

# The Little Maghemite Story: A Classic Functional Material

By *Richard Dronskowski\**

*In memory of Professor Louis Néel who passed away on November 17, 2000 at age 96*

It is presumably one of the curiosities of our modern “information society” that the public at large is virtually unaware of the role of magnetism in everyday life. Ask your next door neighbors and you will find that some may perhaps associate magnetism with ship navigation using a compass; the majority probably consider the topic a long-forgotten elementary school experience. Nonetheless, magnetic information storage, either analog or digital, be it on tapes or on disks, is a truly universal technology and of tremendous importance both in the consumer and professional markets. The possibility of storing and retrieving essential information has become so natural that only a sudden data loss makes us realize how indispensable it really is—especially when your own computer hard disk suddenly crashes. While I personally believe that most digital information is better dumped than preserved, we all would certainly love to keep the audio and video memories of our beloved ones accessible for eternity. Here’s a little story reminding us of one of the materials that made it all possible, and of the science and scientists involved. Because of the opulent scientific literature, the following historical account can only be considered a rough sketch; I leave the more elaborate and competent coverage to the science historians and apologize for any errors of mine.

Fe<sub>2</sub>O<sub>3</sub>, or, depending on the synthetic procedure, *Crocus martis adstringens*, *Caput mortuum (vitrioli)*, *Crocus martis Zwelferi*, or *Eisensafran*, has obviously been known for centuries. According to the 1822 textbook of Schubarth,<sup>[1]</sup> the alchemist Kunckel had already synthesized Fe<sub>2</sub>O<sub>3</sub> by heating metallic iron in air until red-hot. Then, in the early 19th century, the prominent chemist Gay-Lussac made the material first from the reaction of gaseous nitric acid with red-hot iron<sup>[2]</sup> and, somewhat later, by oxidizing molten iron dichloride using elemental oxygen in the presence of humidity;<sup>[3]</sup> there have been many more contributions from other scientists (see below), and the contemporary literature witnesses a rich chemistry evolving in the late 19th century. Hedvall, an early pioneer of solid-state chemical reactivity, eventually demonstrated in 1922 that diverse starting materials lead to Fe<sub>2</sub>O<sub>3</sub>, and he prepared the crystalline phase from pyrophoric iron but also from the chlorides, the nitrate, the sulfides, the sulfate, the carbonate, the

oxalate, and the acetate of iron.<sup>[4]</sup> Before magnetic materials entered advanced technical use, Fe<sub>2</sub>O<sub>3</sub> was simply employed as a catalyst, a paint, or an abrasive material.<sup>[5]</sup>

In 1846 Faraday investigated Fe<sub>2</sub>O<sub>3</sub> and characterized it as being—in today’s language—paramagnetic, i.e., almost non-magnetic but can be attracted to an external magnetic field.<sup>[6]</sup> When it comes to more exciting physical behavior, Malaguti states<sup>[7]</sup> that Pelouze reported to Becquerel the successful synthesis of magnetic Fe<sub>2</sub>O<sub>3</sub>, generated by carefully roasting very fine iron powder in air. Robbins, in 1860, synthesized magnetic Fe<sub>2</sub>O<sub>3</sub> by oxidizing Fe<sub>3</sub>O<sub>4</sub>,<sup>[8]</sup> a process that is actually used nowadays. The same synthetic route was later followed by Baudisch and Welo;<sup>[9]</sup> they recognized that magnetic Fe<sub>2</sub>O<sub>3</sub> seemed to be magnetically superior to the structurally closely related Fe<sub>3</sub>O<sub>4</sub>. In retrospect, it is interesting to see how long it took the struggling scientists to realize that the strong magnetic features of that particular type of Fe<sub>2</sub>O<sub>3</sub> did not go back to impurities of FeO or Fe<sub>3</sub>O<sub>4</sub> but were intrinsic properties; the problem is particularly difficult since our predecessors had to find out that Fe<sub>2</sub>O<sub>3</sub> manifests itself in different—using today’s terminology—crystallographic phases! From a modern perspective, a number of historic observations seem to be especially worth mentioning.

First, the presence of at least two different forms of Fe<sub>2</sub>O<sub>3</sub> was already apparent from their difference in specific densities.<sup>[10]</sup> Second, thermochemist Le Chatelier established their existence as a function of temperature in 1895. After having synthesized one form by decomposing iron acetate at 400 °C and the other form by firing the first one at 1000 °C, he then reduced the two kinds of Fe<sub>2</sub>O<sub>3</sub> with elemental carbon in a calorimeter. It seems truly admirable that, building upon his precise measurements, Le Chatelier clearly demonstrated that the low-temperature form of Fe<sub>2</sub>O<sub>3</sub> is only metastable, distinct from the stable high-temperature form by about 2 kcal/mol.<sup>[11]</sup> Third, it was shown that the magnetic low-temperature form loses its magnetic properties through high-temperature annealing.<sup>[7,8]</sup> Finally, substantial natural deposits of Fe<sub>2</sub>O<sub>3</sub> were recognized as being magnetic, following the account of Hilpert.<sup>[12]</sup>

As we know today, the puzzle of Fe<sub>2</sub>O<sub>3</sub> modifications can at least be partially elucidated by looking at the crystal structures. In the 1987 edition of his book, Wells mentions four different Fe<sub>2</sub>O<sub>3</sub> phases.<sup>[13]</sup> The trigonal corundum structure of thermodynamically stable, almost non-magnetic  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (hematite) was clarified by Pauling and Hendricks in 1925;<sup>[14]</sup> another two, less

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important phases have been dubbed  $\beta$ - $\text{Fe}_2\text{O}_3$ . However, the probably cubic (see below) nature of magnetic  $\gamma$ - $\text{Fe}_2\text{O}_3$  (maghemite) was first understood by Baudisch and Welo, who were also able to distinguish, by X-ray analytical means, the stable  $\alpha$  phase from the metastable  $\gamma$  phase.<sup>[15]</sup> Most of the  $\gamma$  phase's structural characteristics were then elaborated in the thirties.<sup>[16–18]</sup> Since that time,  $\gamma$ - $\text{Fe}_2\text{O}_3$  is usually described as a defect structure of inverse spinel type in which the trivalent iron atoms are distributed over tetrahedral and octahedral sites,<sup>[13,19]</sup> thus, the structural relationship of  $\gamma$ - $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$  is immediately apparent, as is the easy chemical interconversion of these two materials upon reduction/oxidation.

However, insight was not sufficient—taking a look into Klemm's 1936 textbook on magnetochemistry,  $\gamma$ - $\text{Fe}_2\text{O}_3$  is oversimplified as being a “ferromagnetic” material.<sup>[20]</sup> Also, Klemm came up with an ad hoc hypothesis in saying that the “ferromagnetic” properties of the  $\gamma$  phase were due to the presence of “metal–metal bonds”, which he thought were not present in the  $\alpha$  phase. Both questionable statements, however, were quite legitimate at that time, and they simply reflect the 1936 frame of knowledge since a) diamagnetism, b) paramagnetism, and c) ferromagnetism were the only magnetic notions available; also, quantum chemistry was in its infancy. In order to explain the magnetic properties of  $\gamma$ - $\text{Fe}_2\text{O}_3$  the world urgently needed a new idea.

In the same year, 1936, Néel considered the  $\alpha$  phase of metallic manganese and developed his concept of *antiferromagnetism*, although no contemporary material whatsoever followed his theory satisfactorily.<sup>[21]</sup> Two years later, however, the phenomenon was observed for the first time in  $\text{MnO}$ <sup>[22]</sup> and given its name by Bitter.<sup>[23]</sup> It is amusing to note that early on Néel's very much structure-oriented and in some sense “static” picture of the atomic interactions in magnetic materials did not find the approval of his quantum theorist colleagues; Néel modestly rejoined: “Thank God I do not know this quantum mechanics”.<sup>[24]</sup> Another class of materials, the ferrites, seemed to be even more complicated but attracted a lot of attention, so they came under investigation at the Philips laboratories. In 1947, Verwey and Heilmann published a definitive paper in which they showed by X-ray investigations that all iron spinels were inverse spinels;<sup>[25]</sup> tragically, Heilmann had already been deported to a concentration camp in 1944 from which he never returned. Shortly after, in 1948, Néel successfully transferred his model of antiferromagnetism to this structure type and also proposed the term *ferrimagnet* for a compound made up of two magnetized sublattices with spontaneous magnetizations of opposite directions and differing sizes.<sup>[26]</sup> The experimental verification of the phenomenon using neutron diffraction was performed in 1949 but on the basis of  $\text{Fe}_3\text{O}_4$ .<sup>[27]</sup>

Thus, *ferrimagnetic*  $\gamma$ - $\text{Fe}_2\text{O}_3$  (maghemite) seems to have a ferromagnetic Curie point, although its magnetization is lower than if it were a real ferromagnet; the two opposing magnetic lattices do not fully cancel each other out—the phase exhibits a magnetic moment of about 2.5 Bohr magnetons per formula unit.<sup>[19]</sup> Maghemite's ordering temperature, about 675 °C, is much higher than the temperature of its irreversible transformation to hematite; the operational value lies around

400 °C.<sup>[28]</sup> Interestingly, it has been known since 1930 that pure maghemite is unstable even at room temperature and loses its susceptibility with time,<sup>[29]</sup> but it can be stabilized by doping with other metal ions. In the second half of the 20th century, even more delicate structural investigations revealed that maghemite is not cubic but shows an ordered cation vacancy distribution with tetragonal symmetry in which one lattice vector must be tripled;<sup>[30,31]</sup> the superstructure reflections are only observed if the crystallites are not too small. As expected, maghemite is an ideal material for Mößbauer measurements, and the ionic environments and oxidation states were studied in great detail.<sup>[32]</sup> Finally, refined magnetic notions were also applied to  $\alpha$ - $\text{Fe}_2\text{O}_3$  (hematite): this material turned out to be a *tilted antiferromagnet*<sup>[19]</sup> with such a tiny residual magnetic moment that it was falsely regarded as being a paramagnet (remember Faraday) for many decades.

The science–technology relationship emerged through Poulsen's 1897 telegraphon invention,<sup>[33]</sup> a predecessor of our tape recorders, which stored sound on a magnetic steel wire. Nowadays magnetic tapes are the successors of Pflüger's 1934 magnetophone system, jointly developed in Germany by AEG and BASF;<sup>[34]</sup> the first tape was made of carbonyl iron embedded into cellulose acetate. This low-performance magnetic material was soon replaced by cubic  $\text{Fe}_3\text{O}_4$  (magnetite) and later, after the invention of acicular magnetic pigments in the late 1940s, by  $\gamma$ - $\text{Fe}_2\text{O}_3$  (maghemite).<sup>[35]</sup> When anticipating acicular particles and their technology (see below), one might add that the classification of maghemite as the  $\gamma$  phase goes back to a proposal of Haber<sup>[36]</sup> because  $\gamma$ - $\text{Fe}_2\text{O}_3$  can be made from dehydrating needle-shaped  $\gamma$ - $\text{FeOOH}$  crystals. For an extensive overview of the large number of iron oxides and oxide hydroxides, the reader should consult the literature.<sup>[37]</sup>

All kinds of magnetic pigments manufactured today are magnetically hard materials. For optimum performance, they should exhibit both high coercivity and high remanence. Also, the particles should be (uniformly) small, temperature-tolerant, and resistant to corrosion and friction.<sup>[34]</sup> With the exception of platelet-shaped crystals of barium ferrite, acicular particles of  $\gamma$ - $\text{Fe}_2\text{O}_3$ , Co-coated iron oxides, and metallic iron are mostly sought after since the artificially introduced shape anisotropy leads to higher coercivities.<sup>[34]</sup> The diameters of the particles lie around 0.03–0.1  $\mu\text{m}$ , with an aspect ratio of about 5–10.<sup>[38]</sup> Because of its tetragonal rutile structure, crystals of  $\text{CrO}_2$ —the big competitor—grow spontaneously in needle-like shape under hydrothermal synthetic conditions.<sup>[39]</sup> For iron pigments, however, the industrial processes have to start from acicular precursor crystals of either non-magnetic  $\alpha$ - $\text{FeOOH}$  (goethite) or non-magnetic  $\gamma$ - $\text{FeOOH}$  (lepidocrocite); these are dehydrated directly to  $\alpha$ - $\text{Fe}_2\text{O}_3$  (hematite) and further reduced to  $\text{Fe}_3\text{O}_4$  (magnetite). Following Robbins's 1860 approach, magnetite is then carefully oxidized to yield ferrimagnetic  $\text{Fe}_2\text{O}_3$  (maghemite), which makes up by far the largest share of all magnetic pigments; the vast patent literature illustrates its paramount importance. As a final step, an epitaxial surface of cobalt ferrite is often added to boost magnetic coercivity, and these Co-coated maghemite pigments in turn challenge  $\text{CrO}_2$  pigments in performance.<sup>[38]</sup>

The room-temperature saturation magnetization of fine particles of pure maghemite is around 350 G. Acicular particles exhibit a coercivity of order 350 Oe.<sup>[40]</sup> Either poly(ethylene terephthalate) (PET) films or Al/Mg disks serve as substrates for the magnetic material.<sup>[34]</sup> Analog as well as digital magnetic information processing operates by exchanging magnetic signals between an electromagnetic head and a magnetic carrier (the pigment) while the two components are constantly moving relative to each other. In recording mode, the electromagnetic head is magnetized by a signal current representing the information to be stored, thereby writing a corresponding residual magnetization into the pigment. In retrieving mode, the pigment's permanent magnetization electromagnetically induces a varying voltage in the head.<sup>[41]</sup> Grünberg's recent discovery of giant magnetoresistivity in layered magnetic structures<sup>[42]</sup> has presented a radically new and even more promising technique for data storage on hard disks.

A number of points can be extracted from the story of maghemite. First, the successful operation of an advanced functional material can only be safely established if it is based on rock-solid fundamental research. In addition, we have seen that generations of (sometimes eminently prominent) scientists may look at a problem, and all of them contribute in one way or another to the growing knowledge; the necessity of combined experimental and theoretical efforts to both make and understand a new compound is all too obvious, and is equally important in the past, present, and future. A moment's reflection will also reveal that virtually everything related to our "information society" mentioned at the beginning—let alone the exploding growth of the World Wide Web—would simply be non-existent without that "academic" curiosity-driven research of our predecessors. Let us communicate this to science funding agencies, journalists, politicians, and suchlike. Lastly, even this historical sketch would not be here without maghemite because the words you are reading now once rested on a hard disk and a diskette associated with my computer. That's what I call a "recursive" functional material.

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