The Little Maghemite Story: A Classic Functional Material

By Richard Dronskowski*

In memory of Professor Louis Nèel 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 number of historic observations seem to be especially worth mentioning.

First, the presence of at least two different forms of Fe₃O₄ was already apparent from their difference in specific densities.[10] 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 Fe₃O₄ with elemental carbon in a disch and Welo;[9] they recognized that magnetic Fe₃O₄ seemed to be magnetically superior to the structurally closely related Fe₂O₃. 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 Fe₂O₃ did not go back to impurities of FeO or Fe₃O₄ but were intrinsic properties; the problem is particularly difficult since our predecessors had to find out that Fe₂O₃ 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.

As we know today, the puzzle of Fe₂O₃ modifications can at least be partially elucidated by looking at the crystal structures. In the 1987 edition of his book, Wells mentions four different Fe₂O₃ phases.[13] The trigonal corundum structure of thermodynamically stable, almost non-magnetic α-Fe₂O₃ (hematite) was clarified by Pauling and Hendricks in 1925;[14] another two, less...
important phases have been dubbed $\beta$-$Fe_2O_3$. However, the probably cubic (see below) nature of magnetic $\gamma$-$Fe_2O_3$ (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.[15] Most of the $\gamma$ phase’s structural characteristics were then elaborated in the thirties.[16–18] Since that time, $\gamma$-$Fe_2O_3$ is usually described as a defect structure of inverse spinel type in which the trivalent iron atoms are distributed over tetrahedral and octahedral sites[13,19] thus, the structural relationship of $\gamma$-$Fe_2O_3$ to $Fe_3O_4$ 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 magnetoochemistry, $\gamma$-$Fe_2O_3$ is over-simplified as being a “ferromagnetic” material.[20] 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 $\gamma$-$Fe_2O_3$, 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.[21] Two years later, however, the phenomenon was observed for the first time in MnO[22] and given its name by Bitter.[23] 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”.[24] 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 are inverse spinels.[25] 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.[26] The experimental verification of the phenomenon using neutron diffraction was performed in 1949 but on the basis of $Fe_3O_4$. [27]

Thus, ferrimagnetic $\gamma$-$Fe_2O_3$ (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.[19] 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.[28] Interestingly, it has been known since 1930 that pure maghemite is unstable even at room temperature and looses its susceptibility with time,[29] 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.[30,31] 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.[32] Finally, refined magnetic notions were also applied to $\alpha$-$Fe_2O_3$ (hematite); this material turned out to be a tilted antiferromagnet[19] 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 Poul- sen’s 1897 telegraphon invention,[33] a predecessor of our tape recorders, which stored sound on a magnetic steel wire. Nowadays magnetic tapes are the successors of Pfeumer’s 1934 mag- netophone system, jointly developed in Germany by AEG and BASF,[34] the first tape was made of carbonyl iron embedded into cellulose acetate. This low-performance magnetic material was soon replaced by cubic Fe$_2$O$_3$ (magnette) and later, after the invention of acicular magnetic pigments in the late 1940s, by $\gamma$-$Fe_2O_3$ (maghemite).[35] 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[36] because $\gamma$-$Fe_2O_3$ can be made from dehydrating needle-shaped $\gamma$-FeOOH crystals. For an extensive overview of the large number of iron oxides and oxide hydroxides, the reader should consult the literature.[37]

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.[34] With the exception of platelet-shaped crystals of barium ferrite, acicular particles of $\gamma$-$Fe_2O_3$, Co-coated iron oxides, and metallic iron are mostly sought after since the artificially introduced shape anisotropy leads to higher coercivities.[34] The diameters of the particles lie around 0.03–0.1 μm, with an aspect ratio of about 5–10.[38] Because of its tetragonal rutile structure, crystals of CrO$_2$ — the big competitor — grow spontaneously in needle-like shape under hydrothermal synthetic conditions.[39] For iron pigments, however, the industrial processes have to start from acicular precursor crystals of either non-magnetic $\alpha$-FeOOH (goethite) or non-magnetic $\gamma$-FeOOH (lepidocrocite); these are dehydrated directly to $\alpha$-$Fe_2O_3$ (hematite) and further reduced to $Fe_2O_4$ (magnette). Following Robbins’s 1860 approach, magnetite is then carefully oxidized to yield ferri- magnetic $Fe_3O_4$ (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 CrO$_2$ pigments in performance.[38]
The room-temperature saturation magnetization of fine particles of pure maghemite is around 350 G. Acicular particles exhibit a coercivity of order 350 Oe. Either poly(ethylene terephthalate) (PET) films or Al/Mg disks serve as substrates for the magnetic material. 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 electromagnetic head is magnetized by a signal current representing the 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. 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