HISTORY OF THE "MAGNETISM" AT THE NAT.LAB.

Starting situation

1) *At Philips*
Diversification from the incandescent lamp industry towards an electrotechnical-electronic industry has effected a growing interest in magnetic materials.

a) Application of soft magnetic materials in power transformers, in smoothing coils, in filters for different frequency ranges. The materials used are usually electric conductors, i.e. metals and alloys. The construction of components is variable and is of ten aimed at the reduction of eddy current losses (laminations with paper insulation, iron powder with a phosphate coating).
b) Application of permanent magnetic materials for magnets in electrodynamic loudspeakers. Heterogeneous materials, which acquire a sufficiently high coercive force by a complicated heat treatment (whatever this may be).
c) An integrated industry produces the critical materials in its own factories. The permanent magnets served also to ensure full employment of the Philips casting workshops.

2) *In the world*

a) The quantum theory can give an explanation of the a tomic magnetism. A "qualitative" interpretation of the temperature-dependence of saturation can be obtained from Weiss' theory (1907). The molecular field of a model of ferromagnetic metals has been understood by Heisenberg (1928). A physical understanding of the saturation of solids has been gained only exceptionally, i.e. through isolated ions. Here a Dutch (Leyden) tradition of investigation at very low temperatures was established.

Secondary magnetic properties as K, λ and so on are not clearly understood and even more obscure is Hc .
However concepts as Weiss domain and Bloch wall are well-known (1932, Becker) and magnetization processes of a different nature (ca. 1930) were being developed. Widely read authors in this field were Becker and Döring (1939).

b) Since all the magnetic materials relevant to industry are metals, the metal theory and the empiricism of metals and alloys is vitally important for the understanding of magnetism. An insight into metals has been provided by the quantum theory (Mott and Jones, 1036). Understanding of precipitation processes, and empirism was due to Köster, Masing and Mishima in the thirties, and studies on recrystallization were delivered by Burgers (1935).

At the laboratory
1) *Previous history*
Investigation of the grain size and magnetic properties was conducted by Sizoo (1928), Sizoo and Zwikker: determination of R, dR/dT in a Ni-Fe system. Sizoo: measurement on single crystals (1929). Elenbaas: Measurements on ferromagnetic thin films (1932). Also: permanent magnets 1932/33 (?)

2) *Research teams directly or indirectly involved in magnetic research in the years 1935-1945 in the Nat.Lab.*
Notwithstanding that there were no formal groups in these days, one can subdivide the researchers in a number of teams:

<u>Magnetism:</u> Dr. Snoek, J.F. Fast, M.W. Lauwerse, Dr. J. Boeke, Prof. dr. G.W. Rathenau. Dr. E.W. Gorter
<u>Metals and X-ray diffraction research:</u> Prof. W.G. Burgers, J.J.A. Ploos van Amstel, Prof. J.D. Fast, Dr. J.F.H. Custers
<u>Material and metal tests:</u> Dr. P. Clausing, Dr. J.J. Went Hogendoorn, G.T. Breuring
<u>Metal casting and processing</u>: dr. G.B. Jonas, B. Haes, Ir. H.J. Meerkamp van Embden
<u>Investigations on oxydes</u>: Prof. A.E. Van Arkel, M.G. Van Bruggen, dr. J.H. De Boer, Dr. E.J.W. Verwey, Dr. P.W. Haaijman, Dr. F.C. Romeijn
<u>Telephone:</u> Jhr. ir. W. Six, Dr. J.W.L. Köhler, Ir. P.J. Koops
<u>Radio, Television:</u> Ir. H. Rinia, Ir. H.J. Lindenhovius, Jhr. Dr. M. Gevers
<u>Electrical networks</u>: Prof. B.D.H. Tellegen

A broad range of activities is manifest from this list. It was the base for the multidisciplinary approach which proved so successful in the investigation and the development of the magnetic materials, ferrites and permanent magnets, in the laboratory.

Soft magnetic materials

1) Philips became involved in telephony. How did it start? Zwagerman of Six's group rolled for Six, under intermittent annealing, nickel-iron strips of thickness up to ca. 50μm to be used for Pupin coils. Six had learned and felt (?) that this results in suitable core material (reports 782/33 (?), 864/34 (?)). Snoek up to then working in the field of acoustics and dipole liquids (continuing Sizoo's work?) constructs magnetic equipment and tackles this problem. Sometimes the losses and the distortion are low (Report Snoek 842/32?). A typical cooperation was build up between the metal-casting expert Jonas, the X-ray diffraction specialist Burgers and the electrotechnical engineer Six. They found that to keep the losses low the use of 50/50 NiFe strip with a quasi-unicrystalline texture is required; this material should be rolled out in the [100] direction and a non annealed rolling from 100μ to 50μ is necessary to obtain adequate magnetic properties; Snoek found that such properties are associated with a magnetic preferred direction in the plane of the strip normal to the directions of the magnetic field used (Six, Snoek and Burgers, Ingenieur 49; Snoek, Physica 2, 1935). Later (R + Snoek, Physica 8, 1941) this has been attributed to an NiFe structure which could not be demonstrated without the use of neutrons. The solution to this problem was given after the war by Néel-Dautreppe? Because of their highly advanced Pupin coils Philips became an esteemed supplier of telephony components and the like. A factory (......Van Meurs), which cooperated with different P.T.T. 's was founded in Warschau besides that in Hilversum (TDS).

2) Holst conceived non-conducting transformer cores, which only needed to be cast. An extensive program has been set up on ferrites; whose magnetic properties initially were confusing and obscure. Van Arkel, Verwey and Van Bruggen (Rec. Trav. Chim. Pays Bas 21, 1936) attacked the chemical aspects of this problem. Phase diagrams of oxide systems were made. Verwey early started to investigate the structural properties of oxides (Z. Krist. A 91, 1935; in conjunction with Van Bruggen, Z. Krist. A 92, 1935).
Together with De Boer (V. + De Boer, Rec. Trav. Chim. 21, 1936 (?) he was interested in the cation arrangement in spirrels, which will later turn out to be essential for the interpretation of the physical (among which magnetic) properties. Work was performed in conjunction with Heilmann, Haaijman, Romeijn (see also Philips Technical Review) and J.H. van Santen (dito) on the cation distribution, on the arrangement of electrons in Fe_3O_4 (Verwey arrangement) and on the Madelung energy.
Part of this work has not been published until after the war. The investigation carried out in conjunction with Heilmann took place during his detention in the concentration camp of Vught. Establishing the arrangement of the cations (normal or inverse ferrite), in which Verwey made use of earlier work of Barth and Posnjak (1932) has made an essential contribution to Néels theory of ferrimagnetism.

As early as 1936 Snoek published on the ferrites $MeOFe_2O_3$ (Physica 3, 1936). In his book (Elsevier 1947) he summarizes his work done during the war and also refers to the essential contribution made in the field of measuring by Köhler and Koops with their advanced Maxwell bridge. Through Gevers measurements at high frequencies indications were obtained as to ferromagnetic resonance.
The resonance phenomena important for physical understanding, and innumerable new applications (circulators, emitters) were recognized as such by Snoek (Physica 14, 1948) in the curves of μ' as a function of frequency.
Snoek also grasped the possibility of resonance in nonsaturated specimens (ibid). Beljers (Physica 14, 1949) was the first to carry out an exact measurement of the ferrimagnetic resonance in a resonator cavity.

The scientific work of Philips on ferrites has greatly influenced other investigations in the world and has received in turn new stimuli from them. It is remarkable that the most directly verified theory in this connection is Néel's (Gorter and Schulkes, P.R. 90, 1953), but this theory has given just Philips as well as others a guide for work aimed at practical applications. Japanese work on ferrites (T. Takei ...) was already being in progress at the time of Snoek's investigations and was stimulated afterward thereby. American work (Kittel, P.R. 73, 76, 1948 and 1949)in' a wide diversification followed upon the work at Eindhoven. Maybe it is a tragic element that the application of ferrite materials to the gyrator suggested by Tellegen at Eindhoven, the new network element (Ph. Res. Rep. 3, 1948) has not been envisaged, which can be due to an unduly busy condition or lack of communication. This application originated from Bell (Clogston, Rev. Mod. Phys. 52?). In fact the interdisciplinary cooperation at the Philips laboratory between the chemists, physicists, X-ray diffraction, electronic engineers and measuring instrument designers has been excellent and decisive for success. Perhaps failure in the above-mentioned work of Tellegen was due to the fact that he was a "lonely wolf".

The significance of the ferrites for electronics throughout the world was enormous. Quite new wavelength range became available for use (…..) not only for communication technique but also for the scientific and technical measuring technique (e.g. ferrites for accelerators and afterwards for memory cores, etc.). Typically, at the Philips laboratory, it is not the representatives of H.F. technique but the telephony experts, notably Six (the non-conservative aristocrat) who were the pioneers of the application of the new materials and were responsible for their introduction in the factory.
As regards Philips the once established competence on the ferrite field has been fruitful for many years (new ferrites, which were more and more tailored to suit their applications). From the knowledge of the family of soft ferrites competence on the field of permanent ferroxdure magnet could easily be gained (1952).

3) Emerging from the work on magnets was the interest in time effects, after-effects such as those of C and N in Fe (Snoek, Physica 8, 1941, 9, 1942) thus opening up a large scope of scientific research. As Snoek erroneously thought that magnetic after-effects were due only to mechanic causes he concentrated on these. He correctly considered the interstitial sites on the three axes as stable positions for interstitials. He considered the re-establishment of equilibrium after mechanic distortion to occur by redistribution of interstitials over the different interstitial sites. This he recognized as the basis of the after-effect.
Theoretical and quantitative explanation of his experiments by Polder (Philips Res. Rep . 1). This work was widely followed up and extended in the USA (Zener), at the Eindhoven laboratory (J.D. Fast and afterwards, Meijering) and elseqhere resulting in a knowledge of solubilities, of the fundamental interstitial diffusion phenomenon, and so on. The Philips industry was not left with tangible results, except for the knowledge of highly sensitive physical measuring methods (and their application to welding rod production), which have outrun the chemical analyses, as well as technical fame.

Snoek's character

It is justifiable to throw light on Snoek as a human being, who gave such a great contribution to the development of magnetic materials. He was educated at a training college (together with Bouwers), studied at the Utrecht University, and promoted there under Ornstein …....
He performed acoustic work at the Nat.Lab. but especially made a significant contribution to the knowledge of dipole liquids (Van Arkel and Snoek's formula). After this he worked on magnetism and metals. In 1950 he left for the U.S.A., where he was killed in a car accident six month later.

He was a most remarkable character but not particularly sociable. He was possessed by his problems end was anxious to succeed in the project he handled. He had a very good knowledge of the literature but he was not mild in judging other people. Probably owing to his individual characteristics he was not given the honour he was entitled to. His lectures were often confusing, dealing with measurements obtained just the day before. His lectures in English were much more consistent than those in his mother tongue. There he had to concentrate on the language and could not continue to think physics while speaking. His publications however are clear.

Permanent magnets

Also here, in the time of this story, the knowledge is dynamic: application of the quantum theory to metals, but, what is much more important, there starts an understanding of precipitation effects while the cooling od alloys and the like. As said, Philips participated in this science.
P.M. production with Philips started in 1933 for two reasons:
a) Owing to reduction of chromium-iron production, we had some excess metal melting and casting capacity which had to be used.
b) Some need was felt to replace the electromagnet of our loudspeakers by P.M systems (Dijksterhuis).

The best magnet material in that time was so called “Honda” steel (Fe + 25% Co) which normally was made by casting large blocks and subsequent swaging and rolling. We had no swaging and rolling facilities, so tried and succeeded in casting the magnets in their final form.

Very soon the Honda steel was replaced by the better Mishima steel, an alloy of Fe, Ni and Al. Unlike previous materials this alloy derived its magnetic hardness from the shape anisotropy of ferromagnetic particles precipitated in a non-magnetic matrix. Casting this material in our old arc furnace was impossible owing to the very reactive Al. So we shifted to H.F. induction furnaces of our own design with large transmitter tubes (250 kW), in contrast with the normally used motorgenerators (Posthumus and Douma).

In 1938 Oliver and Shedden (England) found that heat treatment in a magnetic field gave a small improvement of 20% in energy product. Their effect was explained in terms of magnetostriction which gave 20% as about the maximum obtainable effect. This explanation at first satisfied our scientists but when repeating Oliver and Shedden's experiment a somewhat larger effect was found (23%). This made Jonas suspicious about 20 being the maximum obtainable. Within two weeks he obtained an improvement of more than 300% by adding more Co than O. & S. did. This result made him very sad because it did not fit into the magnetostriction explanation. However, adding more cobalt was the result of Heerkamp van Embden's consideration that a higher temperature facilitated diffusion. But also the material had to be ferromagnetic at that temperature. So the Curie temperature had to be elevated and a well-known way to do that was cobalt addition. This was 1939. The alloys were investigated in various scientific institutes and much knowledge was gained about the metallography of this class of heterogeneous alloys. It was found that the magnetic field had an orienting effect on the precipitates but it was not before 1959 that work done in our laboratory gave the insight that increasing the Curie-temperature was not the first important effect of cobalt addition, but that decreasing the interface tension between the precipitated phase and the matrix was an essential additional effect.

The new material was quickly put into production under the name Ticonal G (BHmax = 4,5 MGOe). There was much trouble because of carbon which occasionally spoiled the material. Addition of Ti cured the disease by binding the carbon, although the nature of disease and cure were not understood then. When proper insight occurred the use of low-carbon iron was the logical remedy.

In 1939 a production unit of Ticonal G steel was established in Blackburn (England) to secure production in case Holland were occupied. This factory has produced largely for the war effort during the war. In contrast with this Allied interest, the Germans did not see much in the new magnet.

After the war we had a considerably income from licensees in U.S.A. and Europe, except for Great Britain who never paid anything for producing our magnet. One of the reasons for the latter was that in our patent the lower limit of the Ni content was put too high (13%). It proved possible to make good magnets with 12,5% Ni.

During the war and the German occupation Co and Ni could not be obtained for civil purposes and we made P.M. from an alloy of Fe, Al and C, specially for loudspeakers and for handoperated small dynamo's to replace flashlight for which no batteries were available. The mechanical properties of this alloy could be improved by adding ½% Ni (forbidden by the Germans) which Ni was stolen from the German-controlled Ticonal E production by slightly pinching the Ni content of the latter material.

After the war new developments increased the quality of the magnet steel. As no good theory about the origin of the magnetic hardness existed and also the relation between magnetic properties and metallography was largely unknown the progress was obtained purely empirically by gradually varying the composition and the temperatures of heat treatment and observing the improvement. This tedious method of optimization which, however, led to success (as shown in the figure, page 5) was common practice in the metallurgy of those days.

In 1951 a hexagonal oxydic material, which was prepared by accident, was discovered to have an exceptional (for that time) high magnetocrystalline anisotropy. The importance of this was soon recognized and the material was taken into production under the name "Ferroxdure" in 1952. The energy product of this material was not so high as that of Ticonal G, but its higher coercivity made it suitable for dynamic applications. Moreover, it was very cheap.

Apart from the prime interest of Philips in applying P.M. in loudspeakersystems magnets were also made for small generators, electric motors and meter systems. The continuous improvement of the energy density of the materials made smaller and smaller systems possible. A loudspeakersystem made of Honda steel weighing about 10 lbs is now replaced by an equivalent system of 1 lb. However, this smaller system was once considered less attractive commercially as clients associated a voluminous magnet with better sound quality!

Summing up:
a) Interdisciplinary work is recommendable, as well as an interaction between the university and industrial laboratories.
b) Success makes success.
c) Believe in scientists, but not entirely.

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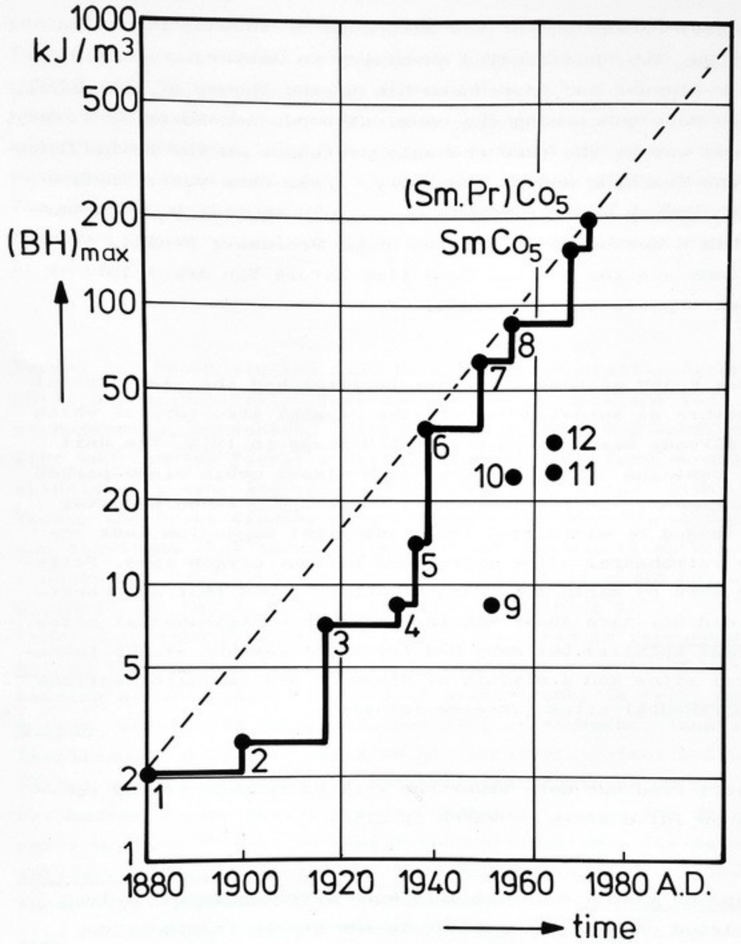
1973-10-10



Maximum energy product $(BH)_{max}$ of permanent magnet materials plotted against time. The dotted line suggests an exponential growth. Legend : 1 = carbon steel, 2 = tungsten steel, 3 = cobalt steel, 4 = Fe-Ni-Al alloy, 5 = 'Ticonal 2', 6 = 'Ticonal G', 7 = 'Ticonal GG', 8 = 'Ticonal XX', 9 = Ferroxdure 100, 10 = Ferroxdure 300, 11 = Ferroxdure 330, 12 = Ferroxdure 360.