Scanning Our Past From The Netherlands

Early Investigations on Ferrite Magnetic Materials by J. L. Snoek and Colleagues of the Philips Research Laboratories Eindhoven

Ferrite magnetic materials have found wide applications in the electronic world, but only after intensive research activities over a long period of time. Two specific areas of application are to be distinguished:

1) soft magnetic ferrites with a cubic spinel structure for use in high-frequency inductances and transformers;
2) hard ferrites with a hexagonal structure, mainly to be used as permanent magnets in loudspeaker and electro motors.

The commonly used iron powder cores in inductances caused high losses resulting from the induced eddy currents—a very disturbing phenomenon, causing resistive losses by the pure iron powder in the conventional cores. Although it was known that the—later called—nonconducting soft ferrites were a suitable replacement for the common iron-powder cores, a clear understanding of the design parameters of this material was not yet available. At the same time, cheaper permanent magnetic material to be used for loudspeakers was highly requested. Other applications of ferrites were small square loop ferrites, which had a revolutionary effect on the miniaturization of the very early computer systems, as well as recording heads, synchrotron accelerators, etc.

Fig. 1. *Dr. J. L. Snoek (1902–1950).*

In 1933 Dr. J. L. Snoek was invited to investigate the complex nature of magnetic material and this article reviews the challenges of this investigation by a critical but very inventive scientist and his colleagues.

I. SOFT MAGNETIC FERRITES

In 1933, Dr. J. L. Snoek was invited to investigate the complex nature of magnetic material. This short historical overview shows the difficult and laborious route of such a development, carried out by a critical but very inventive scientist and his colleagues.

Snoek started the research on ferrites by reviewing the early work of S. Hilpert, who already in 1909 published magnetization curves as a function of temperature for nickel, copper, magnesium, and zinc ferrites. Because of the losses in these ferrites, the initial results were not very promising and the interest died out. However, new developments in equipment for long-distance multiplex telephony systems renewed the interest. Initially, Snoek followed an experimental approach to learn all the properties of the different kinds of ferrites known at that time.

In 1937, Snoek noticed that removing carbon and nitrogen from iron and iron alloys reduced the hysteresis losses and the annoying magnetic after effects. He also succeeded in creating an iron nickel cobalt (Fernico) alloy with less than .001% carbon and less than .001% nitrogen. Wound cores of a thin rolled sheet of this Fernico alloy were a breakthrough for Pupin coils used in communication cables, having no after effects, very low hysteresis losses, and a high permeability.

In 1939, a core of Fernico wire with high quality and excellent

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stability was introduced in telecommunication filters. A volume reduction from 500 to 220 cm^3 was realized for filter coils, raising the magnetic quality factor Q from 90 to 200.

In Japan, Kato and Takei also patented soft magnetic ferrites. However, at that time, the Japanese industry did not see practical utilization for soft ferrites with lower performances, and no patents were applied for outside Japan.

In early 1940, the existence of copper zinc ferrite as soft-magnetic core material was brought to the attention of Dr. Snoek. This material with an effective permeability of 10 would lead to acceptable Q values. Snoek succeeded in making great improvements in the magnetic performance of mixed cubic ferrite materials containing zinc ferrite. He realized further improvements by interchanging ferro ions in the ferrite structures by other metal ions, preventing unwanted electrical currents within in the crystals. Snoek realized these improvements by starting from fine-grained pure raw materials and proper processing for homogeneity and the properly required oxidation state. Based on the insights collected before 1940, Snoek shifted his research work from product properties to material properties of magnetic material. The cooperation between Snoek and the partners of the telecom research group also resulted in the determination of the design parameters when using an air gap for fine tuning. In the same manner, material factors were derived for the hysteresis losses, the temperature coefficient of the permeability, and the time stability of the permeability. Snoek showed that by tailoring the zinc content in mixed ferrites, he could influence the magnetic saturation, the permeability, and the coercive force in such a way that the losses, including hysteresis losses, could be minimized to rather low values. Processing of homogeneous stress-free ferrites with no or very small inclusions of impurities was realized by using pure fine-grained raw materials and sintering the material grades in accordance with the required chemistry.

The introduction of these nonmagnetic zinc ferrites in the ferrite structure is considered a basic invention. The work of Snoek *et al.* on soft magnetic ferrites with a spinel structure stimulated the research in understanding the fundamentals of the magnetism in oxidic ferrite materials. Neél (Polytech, Grenoble, France) used these results as an experimental proof of his theory on ferrimagnetism in 1948. Neél's theory, for which he was granted the Nobel Prize (1970), was of great help to understand and explain the magnetic behavior of ferrite materials. The understanding of Snoek about the phenomenon of magnetostriction led to his investigation on the compensation of the negative magnetostriction of mono ferrites and mixed-metal zinc ferrites by mixing them with ferro ferrite that has a positive magnetostriction. This research led to the manganese zinc ferro ferrites that have found the widest application of the soft ferrites. Tailoring the zinc content and an excess of iron oxide, which would transfer to ferrous ferrite during the sintering process, created a great variety of materials with excellent magnetic properties.

The ferrite material research delivered basically four material groups in the frequency range up to 100 MHz, i.e., copper zinc, magnesium zinc, manganese zinc, and nickel zinc ferrites. The first industrial breakthrough in 1946 for a telecom application is shown in Fig. 2.

The great reduction in volume of the telephony filter systems was of great economic importance. It reduced investments, for instance, in telephone exchange buildings, where the fast growing numbers of telephone subscribers could be served by a continuous reduction of space per subscriber.

The soft magnetic ferrite patent position was not only of paramount importance for that application but soon other electronic applications of ferrites were recognized as well. This eminent position on ferrites led, as early as 1947, to a cross-licence agreement with Western Electric and with their later patents on transistors,

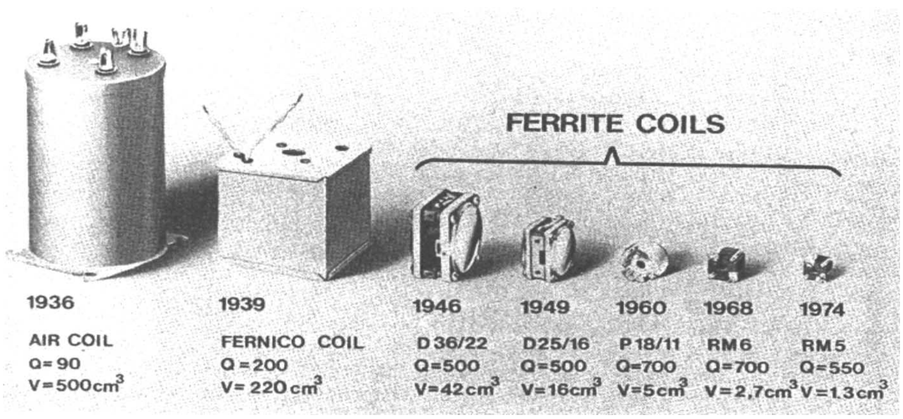

Fig. 2. *Filter coil developments from 1936 to 1974.*

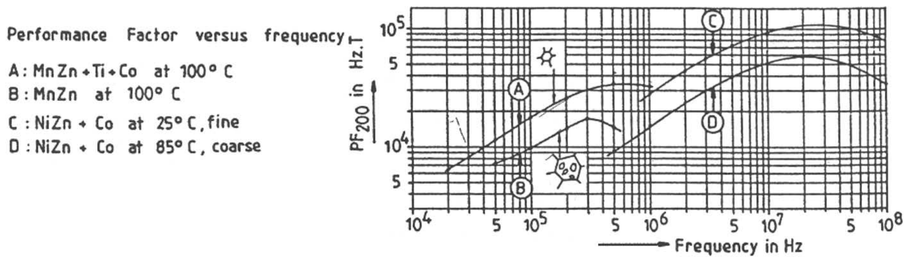

Fig. 3. *Performance factor 200 mW/cm³ versus frequency.*

which was very advantageous and fruitful for both parties. Other licences and cross-licences followed, overcoming the hesitation to change from powder iron cores and metal sheet cores to ferrite cores in radios, antennas, and transformers over a wide range of frequencies. With the introduction of television, a market opened for rather heavy ferrite products in the line output transformer and the deflection coil, both being overruled now by the introduction of flat screens.

A growing important application is that of switch mode transformers, where ferrites are widely used. A performance factor (PF), expressed in hertz tesla for different ferrite materials, was defined for maximum power throughput. The transformer volume for a certain throughput power is proportional to the PF.

Fig. 4 illustrates the great weight reduction of a 100-W transformer starting from 1960 onwards for time optimal core material of that time and other components and the corresponding optimal switching frequency. Modern flat designs allow an additional volume reduction resulting in a performance factor of 500 mW/cm^3.

II. PERMANENT MAGNETS

Later in the investigations of Snoek on oxidic magnetic materials, the magnetic research group, together with a group scientists from various disciplines, investigated possible interesting compounds with magnetic properties, such as the compound barium hexaferrite starting from barium carbonate and iron oxide $BaFe_{12}O_{19}$. The development of the hard ferrites, called ferroxdure (fer = iron, ox = oxygen, and dure = hard), followed the same unpredicted course as the soft ferrites.

G. W. van Oosterhout worked in 1949 on semiconducting perovskite materials based on iron oxides ($AFeO_3$), where A is a divalent or trivalent ion or a mixture of those ions. During the tests on lanthanum barium iron oxide compositions, a weighing error was made by putting double the amount of very pure iron oxide in a sample. His routine to check whether the sintered samples would be magnetic brought him, much to his surprise, to the finding that the sample made with very pure iron oxide showed magnetism. After recalculating his recipe, it became clear that a double amount of iron oxide had been used and it was concluded from the phase diagram that the magnetoplumbite phase of $BaFe_{12}O_{19}$ was the most probable candidate. Comparing the X-ray diagrams with older "perovskite" experiments in an attempt to make a soft magnetic ferrite with barium hexaferrite led to the same conclusion, and so a new class of material was born.

It was also discovered that the magnetic saturation was much higher than might be expected from earlier measurements, and it was found

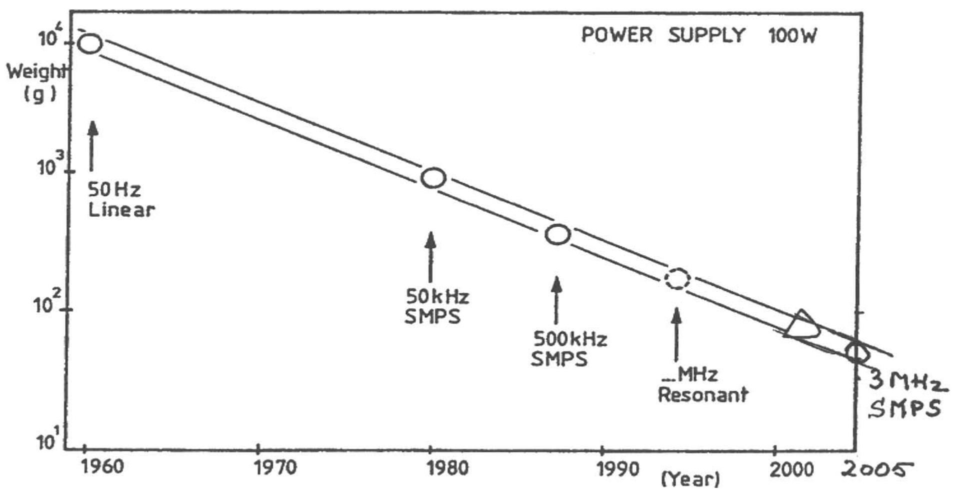

Fig. 4. *Weight of 100-W transformer from 1960 to 2005.*

Fig. 5. *G. W. van Oosterhout, professor of inorganic chemistry at the Technical University of Delft, in 1967.*

that, surprisingly, the coercivity was increasing with rising temperature. These observations informed the researchers that they had found a material with special magnetic properties.

Further research showed that the same type of properties can be obtained by replacing barium by strontium or lead. At the same time, it was discovered that pressure on the die material improved the magnetic orientation. The new material arrived in time to replace cobalt, which had become a rather strategic material.

The idea arose to improve the magnetic strength of the permanent magnets for the application of, e.g., loudspeakers by magnetic aligning of the small single crystals during the forming process. In 1951, A. L. Stuijts realized alignment in a wet-pressed product and found to his pleasant surprise that by sintering this product, the alignment further improved. This oriented material has a much higher saturation magnetization in the direction of the orientation compared to the nonoriented material. The quality of hard magnetic ferrite materials can be expressed by the quality factor Q, which is the sum of the remanence B_r plus the coercivity H_{cj} times 0.4 ($Q = B_r + H_{cj} \times 0.4$). The progress of the Q value since 1950 is illustrated in Fig. 6.

The advantage of the new types of permanent magnetic is that raw materials, iron oxide, barium carbonate, and strontium carbonate are readily available and cheap, while cobalt is an expensive and strategic material. The very competitive hard magnetic ferrite magnets are widely used in loudspeakers, motors, and generators.

An example of the impact of magnets of strontium ferroxdure is the application as stator segments in the starter motor of motorcars. This design with permanent Fxd-magnets reduces the start current by a factor of two. This means a smaller battery with considerable cost saving and a weight reduction of at least one kilogram.

In 1999, an important further improvement of the Q was realized by substitution lanthanum and cobalt

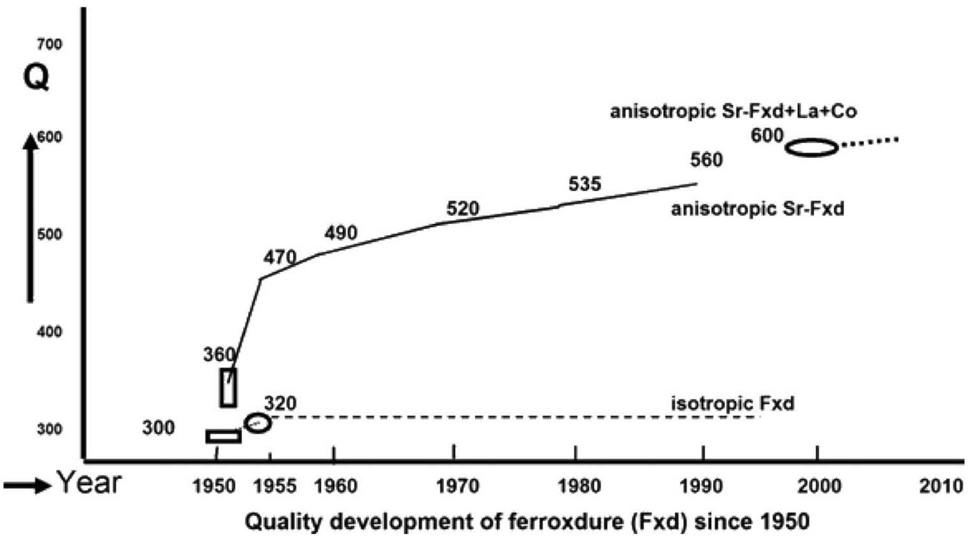

Fig. 6. *Progress of Q value since 1950.*

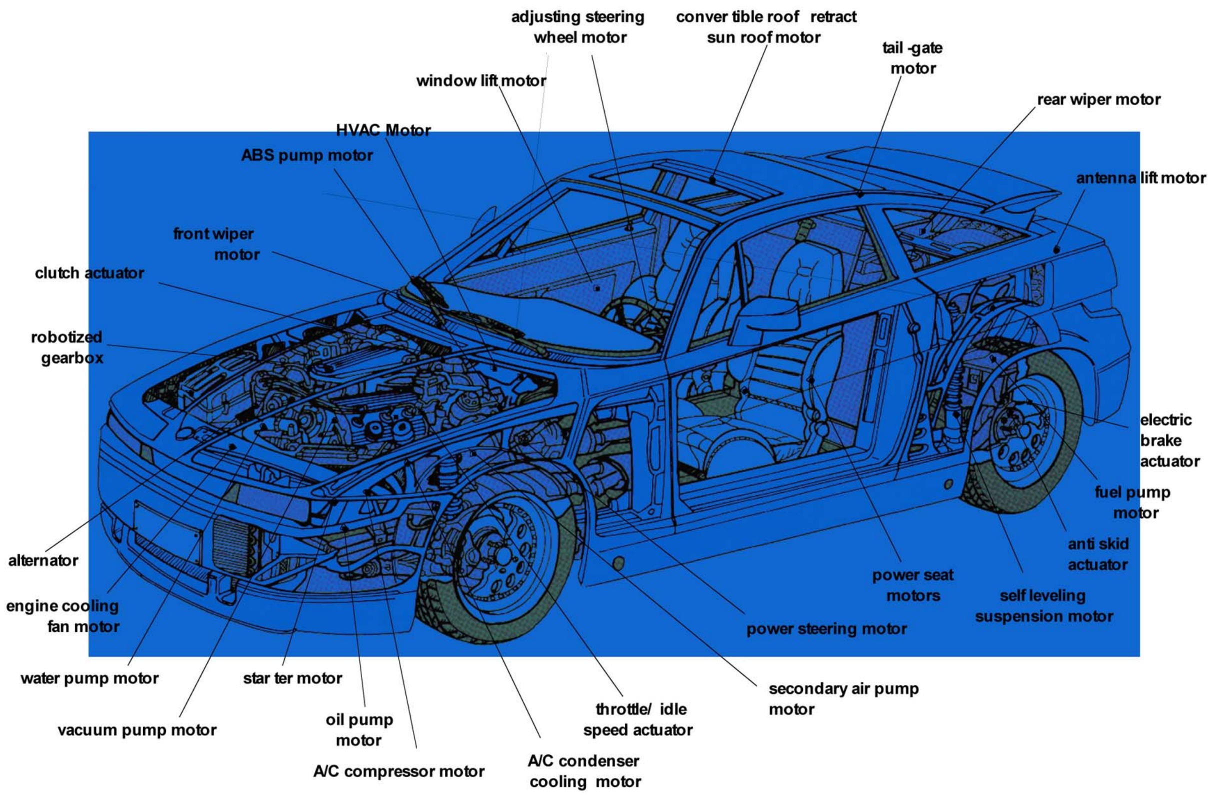

Fig. 7. *Commercial publication of use of permanent magnets in cars.*

in strontium hexaferrites (Sr-Fxd) as a result of research in Japan and Europe. As these substituted materials are more expensive and the cobalt also strategic, there is some hesitation in using this new material on a large scale. Because of the higher Q of this material that has a high coercivity combined with a high remanence, it will be possible to reduce the weight of magnets for the same function by 40%–50%. This makes the new material attractive for new designs with a smaller overall volume and weight.

The great variety of Fxd applications in the automotive industry is shown in Fig. 7.

The hard and soft ferrites will still have a good future and a much longer life. Note that in 1997 the hard magnet section was sold to Ugimag (France) and the ferroxcube activity in 1999 to Yageo (Taiwan). ■

Theo Stijntjes
Bob van Loon