291
- Cazin, M. Achille. 1875. Mémoire sur les effets thermiques du magnétisme. *Ann. Chem. Phys.* **6**: 493-554
- Debye, Peter. 1926. Einige Bemerkungen zur Magnetisierung bei tiefer Temperatur. *Ann. Phys. (Leipzig)* **386**: 1154-1160
- Delere, Heinrich. 1905. *Über die Wärmeentwicklung bei cycklischer Magnetisierung von Eisenkernen. Inaugural-Dissertation.* Westfälischen Vereinsdruckerei, Münster i. Westf., pp. 21-30
- Edison, Thomas. 1888. Pyromagnetic Motor. *US Patent* US380100
- Edison, Thomas. 1892. Pyromagnetic Generator. *US Patent* US476983
- Ewing, J.A. 1882. On Effects of Retentiveness in the Magnetisation of Iron and Steel. (Preliminary Notice.) *Proc. Roy. Soc.* **24**: 39-45
- Ewing, J.A. 1885. Experimental Researches in Magnetism. *Phil. Trans. R. Soc. Lond.* **176**: 523-640
- Faraday, Michael. 1856. Experimental Researches in Electricity. Thirtieth Series. *Phil. Trans. R. Soc. Lond.* **146**: 159-180
- Giauque, W.F. 1927. A Thermodynamic Treatment of Certain Magnetic Effects. A Proposed Method of Producing Temperatures Considerably Below 1° Absolute. *J. Am. Chem. Soc.* **49**: 1864-1870
- Giauque, W.F. and D.P. MacDougall. 1933. Attainment of Temperatures Below 1° Absolute by Demagnetization of  $\text{Gd}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$ . *Phys. Rev.* **43**: 768
- Gross, Alan G. 1998. Do Disputes over Priority Tell Us Anything about Science? *Sci. Context* **11**: 161-179
- Gschneidner Jr., K.A. 1984. Past, Present and Future of Rare Earth Metallurgy. *J. Less-Common Met.* **100**: 1-13
- Gschneidner Jr., K.A., V.K. Pecharsky, A.O. Pecharsky and C.B. Zimm. 1999. Recent developments in magnetic refrigeration. *Materials Science Forum* **315-317**: 69-76
- Heydweiller, Adolf. 1906. Über die Thomsonsche Magnetisierungswärme; Entgegnung auf eine Bemerkung des Hrn. E. Warburg. *Ann. Phys. (Leipzig)* **325**: 207-208
- Herwig, Hermann. 1878. Ueber Wärmeentwicklung durch Drehen von Moleculärmagneten. *Ann. Phys. (Leipzig)* **4**: 177-187
- Joule, James. 1843. On the Calorific Effects of Magneto-Electricity, and on the Mechanical Value of Heat. *Phil. Mag., Ser. 3*, **23**: 263-276
- Keith, Stephen T. and Pierre Quédec. Magnetism and Magnetic Materials. 1992. *Out of the Crystal Maze: Chapters from the History of Solid-State Physics*, Lillian Hoddeson et al. (eds.). Oxford University Press, New York, pp. 359-442
- Kuhn, Thomas S. 1962. Historical Structure of Scientific Discovery. *Science* **136**: 760-764
- Kuz'min, M.D. and A.M. Tishin. 1992. Magnetocaloric Effect. Part 1: An introduction to various aspects of theory and practice. *Cryogenics* **32**: 545-558
- Langevin, M.P. 1905. Magnétisme et théorie des électrons. *Ann. Chim. Phys.* **5**: 70-127
- Merton, Robert K. 1957. Priorities in Scientific Discovery: A Chapter in the Sociology of Science. *Am. Sociol. Rev.* **22**: 635-659

- Myers, H.P. and W. Sucksmith. 1951. The spontaneous magnetization of cobalt. *Proc. Roy. Soc. A* **207**: 427-446
- Oxford English Dictionary 3rd edn. 2000. Accessed online ([www.oed.com](http://www.oed.com)), entry 'magnetocaloric'
- Potter, H.H. 1934. The Magneto-Caloric Effect and Other Magnetic Phenomena in Iron. *Proc. Roy. Soc. A* **146**: 362-387
- Schwarzschild, Bertram M. 1979. Magnetic refrigerator-heat pump. *Phys. Today* **32**: 18-20
- Simkin, M.V. and V.P. Roychowdbury. 2003. Read before you cite! *Complex Syst.* **14**: 269-272
- Simkin, M.V. and V.P. Roychowdbury. 2012. Theory of citing. *Handbook of Optimization in Complex Networks: Theory and Applications*, M.T. Thai and P.M. Pardalos (eds.). Springer, Dordrecht, The Netherlands, pp. 463-505
- Smith, Anders et al. 2012. Materials challenges for high performance magnetocaloric refrigeration devices. *Adv. Energy Mat.* **2**: 1288-1318
- Stefan, J. 1871. Ueber die Gesetze der elektrodynamischen Induction. *Wien. Ber.* **64**: 193-224
- Stefan, J. 1889. Ueber thermomagnetische Motoren. *Ann. Phys.* **274**: 427-440
- Steyert, W.A. 1978. Stirling-cycle rotating magnetic refrigerators and heat engines for use near room temperature. *J. Appl. Phys.* **49**: 1216-1226
- Tesla, Nikola. 1889. Thermo-Magnetic Motor. *US Patent* US396121
- Tesla, Nikola. 1890. Pyromagneto-Electric Generator. *US Patent* US428057
- Thomson, William. 1860. *Cyclopedia of the Physical Sciences*, 2nd edn., J.P. Nichol (ed.). Richard Green and Company, London and Glasgow, 838
- Thomson, William. 1878. On the Thermoelastic, Thermomagnetic, and Pyroelectric Properties of Matter. *Phil. Mag.*, Ser. **5**: 4-27
- Tishin, A.M., K.A. Gschneidner Jr., and V.K. Pecharsky. 1999. Magnetocaloric effect and heat capacity in the phase-transition region. *Phys. Rev. B* **59**: 503-511
- Urbain, Georges, Pierre Weiss and Félix Trombe. 1935. Un nouveau métal ferromagnétique, le gadolinium. *Comptes Rendus* **200**: 2132-2134
- Warburg, Emil. 1881. Magnetische Untersuchungen. Ueber einige Wirkungen der Coërcitivkraft. *Ann. Phys. (Leipzig)* **249**: 141-164
- Warburg, Emil and L. Hönig. 1882. Ueber die Wärme, welche durch periodisch wechselnde Kräfte im Eisen erzeugt wird. *Ann. Phys. (Leipzig)* **256**: 814-835
- Warburg, Emil. 1906. Bemerkung zu der Arbeit des Hrn. Delere über die Wärmeentwicklung bei zyklischer Magnetisierung von Eisenkernen. *Ann. Phys. (Leipzig)* **324**: 643-644
- Weiss, Pierre. 1907. L'hypothèse du champ moléculaire et la propriété ferromagnétique. *J. Phys. (Paris)*, 4th Ser. **6**: 661-690
- Weiss, Pierre and Paul-N. Beck. 1908. Chaleur spécifique et champ moléculaire des substances ferromagnétiques. *J. Phys. (Paris)*, 4th Ser. **7**: 249-264
- Weiss, Pierre and Auguste Piccard. 1917. Le phénomène magnétocalorique. *J. Phys. (Paris)*, 5th Ser. **7**: 103-109
- Weiss, Pierre and Auguste Piccard. 1918. Sur un nouveau phénomène magnétocalorique. *Comptes Rendus* **166**: 352-354
- Weiss, Pierre. 1921. Le phénomène magnéto-calorique. *J. Phys. Radium* **2**: 161-182
- Weiss, Pierre and R. Forrer. 1924. Phénomène magnétocalorique. Aimantation apparent et aimantation vraie. *Comptes Rendus* **178**: 1448-1452
- Weiss, Pierre and R. Forrer. 1926. Aimantation et phénomène magnetocalorique du nickel. *Ann. Phys. (Paris)* **5**: 153-213