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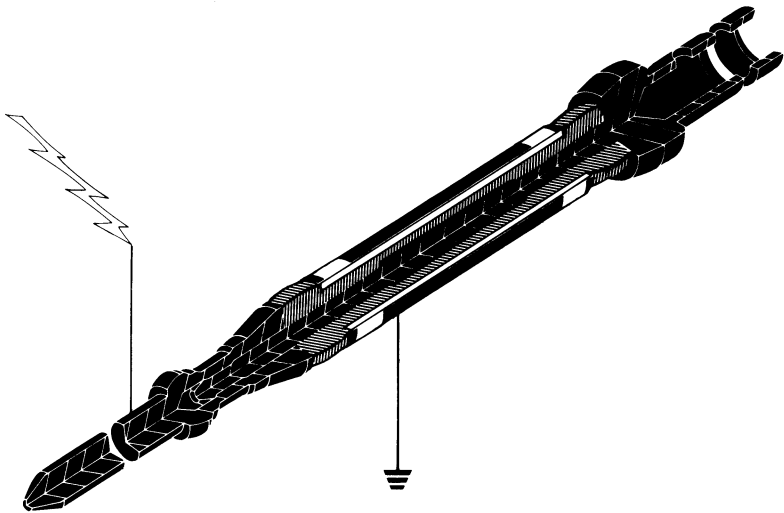
Ceramics

Properties, Devices, and Applications

edited by
Lionel M. Levinson

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General Electric Company
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3
Magnetic Ceramics

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3.1 INTRODUCTION

3.1.1 What Is a Ferrite?

Magnetic ceramics, most often represented by ferrites, are becoming increasingly important materials for electronic components. Metallurgically, a ferrite is a solid solution of metals containing iron as the main element. Ceramically, what is referred to as a ferrite may be one of a whole family of magnetic ceramics, including spinels, magnetoplumbites, garnets, orthoferrites, or variations of these, such as γ-Fe_2O_3. These are classified as ferrimagnetic or a special case of ferromagnetic materials. There is, however, an important difference between the ferromagnetism in metallic materials and the ferrimagnetism in ceramic materials with regard to the mechanism producing the magnetic phenomenon. Because the subject is so broad, the main emphasis of this chapter is on only one class of materials, the soft ferrites, primarily of the manganese-zinc variety because of their predominant position in electronic applications. The other classes will be dealt with in lesser detail, although much of the information about manganese-zinc soft ferrites also applies to the other classes.

3.1.2 History of Ferrites

Although the naturally occurring ferrite, magnetite, has been known for a very long time, the first practical use of a synthetic ferrite was not until the twentieth century. The discovery of modern ferrites is attributed to Kato and Takei (1), who examined some cobalt ferrites

in the early 1930s. Shortly after that, Snoek (1936) and his coworkers (2) at the Philips Research Laboratories in the Netherlands developed the first soft ferrites for commercial applications. Néel (3) published the first explanatory theories on the origin of magnetism in ferrites. Further investigation on the technology of ferrites was made by Guillaud (4) and his coworkers. After World War II, there was rapid development of many types of ferrites, including those for high-frequency uses, for microwave applications, and as permanent magnets. With the availability of purified raw materials and highly developed ferrite technology of powder making and sintering, magnetic properties have improved significantly so that they compete strongly with metallic magnetic materials. The present heightened interest in ferrites is brought about by the recent growth in the use of high-frequency power supplies, primarily for computers and other digital devices. This type of power supply uses transistor switching and is therefore called a switched mode power supply.

3.2 SOURCES OF MAGNETIC EFFECT

3.2.1 Ferromagnetism

In a magnetic material, magnetic phenomena originate in the unpaired electronic spins of atoms or ions. In atoms, these unpaired spins are oriented parallel and can be added vectorially, producing a paramagnetic moment or polarization (see Fig. 1). However, this effect is
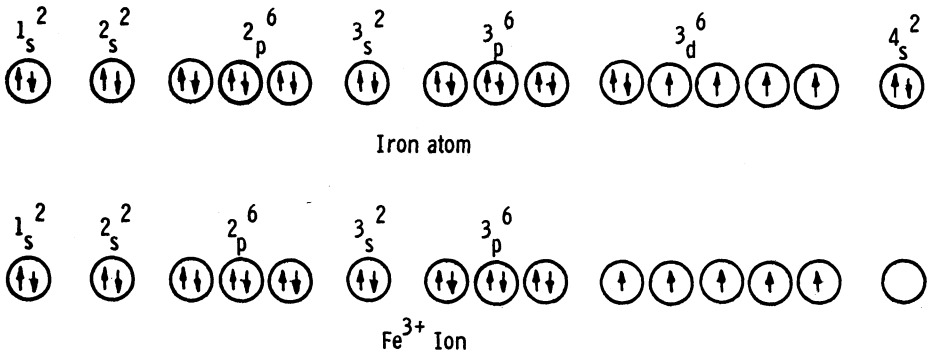

FIGURE 1 Electronic configuration of atoms and ions. Electrons are inserted into the energy levels and atomic orbitals from left to right. While filling a particular energy level, the electrons go in with parallel spins until the band is half-filled. Then pairing occurs. Note the unpaired electrons in the third band that are responsible for the magnetic behavior.

very weak and has no real practical significance. Large-scale magnetic effects resulting in commercially important materials occur in atoms (and ions) of only a few metallic elements, notably Fe, Co, Ni, and some of the rare earths. In some materials containing these elements, there is great enhancement of the atomic spin effect, which comes about from the cooperative interaction of large numbers (10^{13}-10^{14}) of these atomic spins, producing a region where all atomic spins within it are essentially aligned parallel (positive exchange interaction). These materials are called ferromagnetic. The regions of the materials in which the cooperative effect extends are known as magnetic domains. Weiss (5) first proposed the existence of magnetic domains to account for certain magnetic phenomena. He postulated the existence of a "molecular field" that produced the interaction aligning spins of neighboring atoms parallel. Heisenberg (6) attributed this "molecular field" to quantum mechanical exchange forces. Domains have been confirmed by many techniques and can be made visible by several means.

In a domain, the net unpaired spins of ferromagnetic atoms are oriented parallel. Each domain then becomes a magnet composed of smaller magnets (atomic spins). Adjacent domains have their respective spins oriented 180° or, less frequently, 90° to each other. Under unexcited condition, the domains are arranged in a manner that depends on crystallographic and stress states of the material. Under an increasing DC magnetic field, the domains whose magnetizations lie in the direction of the applied field (or closest to that direction) will progressively grow at the expense of those having other magnetization directions. The boundaries between neighboring domains are called domain walls (7). If sufficient external magnetic field is applied, the material can be completely polarized or saturated. During the course of this process, domain walls disappear and the magnetization of the entire specimen rotates in line with the applied field. Under AC magnetic fields, such as those produced by an alternating current flowing through a wire, the domain walls move in response to the variations in the field strength resulting in alternating growth and contraction of the domains with the changes in direction of the exciting field. The movement of the domain walls through a magnetic material gives rise to losses, which are usually dissipated as heat. The degree of polarization or magnetization of the material per unit of magnetizing field is called the relative magnetic permeability. This permeability is a measure of the ease of movement of the domain walls through the medium.

3.2.2 Ferrimagnetism

In ferromagnets, the positive exchange force aligns spins of neighboring atoms parallel. In oxides, the interaction of the unpaired spins of

two neighboring metal ions is through an intermediate oxygen ion, leading to an indirect exchange called superexchange (8) or double exchange (9). However, this leads to a negative exchange force producing a phenomenon called antiferromagnetism, which orients spins of neighboring metal ions antiparallel. In antiferromagnetic materials, the negative interaction occurs between equal numbers of magnetic metal ions on two different lattice sites, and thus complete cancellation of ionic spin moments is accomplished. However, if there are unequal numbers of magnetic ions on the two sites, antiparallel alignment between them will still occur, except that, in this case, there will be a net moment due to the uncompensated spins on the excess ions. This phenomenon is called ferrimagnetism (10) or uncompensated antiferromagnetism. The net moments due to this ferrimagnetism can be treated the same as the ferromagnetic moments and thus form magnetic domains in a similar manner.

3.3 CLASSES OF MAGNETIC CERAMICS

Magnetic ceramics or ferrites are classified according to their different crystal structures and, further, by the metal ions whose oxides occur in these structures. As the name "ferrite" infers, iron oxide (Fe_2O_3) is the oxide that is generally common to all ferrites (although there are a few "ferrites" that contain Mn, Cr, or Al as the main oxide). The elements that combine with iron oxide may determine the crystal structure or class. Some oxides, such as yttrium (Y_2O_3), may form more than one class depending on the ratio of Y_2O_3 to Fe_2O_3. Very often, the crystal structure is related to the ultimate application. For example, BaO combines with Fe_2O_3 to form a hexagonal structure with a unique crystal axis predisposing to a permanent magnet application.

3.3.1 Spinel

This is by far the most widely used magnetic ceramic and is almost synonymous with the term "ferrite." The spinel structure derives its name from the nonmagnetic mineral, spinel $MgAl_2O_4$ (or $MgO \cdot Al_2O_3$) and is a complex cubic structure. In the magnetic spinels, the divalent Mg^{2+} can be replaced by Mn^{2+}, Ni^{2+}, Cu^{2+}, Co^{2+}, Fe^{2+}, Zn^{+2}, (Li^+), or more often by combinations of these. The trivalent Al may be replaced by Fe^{3+} or by Fe^{3+} in combination with other trivalent ions. Magnetic spinels have the general formula $MO \cdot Fe_2O_3$ or MFe_2O_4. The unit cell of the spinel structure consists of eight formula units with the metal ions coordinated by either four or six oxygen ions. This gives rise to two different lattice site classifications,

namely, tetrahedral for the four-coordination or octahedral for the six-coordination arrangements.

3.3.2 Magnetoplumbite Structure

The magnetoplumbite structure is hexagonal and therefore has one major axis, the c axis, which is important magnetically. The magneto-plumbite formula is $MFe_{12}O_{19}$, or $MO \cdot 6Fe_2O_3$, where M can be Ba, Sr, or Pb. The Fe_2O_3 can be partially replaced with Al, Ga, Cr, or Mn. Variations of the magnetoplumbite structure involve combinations of the Ba, Sr, or Pb oxides with spinel, forming oxides to produce new complex layered structures.

3.3.3 Garnets

Magnetic garnets crystallize in the dodecahedral structure related to the mineral garnet. The general formula is $3M_2O_3 \cdot 5Fe_2O_3$, or $M_3Fe_5O_{12}$. Note that in this case the metal ions are all trivalent, in contrast to the other two classes. In the magnetic garnets of impor-tance, M is usually yttrium (Y) or one of the rare earth ions.

3.4 CHEMICAL CONSIDERATIONS

One of the most important attributes or advantages of ferrites is their very high degree of compositional variability. We have spoken of the stoichiometric simple ferrites, such as $MnFe_2O_4$, $CoFe_2O_4$, and $NiFe_2O_4$. However, most commercially important ferrites are of the mixed variety and actually consist of solid solutions of the various simple ferrites, with an infinite number of combinations possible. Depending on the ultimate application, various parameters can be optimized by judicious choice of the component oxides and their ratios. The great variety of possible combinations was proposed by Gorter (11) and has been the subject of much subsequent research in ferrites.

3.4.1 Effect of Iron Variation

The principal source of magnetic effect in most ferrites comes from the Fe^{3+} ions. Although we have stressed the great variety of mixed fer-rites possible, it is in the molar percentage of the iron oxide that we find the least variation. Since the empirical formula for a spinel fer-rite is $MO \cdot Fe_2O_3$, theoretically there should be 50 mol% Fe_2O_3 and 50 mol% MO. In many commercially useful materials, the starting mix may contain slightly more than 50% Fe_2O_3. The purpose of the extra iron is to improve the magnetic properties. One such basic property is

the magnetostriction, which is the change in the length of a material when it is subjected to a magnetic field. With AC excitation, the rapid expansion and contraction of the lattice gives rise to losses. The magnetostriction can be minimized by incorporation of ferrous ferrite as part of the solid solution. Ferrous ferrite ($FeO \cdot Fe_2O_3$ or Fe_3O_4) is actually magnetite, a naturally occurring but technically unimportant ferrite. The additional iron for the divalent Fe^{2+} is usually added in the original mix as Fe_2O_3 but then is reduced to FeO in the sintering or firing processes to maintain the 50% Fe_2O_3 requirement. The molar excess of iron oxide may be as high at 5%. There is, however, a drawback to the incorporation of excess iron in that the high-frequency performance may be reduced considerably, as will be discussed later. Consequently, in these applications, iron excess may be reduced to zero, and in some cases a deficiency of iron is indicated. To illustrate the great impact of iron content, the resistivity of nickel ferrite drops from 10^9 to 10^3 Ω-cm abruptly at 50 mol% iron oxide composition as the iron content is increased. The reason for this great decrease of resistivity or increase in conductivity is an electron-hopping mechanism from Fe^{2+} to Fe^{3+} ions.

In some cases, the substitution of Al^{3+}, Ga^{3+}, or Cr^{3+} for Fe^{2+} is made for special magnetic functions, such as lowering the magnetic saturation value or increasing temperature stability.

3.4.2 Effect of Divalent Ion Variation

We have mentioned that, in spinel ferrites, the divalent ion can be Mn^{2+}, Ni^{2+}, Co^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+}, or Fe^{2+}. The choice is determined by the specific application. For materials for which large magnetic moments are needed, for example in power applications, the magnetic metal ions with the most unpaired spins are chosen. As seen from Table 1, this is one reason manganese ferrite is useful. Although Ni^{2+} has a lower moment, nickel ferrite has a higher resistivity for high-frequency operation and also can operate at higher temperatures. Most commercially important low-frequency ferrites contain zinc. As will be explained later in the section on crystallographic site preferences, zinc oxide substitution for other divalent ions can increase the effective magnetic moment. It also contributes to an increase in magnetic permeability. Very often, it is the ratio of ZnO to the other divalent oxides, as well as the degree of divalent Fe substitution, that gives ferrite materials developers the greatest latitude in optimizing the properties of a specific ferrite. Lithium ferrite is a special spinel in which, instead of the divalent metal for the MO in $MO \cdot Fe_2O_3$, the combination of $Li^+_{.5}Fe^{3+}_{.5}$ is used. The equal amounts of 1+ and 3+ of the two ions average out to be a 2+ charge. Another special case of spinel structure is γ-Fe_2O_3, which will be discussed

TABLE 1 Theoretical and Experimental Metal Ion
Magnetic Moments

Metal ion	Theoretical moment[a]	Actual moment
Mn^{2+}	5	4.6
Fe^{2+}	4	4.1
Co^{2+}	3	3.7
Ni	2	2.3
Cu^{2+}	1	1.3
Mg	0	1.1

[a]Theoretical moment is the number of unpaired
electrons.

later under Recording Media. Here there are no divalent iron ions,
but lattice vacancies combine with Fe^{3+} to again produce a required
number of effective 2+ ions. Another case of charge compensation
occurs in the garnets, where two Ca^{2+} are combined with one V^5 to
produce the equivalent of three ions of trivalent charge.

3.4.3 Effect of Minor Elements

One factor distinguishing ferrite preparation from the counterpart in
metals is the lack of any purification scheme once the processing has
started. In metals, such impurities as C, S, and O, as well as for-
eign inclusions, can be removed during the melting and subsequent
heat treatment. In ferrites, the impurities present in the raw materi-
als will be present in the finished ferrite. This puts a considerable
burden on the ferrite producer to use raw materials that are as pure
as is economically reasonable. Ironically, the addition of some minor
elements in low concentration can increase the quality of the ferrite
to a large degree. We will discuss the useful minor elements and note
those that are detrimental.

In case of the Mn-Zn ferrite, minor additions are common in com-
mercial practice. Early in the exploitation of ferrites, Guillaud (4)
discovered that the addition of CaO to the ferrite in small quantities
produced significant decreases in losses of Mn-Zn ferrite as well as
increased permeability. The use of Ca was unique in that other

divalent alkaline earths in the same column of the periodic table did not produce similar effects. The use of Ca optimized at a specific concentration, and then with further increase properties declined. Another oxide that later was found to improve properties and appears to work in conjunction with CaO, but at a significantly lower concentration, is SiO_2 (12). More recently, materials such as SnO_2 and TiO_2 (13) have also lowered losses and have increased temperature stability. The Sn^{4+} and Ti^{4+} are thought to function by localizing the effect of the Fe^{2+} ions, thus increasing the resistivity. The tetravalent ion can oxidize the Fe^{2+} and prevent the electron conduction mechanism. Li^+ can act similarly. Small additions of CoO have been used to modify the temperature coefficient along with the previously mentioned Sn and Ti.

Other additives may be used to improve ceramic processing by acting as sintering aids. Among those frequently used for this purpose are CuO and V_2O_5.

Guillaud (4), in his research on Mn-Zn ferrites, made a study of the effect of alkali and alkaline earth impurities. He found that the reduction in permeability of alkali metals increased with ionic radius, and a similar but greater effect was seen in the alkaline earth metals. The only exception was in the case of CaO, which has been mentioned previously as an exception and which shows improved electrical properties. It should be noted that the beneficial effect of CaO extends to a concentration of about 0.2 wt%, after which the properties slowly degrade. The same is true for SiO_2, as shown by Akashi (12). With the alkali and alkaline earths, the degradation increased with concentration until the solubility of that element had been reached. Many metallic elements, such as Mo, V, Cu, Cd, and Al, show increases in permeability of up to 50% at very low concentration (14), then peak at a certain concentration, and finally decrease as in the case of SiO_2. At higher concentrations, such impurities as SiO_2 create a duplex structure of giant grains within a fine-grain matrix, which is very detrimental to the permeability (see Fig. 2).

3.5 CRYSTALLOGRAPHIC PREFERENCES

3.5.1 Spinel

We have previously mentioned (Sec. 3.3.1) that the mechanism of ferromagnetism involves the negative exchange interaction of atomic moments of ions on two different lattice sites. In the spinel case, some properties of useful ferrites can be predicted by an understanding of these interactions and the site preferences of the metallic ions.

As a first approximation, the site preference can be explained by the ionic radius and the size of the lattice site. The divalent ions
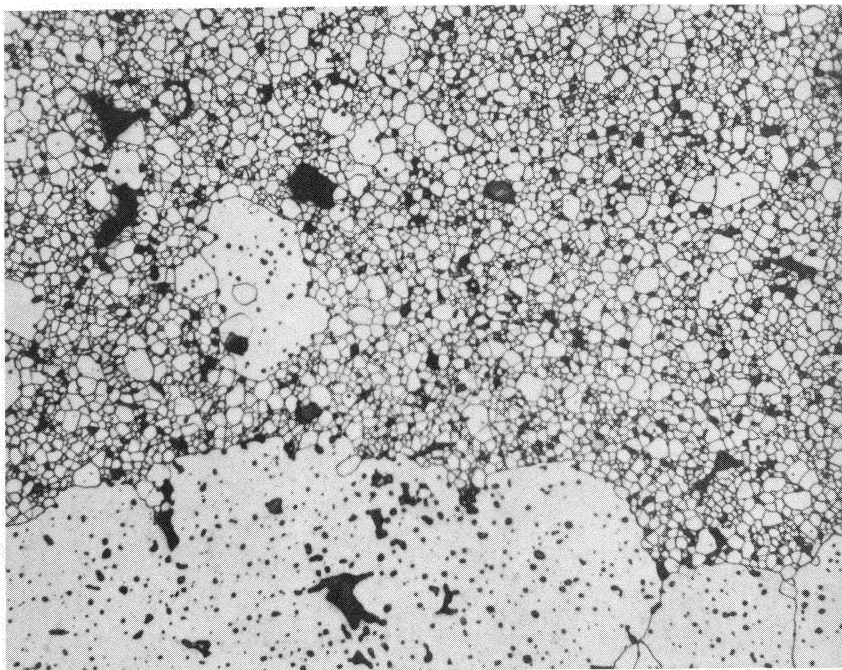
FIGURE 2 Duplex structure in a Mn-Zn ferrite. This type of growth of giant grains in a fine-grained matrix is caused by the localized fluxing action of an impurity, probably SiO_2.

are generally larger than the trivalent, and the octahedral sites are larger than the tetrahedral (see Table 2). Therefore, it would be reaconable that the trivalent ions, such as Fe^{3+}, would go into the tetrahedral sites and the divalent ions would go into the octahedral. Two exceptions are found in Zn^{2+} and Cd^{2+}, which prefer tetrahedral sites because the electronic configuration is favorable for tetrahedral bonding to the oxygen ions. Thus Zn has preference for tetrahedral sites over the trivalent Fe^{3+}.

We have previously mentioned there are two types of sites for metal ions in spinel ferrites. These are the tetrahedral sites, which we call A sites, and octahedral sites, which we call B sites. The negative interaction or exchange force between the moments of two metal ions on different sites depends on the distances between these ions and the oxygen ion that links them and also the angle between the three ions. The interaction is greatest for an angle of 180° and also when the

TABLE 2 Ionic Radii

Metal ion	Ionic radius (Å)
Mg^{2+}	0.78
Mn^{2+}	0.91
Mn^{3+}	0.70
Fe^{2+}	0.83
Fe^{3+}	0.67
Co^{2+}	0.82
Ni^{2+}	0.78
Cu^{2+}	0.70
Zn^{2+}	0.82
Cd^{2+}	1.03
Al^{3+}	0.57
Cr^{3+}	0.64

interatomic distances are the shortest. The interaction between moments on A and B sites is greatest. the BB interaction is very much less stable, and the most unfavorable occurs in AA interactions. By examining the interactions of the major contributor, or the AB interaction that orients the unpaired spins of these ions antiparallel, Néel (3,10) was able to explain the ferrimagnetism of ferrites.

In a unit cell of spinel lattice there are eight tetrahedral and sixteen octahedral sites occupied by metal ions, or 1 tetrahedral and 2 octahedral for each formula unit. In the case of zinc ferrite, the tetrahedral sites are occupied by zinc ions, which, being nonmagnetic (having no unpaired electronic spins), do no ordering of the ions on the octahedral sites occupied by Fe^{3+} ions. The Fe^{3+} (BB) interactions are so weak as to be unimportant. Therefore, zinc ferrite is not ferrimagnetic. This type of arrangement is called a normal spinel structure (Fig. 3).

Let us consider the case of nickel ferrite in which eight units of $NiFe_2O_4$ go into a unit cell of the spinel structure. The ferric ions fill the tetrahedral sites, but there is room for only half of them (eight). The remaining eight go on the octahedral sites, as do the eight Ni^{2+} ions. The antiferromagnetic interaction orients these eight

METAL ION DISTRIBUTION IN FERRITES

Type of ferrite	Metal Ions on Lattice Sites				Resultant moment
	A (Tetrahedral sites)		B (Octahedral sites)		
	Ions	Moments	Ions	Moments	
Zinc ferrite-- $ZnFe_2O_4$ (Normal spinel)	Zn^{2+}	--	Fe^{2+}	↑ ↓	0
Nickel ferrite-- $NiFe_2O_4$ (Inverse spinel)	Fe^{3+}	↓	Fe^{3+} Ni^{2+}	↑ ↑	↑
Nickel-zinc $Ni_{.5}Zn_{.5}Fe_2O_4$	Fe^{3+} Zn^{2+}	↓	Fe^{3+} Ni^{2+}	↑ ↑	↑

FIGURE 3 Ionic distribution in spinels. The line vectors represent the net magnetic moment of the individual ions. The antiferromagnetic coupling of A and B sites is shown with the resultant moment of the ferrite.

Fe^{3+} moments and eight nickel moments antiparallel to the eight Fe^{3+} moments on the tetrahedral sites. The Fe^{3+} ion moments will just cancel, but the moments on the nickel ions give rise to an uncompensated moment or magnetization. This type of ferrite is called an inverse ferrite (Fig. 3).

The preference of Zn ions for tetrahedral sites is used to good advantage in mixed Zn ferrites in which Zn replaces some of the magnetic divalent ion with the same stoichiometric amount of Fe^{3+} present. Let us assume that 50% of the divalent magnetic ion (e.g., Ni^{2+} and Mn^{2+}) is replaced with Zn^{2+}. The Zn^{2+} goes on to half the tetrahedral (A) sites, leaving room on the other half of the A sites for Fe^{3+} ions. The remaining Fe^{3+} ions go on the octahedral sites. The Fe^{3+} moments on the tetrahedral sites orient all the octahedral site moments antiparallel to them so that the Fe^{3+} moments on the tetrahedral sites neutralize only one-third of the octahedral Fe^{3+} ions, leaving a large

percentage (the other two-thirds) oriented but uncompensated, giving a net magnetic moment. Additional magnetic moment comes from the magnetic M^{2+} ions, which have also been oriented antiparallel. The total uncompensated oriented ions consist of one-half of all the Fe^{3+} ions originally present plus all the M^{2+} ions (except Zn^{2+}), giving a large magnetic moment. The nonmagnetic Zn ions cannot be substituted for the magnetic M^{2+} ions without limit as the AB interaction weakens because of great dilution. The use of neutron diffraction has confirmed the structure of normal and inverse spinels (15, 16).

3.5.2 Garnets

Magnetic garnet structure was elucidated by Geller and Gilleo (17). In garnets there are three different sites. These are tetrahedral, octahedral, and dodecahedral sites. The unsubstituted garnets have only trivalent ions, and these are very stoichiometric so that preparation problems are more simple than with spinels. Fe^{3+} is the only ion that enters tetrahedral sites in appreciable amounts. The iron ions on the tetrahedral and octahedral sites are coupled antiferromagnetically as in other ferrites. The resultant magnetic moment is due to the iron ions on the tetrahedral sites.

3.5.3 Magnetoplumbite Structure

Whereas the spinel crystal structure is cubic, that for the magnetoplumbite structure is hexagonal, which has a preferred uniaxial direction as one would expect from a permanent magnet material. There are octahedral and tetrahedral sites plus one more type not found in the spinel structure in which the metal ion is surrounded by five oxygen ions forming a trigonal pyramid. In the case of $BaFe_{12}O_{19}$, the net moment is equal to the sum of the moment of five of the seven octahedral ions and the ion in the layer containing Ba minus the moments of the two octahedral and two tetrahedral ions.

3.5.4 High-Temperature Site Preference

The site preference can be temperature dependent, some sites particularly favoring certain ions over others at high temperatures but reversing the order of preference at low temperatures. Such a ferrite is Mg ferrite, which because Mg^{2+} is a nonmagnetic ion should not give any net moment if the Fe^{3+} ions are equally split between the tetrahedral and octahedral. However, at high temperatures, some Mg^{2+} goes into the tetrahedral site, leaving the remaining tetrahedral (A) sites for only part of the Fe^{3+} ions. The remainder (more than half)

of the original Fe^{3+} goes to octahedral sites. This gives rise to a disproportionation of Fe^{3+} moments similar to that in the mixed Zn ferrites. If the high-temperature site distribution can be maintained at room temperature by rapidly quenching the Mg ferrite from a high temperature, an inverse structure (18) with respectable magnetic moment (3,10) can be obtained. A similar situation exists for Ca ferrite.

3.6 MICROSTRUCTURAL CONSIDERATIONS

Some factors, such as saturation magnetic moment, are a function only of a chemical composition and crystal structure. Others, such as permeability and losses, are dependent on additional considerations, the foremost being the microstructural conditions. This is primarily true during excitation by alternating currents and becomes extremely important at very high frequencies. Since AC excitations produce rapid movement of the magnetic domain walls and since the permeability is related to the ease of movement of these walls, the presence of any imperfections in the ceramic structure will reduce the permeability.

3.6.1 Grain Size Effects on Permeability

Referring back to domain consideration, if only high magnetic permeability is desired without regard to high-frequency losses, the grain boundaries act as impediments to domain wall motion. The fewer grain boundaries there are, the larger the grains will be and the higher the permeability (see Fig. 4). This is, in general, consistent with metallic magnetic materials. There are several differences here between the two types of materials, as we have noted previously. The main difference is that metals have few of the "dirty" features found in ferrites. Inclusions are few, porosity is extremely slight, and grain boundaries are relatively clean and unobtrusive. As pointed out by Tebble and Craik (19), in very high permeability metallic materials, such as permalloy (an 80% Ni-Fe alloy), grain size is not an important factor for high permeability. This is because domain walls appear to be able to move across the grain boundaries easily. In ferrites, where the grain boundary is thicker, the same unhindered movement does not occur. Again, the lack of a purification scheme in processing, the presence of pores and inclusions, as well as greater chemical inhomogeneity prevent the attainment of very high permeabilities, which extend up to 100,000 in metals.

The first demonstration of the relation of grain size to permeability was made by Guillaud and Paulus (20) on nickel zinc ferrite. It has been confirmed on Mn-Zn ferrites by Beer and Schwartz (21), Perduijn and Peloschek (22), and Roess (23).
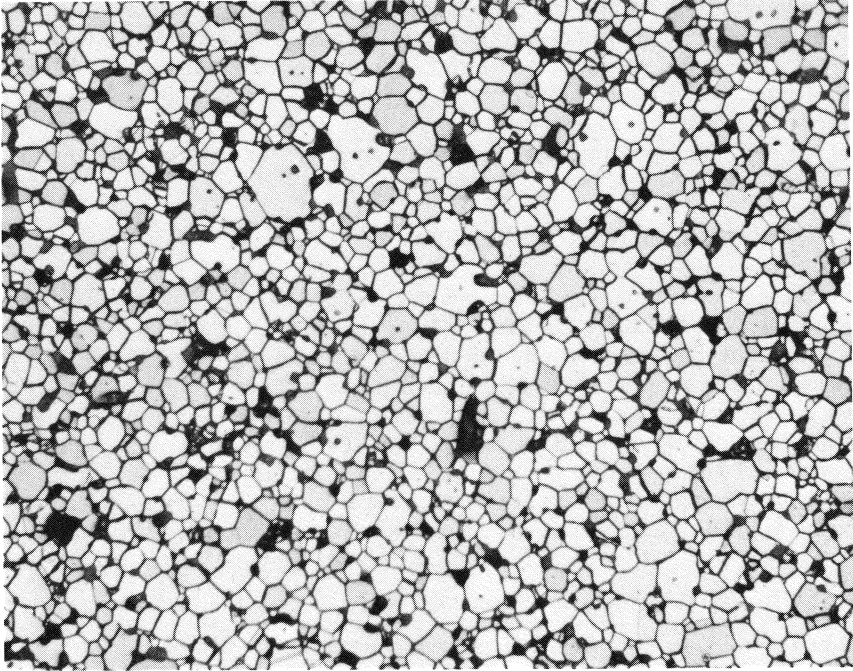
(A)

FIGURE 4 Effect of grain size on permeability. Sample A is the struc-
ture of a 2000 permeability Mn-Zn ferrite; sample B is the structure of
a 11,300 permeability Mn-Zn ferrite. Note the correlation of permea-
bility with grain size.

3.6.2 Effect of Porosity on Permeability

Other imperfections limiting the movement of domain walls are pores,
which again are not encountered in metals. Pores do pin domain walls
and prevent their movement.

A problem encountered in growing large grains in ferrites is that
during the course of growing large grains many pores are swept over
by the grain boundary and remain inside the large grains. The in-
tragranular porosity is more troublesome than the intergranular.

Guillaud (4) showed in nickel zinc ferrites that although the per-
meability increased with grain size up to 15 μm, it decreased there-
after and that this decrease was due to included porosity.
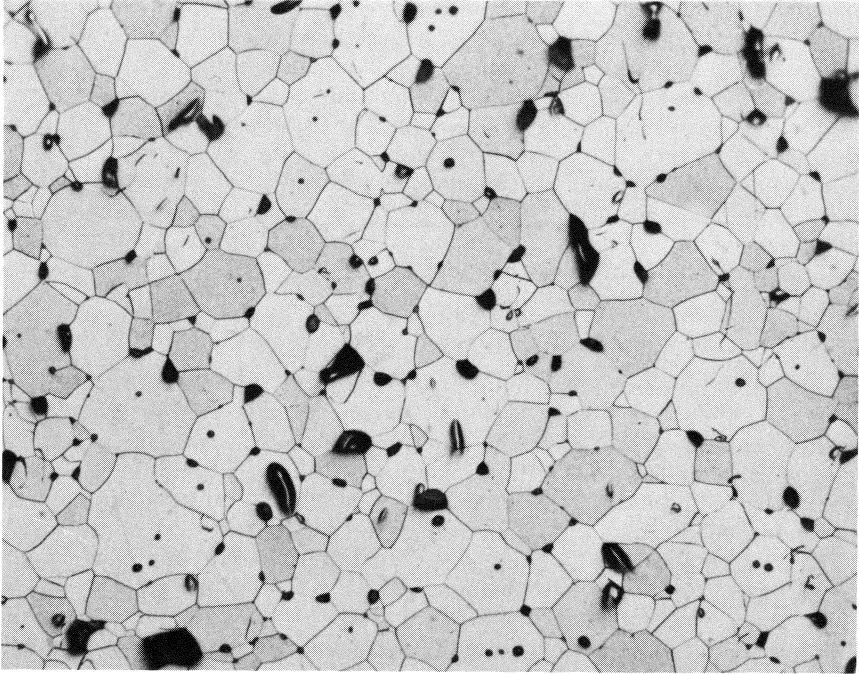
(B)

3.6.3 Imperfections

In addition to grain boundaries, there are the usual ceramic imperfec-
tions that can impede domain wall motion, and these reduce the per-
meability. These include pores, cracks, inclusions, and second phases,
as well as residual strains. These also act as energy wells that pin
the domain walls and require higher activation energy to detach.

3.6.4 High-Frequency Materials

We have previously mentioned the lowering of the starting iron content
as a means for increasing the resistivity for high-frequency operation.
We have also shown that Guillaud increased the resistivity by the addi-
tion of CaO, which increased the resistance of the grain boundaries.
Guillaud (4) measured the resistance across a grain boundary and
found it the dominant resistivity influence.

For high-frequency materials, the eddy current effects become
quite important. The skin depth to which alternating magnetic flux

can penetrate becomes thinner as the frequency rises. Beyond this depth, a phenomenon known as eddy current loss reduces the effectiveness of the material to support the frequency increase. To minimize these losses, thin sheets, fine particles, or small grains are needed. Processing steps are taken to maintain small grains by limiting grain growth and even producing a significant porosity. It is found that, in this case, eddy currents are reduced. It is apparent that there is a compromise between the large-grain dense ferrites for high permeability at low frequencies and the small-grain, porous ferrites for low losses at high frequencies.

3.6.5 Consideration for Microwave Ferrites and Garnets

Many of the same considerations posed for high-frequency ferrite materials apply to microwave ferrites, except to a larger extent. The overlap frequency between the two is somewhat diffuse but probably occurs at about 500-1000 MHz. Because of the high resistivity needed in microwave materials, the iron content must be controlled to prevent the presence of Fe^{2+}. As a matter of fact, for the best microwave properties, overall composition must be maintained within very narrow limits. There is also the beneficial effece of fine grain size, which is difficult to obtain consistently with low porosity. As Nicholas (24) points out, because of this difficulty the use of substituted garnets has outmoded the need for the ultrafine-grain materials. For microwave ferrites, the material must be single phase, stoichiometric, and imperfection free.

3.6.6 Ceramic Consideration of Hexagonal Ferrites

For permanent magnet materials it is most critical to have the final grain size of the order of 1 μm. This is the critical domain size that prevents the existence of domain walls that could cause demagnetization by domain wall movement. Since there is an easy axis along which the magnetization tends to align, the only mechanism for demagnetization is rotation of the magnetization direction, which is made difficult by the high anisotropy. To get a high remanence value, the porosity should be low. This is also needed to prevent internal demagnetizing effects. However, in sintering there is a conflict between the need for fine particles and the high density, and some compromise must be sought. There are two types of ceramic permanent magnets, isotropic and oriented. In the case of the oriented magnet, the remanence is almost doubled by alignment of the crystal axis with the magnetic field. In the isotropic case, the remanence is lower but the coercive force is usually higher. Additions of SiO_2 are used in strontium ferrite to assist in sintering without significant grain growth.
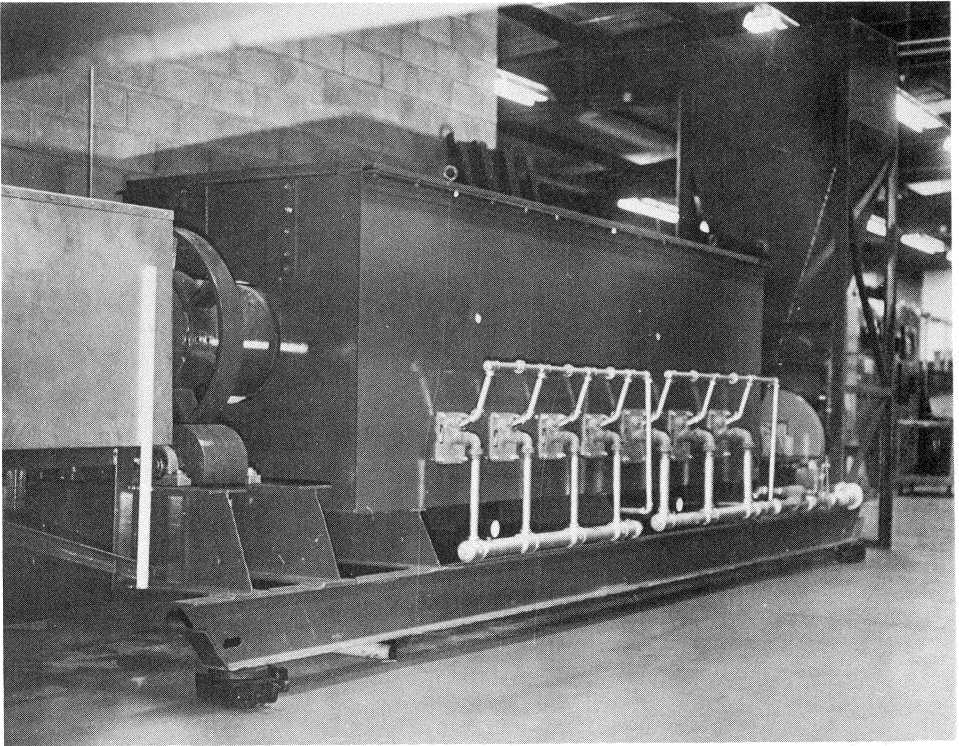
FIGURE 5 A ballmill for production of ferrites. (Photo courtesy of Magnetics, Division of Spang & Co., Butler, PA.)

3.7 FERRITE PROCESSING

3.7.1 Conventional Processing

Ferrites can be processed according to one of several schemes. The conventional technique starts with mixing the oxides or carbonates in the proper ratio. If the starting material is coarse, milling may also be required. The mixing or milling can be done dry or wet using one of a variety of different pieces of equipment, such as ballmills, mullers, high-shear blenders, attritors, or pelletizers. The blended material is then calcined (see Fig. 5) or presintered to start the inter-diffusion of the component materials to form the final spinel lattice. There are low-cost ferrite materials, such as those used for radio and television applications, for which this step (presintering) is omitted,

and there are also materials for very high quality ferrites (microwave ferrites) for which the presintering step is done two or more times with intermediate grinding operations. The calcining is usually done at about 200°C below the final firing temperature.

After the calcining step, the granules are milled [ballmills (see Fig. 6) or attritors] to achieve an optimum particle size. This can vary depending on the applications, but may be of the order of 1 μm. During the last stages of milling, binders and other additives may be put into the slurry.

The milled slurry must then be dried, normally by granulation or spray drying. The latter produces spherical granules that flow well to aid the reproducible filling of die cavities in the pressing of the molded part. The powder is pressed in either hydraulic or mechanical presses (see Fig. 7). In the design of the dies for pressing ferrites, account must be taken of the shrinkage involved in the ensuing firing operation. Depending on the powder processing and firing conditions, shrinkages can vary between 10 and 20% on a linear scale.

Firing may be done in one of many different types of furnaces or kilns. For periodic firing, there are box furnaces, tube furnaces, and elevator furnaces. For the continuous types there are pusher kilns (see Fig. 8), roller hearth kilns, and sled kilns with such provisions as elevators or offsets to separate the binder burnoff from the firing sections.

Because of uncertainty in reproducing temperature and atmosphere profiles and because of variations in temperature and atmosphere in different parts of a kiln, the variation in properties in a periodic kiln may be greater than in a continuous kiln. However, other considerations, such as maximum temperature, equipment cost, and operation cost, must be made.

The first section of a continuous kiln, as well as the first period of time in a periodic kiln, is devoted to the binder burnoff. The percentage of binder and the size of the part will determine the length and temperature profile of the burnoff section or the time and temperature in a periodic kiln. For binder burnoff, the atmosphere is oxidizing (for example, air). After burnoff, the temperature is gradually raised to the final firing temperature. At this point, consideration must be made of the atmosphere in equilibrium with the particular ferrite at that particular temperature. The higher the temperature, the higher is the equilibrium partial pressure of oxygen, pO_2. Studies by Blank (25), Slick (26), and Morineau and Paulus (27) have dealt with the treatment of this oxygen-temperature equilibrium.

The most critical step in firing is the cooling portion as this is the region where the oxidation states of Fe, Mn, and other multivalent ions are fixed. This is done by controlling the O_2 partial pressure, pO_2, as the temperature is lowered. Even if the proper equilibrium
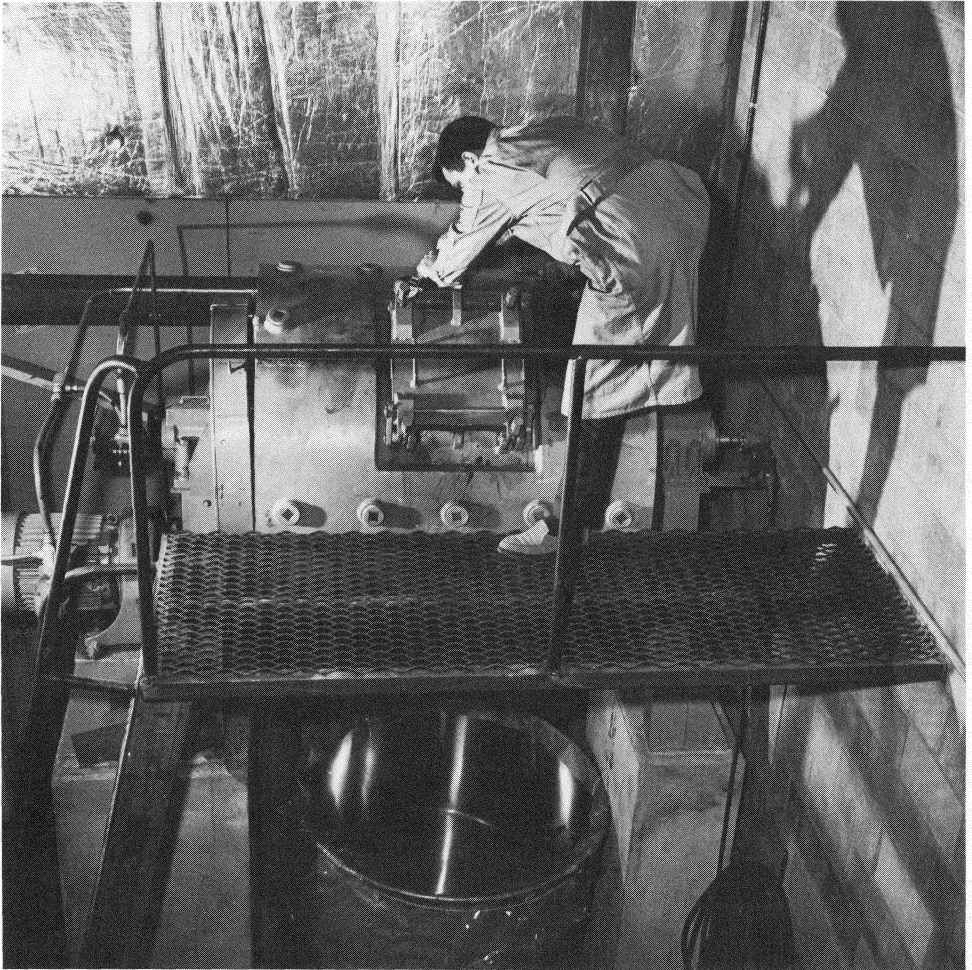
FIGURE 6 Calciner for production of ferrites. Rotary calciners of this type are used to initiate the solid-state reaction between the component oxides. Temperatures are usually between 800 and 1000°C. (Photo courtesy of Magnetics, Division of Spang & Co., Butler, PA.)

is established during the high-temperature hold, improper cooling may negate the previous oxidation state. Conversely, if the hold is not in equilibrium, there is still a chance to establish the proper equilibrium during the cooling period if sufficient time is scheduled.
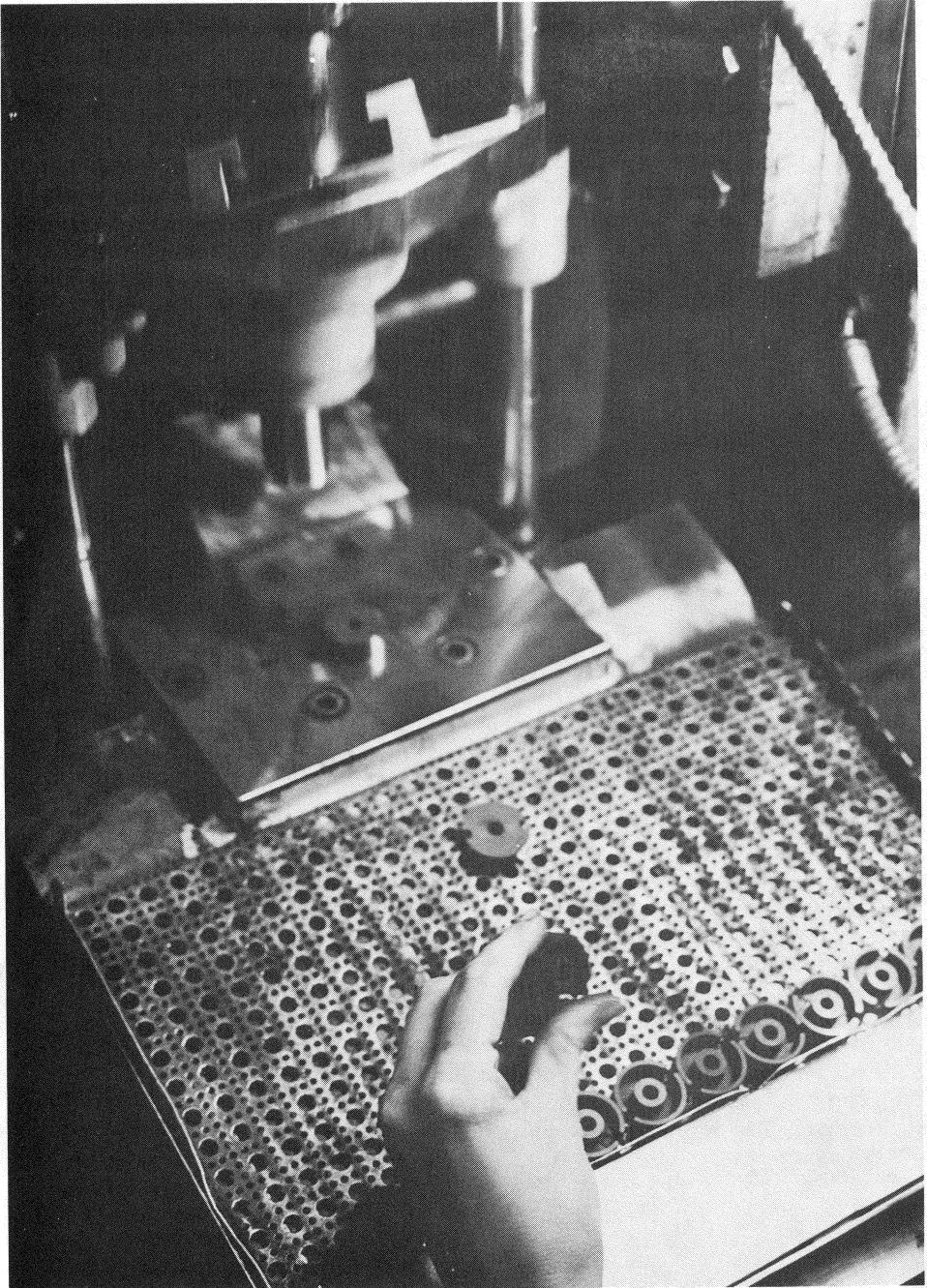
FIGURE 7 Mechanical press for ferrite production. This press is of the double-action type used with a secondary lower punch to press complex parts, such as pot cores. (Photo courtesy of Magnetics, Division of Spang & Co., Butler, PA.)
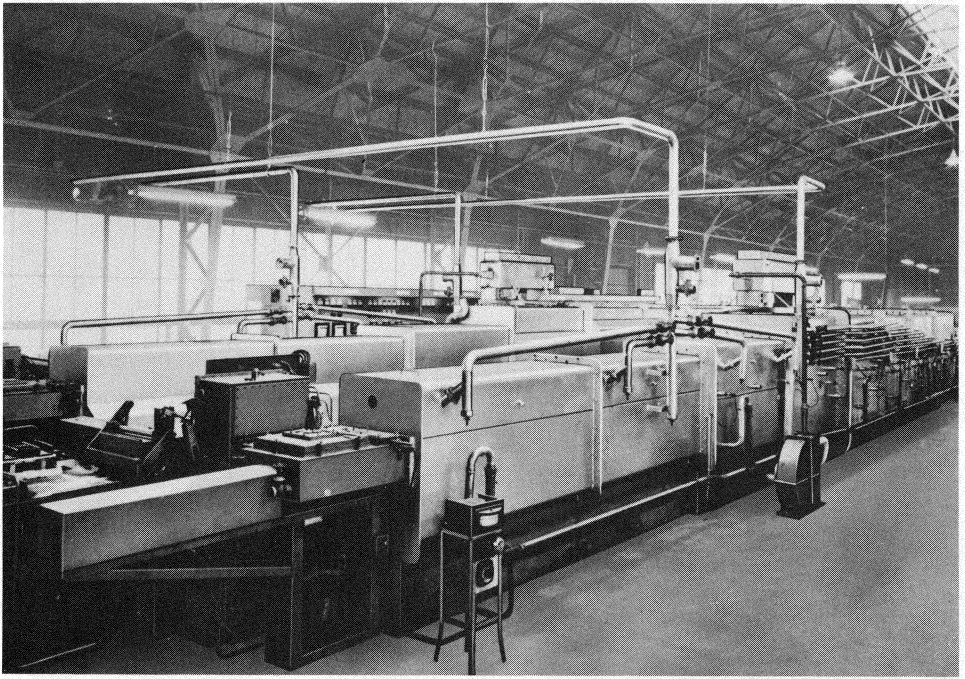
FIGURE 8 Ferrite pusher kiln. This is a controlled-atmosphere kiln for the firing of Mn-Zn ferrites. The first section with exhausts is for binder removal. The next sections contain the heat-up and high-heat zones. (Photo courtesy of Reidhammer Furnace Co., Nurenburg, West Germany.)

Following the firing, there are further machining, grinding, lapping, or tumbling steps to finish the component's manufacture. Finally, the components are measured for magnetic properties (see Fig. 9).

3.7.2 Nonconventional Processing

The previous processing steps are more or less standard ceramic steps especially applied to ferrites. There are, however, some nonconventional processing schemes for forming ferrites. These include coprecipitation, flame spraying, cospray roasting, and activated sintering.

Coprecipitation is a technique of producing a powder by chemical means rather than by blending of oxides (28,29). Here a solution

FIGURE 9 Magnetic measurement of ferrite cores. Here, pot core halves are assembled and measured for permeability. (Photo courtesy of Magnetics, Division of Spang & Co., Butler, PA.)

containing the metal ions is mixed with a precipitant solution to pro-
duce a mixed precipitate of hydroxides, carbonates, oxalates, or some-
times other salts of organic acids. They are then heat treated to pro-
duce the mixed oxides, and the rest of the treatment may be the same.
Some advantages of coprecipitation are the availability of very pure
raw materials and the increased homogeneity, which leads to lower en-
ergy for interdiffusion and ferrite formation. In some cases, the need
for the calcining step can be circumvented. Although coprecipitation
has been known for some time and even used as a production process,
no large-scale use of this technique has been made. The use of co-
spray roasting was described by Ruthner (30) and Akashi et al. (31)
and then by Ochiai (32), but very little has been reported since then.
Reactive sintering (33) involves the spraying of a slurry of the com-
ponent oxides into a hot reactor vessel to accomplish rapid calcining
of the material. Flame spraying (34) has been described for the pro-
duction of very fine powders, but no real commercial applications have
been made.

3.7.3 Processing of Microwave Ferrites

Because of the critical nature of microwave ferrites, pure materials
must be used with careful processing to yield a homogeneous, single-
phase material. The steps are the same as for conventional ferrites.
In the case of garnets, the presintering step as well as the firing step
is done at higher temperatures (1200 and 1500°C, respectively) than
ferrites. Firing is usually done in 100% O_2 to prevent Fe^{2+} formation.
Because there is iron pickup in the grinding steps, compensation must
be made in the final stoichiometry. Hot pressing, especially of the
isostatic variety, has been used to make dense, fine-grained materi-
als, but this process is costly. Such additives as Ca and V are also
used to improve sintering. Control of the magnetization can be made
by substitution for either the Fe_2O_3 or the rare earth ions.

3.7.4 Processing Permanent Magnet Ferrites

The general process is again similar to conventional ferrite processing.
For optimum properties, the final grain size must be controlled to be
about 1 μm. In going from 10 to 1 μm, the coercive force increases
from 100 to 2000 Oe. This grain size can be controlled by the final
grind and also by the sintering process. Oriented (anisotropic) mag-
nets are made by alignment of the particles (wet or dry) in a high-DC
magnetic field during the pressing operation. In the case of wet press-
ing, the water is squeezed out through a porous plate in the die. This
operation takes a longer production time than isotropic magnet produc-
tion so that the cost of these magnets is somewhat higher.

3.8 APPLICATIONS

Magnetic ceramics are used for a great variety of different applications, and they are designed and tailored specifically for each purpose.

1. Permanent magnet materials. These generate a permanent magnetic field to either attract, repel, or lift other magnetic materials. Examples of applications are speaker magnets, field magnets for electrical motors (especially for automotive and cordless appliances), refrigerator gaskets, and repulsive suspension for use in a levitated railway.
2. Cores for high-frequency power supplies. The use here is particularly for the so-called switching power supplies for microprocessors and computers.
3. Cores for low-level inductors for telecommunications filters. These are used to separate specific frequencies in telephone and other telecommunication applications.
4. Deflection yokes for television, to sweep the electron beam across the picture tube as well as vertically.
5. High-frequency transformers for various stages in radio and television circuits.
6. Recording heads for both audio and digital magnetic recording.
7. Memory cores in logic-digital computers.
8. Recording media: γ-Fe_2O_3 and CrO_2.
9. Radar-absorbing paint, shielding.
10. Sensors: temperature, proximity.
11. Microwave components: switch, alternator, phase shifter.
12. Copier powders.
13. Electrodes.
14. Ferrofluids.
15. Magnetostrictive transducers.

In order to discuss the electrical and electronic applications of magnetic ceramic materials, it is necessary to describe the magnetization process in a quantitative manner. If a demagnetized specimen is subjected to an external magnetic field (by a permanent magnet or by a winding through which a direct current is passed), there will be induced in the specimen a bulk polarization or magnetization that, of course, is related to our atomic and domain polarization. This bulk polarization will increase with the strength of the applied field. Figure 10 shows such a magnetization curve. After a sufficient field is applied, the polarization will reach a limiting value that corresponds to complete polarization or saturation. The unit for the magnetizing field (the abcissa) is amperes/per meter (SI units) or oersteds (cgs units; 1 Oe = 79.6 A/m). The units of induction B (which includes
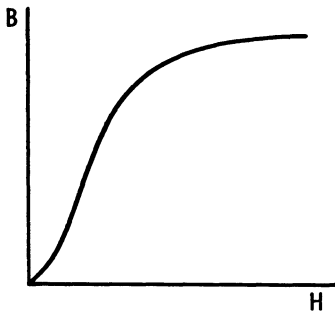
FIGURE 10 Magnetization curve. The initial slope is indicative of the initial permeability. This increases to a maximum at the inflection point and then flattens out at saturation.

the polarization plus the magnetizing field) are teslas (SI units) or gauss (cgs units; $1 T = 10^4$ gauss). The ratio of B to H is called the permeability, which of course can be measured at many different locations on the curve. The limiting B level is called the saturation induction or B_s. If the magnetizing field is reduced to 0 and an increasing reverse field applied, the original magnetization curve is not followed but a lag (hysteresis) of the induction to magnetizing field occurs. Increasing the reverse field leads to saturation in the reverse direction, and if the field is again returned to the original direction a complete cyclic loop is obtained, as shown in Fig. 11. This loop is called the B-H loop and is characteristic of a magnetic material under alternating magnetization conditions. This, of course, now relates directly to AC applications. The area inside the loop is indicative of the losses occurring during the traversal of the loop and are the same losses we mentioned earlier.

As the frequency of traversal is increased, the width of the loop will increase owing to increased eddy current losses. In an AC application, the magnetizing field may not be high enough to saturate the material so only part of the magnetization curve is traversed and the B value reached will not be B_s but a value called B_{max}, the maximum induction.

3.9 POWER TRANSFORMERS

The large increase in ferrite use has been due to its application as power transformers in switched mode power supplies. To explain why ferrites were made to order for this application, we must understand
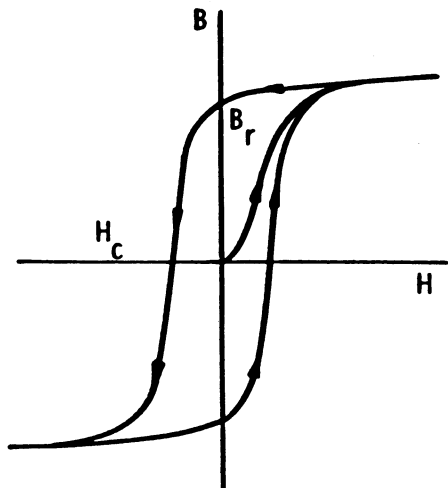
FIGURE 11 Hysteresis loop with magnetization curve. This loop shows
the lag or hysteresis of the induction B to the magnetizing field H dur-
ing cyclic magnetization.

the implications of going to higher frequency operation. Ferrites have
low saturation compared with metals and also have much lower perme-
abilities than such materials as 80% Ni-Fe (see Table 3). The low sat-
uration of ferrites comes about because the large oxygen ions in the
spinel lattice contribute no moment and so dilute the magnetic metal
ions compared with a metal, such as iron, in which there is no such
dilution. In addition, because of the antiferromagnetic interaction,
not all magnetic ions contribute to the moment in ferrites.

3.9.1 Frequency-Voltage Considerations

We described in Sec. 3.2.1 how an alternating electric current in a
winding provides an alternating magnetizing field that creates a cor-
responding alternating magnetic induction in a magnetic material. This
will induce in another (secondary) winding an alternating voltage given
by

$$E = -N \frac{d\phi}{dt} = -N \frac{d(BA)}{dt}$$

For a sine wave, the induced voltage is given by

$$E = 4.44 \, BNAf \times 10^{-8}$$

TABLE 3 Saturation Inductions and Permeabilities of Various Magnetic Materials

Material	Saturation induction		Permeability
	Gauss	Teslas	
CoFe	24,000	2.4	70,000
SiFe	18,000	1.8	1,800
50% Ni-Fe	15,000	1.5	10,000
80% Ni-Fe	7,500	0.75	100,000
Ferrites	4,000-5,000	0.4-0.5	2,000-18,000
Amorphous metal alloy	7,000-15,000	0.7-1.5	10,000

where

    E = induced voltage, volts
    B = maximum induction, gauss
    N = number of turns in winding
    A = cross section of magnetic material, square centimeters
    f = frequency, hertz

For a given voltage the trade-offs can be numerous.

1. Increasing B by using a material with high induction, such as 50% CoFe. This material is used in aircraft and space applications where space and weight are important. However, there is a material limitation on how high the B can go. Ferrites may have saturation of 4000-5000 gauss. Because 50% CoFe has the highest RT saturation, about 23,000 gauss, there is only a possible 4:1 or 5:1 advantage there.
2. N can be increased. This leads to increased wire resistance losses, and in addition there is a maximum number of turns that can be wound around a core that has a window. Using a small wire size yields more turns, but the increased resistance limits the current through the wire.
3. A can be increased. This requires more wire, leading to higher wire losses and making the device larger and heavier. In addition, with poor thermal conductors, such as ferrites, there is the problem of removing the heat produced in a large core.

  If heat is not removed, the temperature rise lowers the satura-
tion of the ferrite and can also damage wire and other compo-
nents.

4. f can be increased. Here the effect can be quite dramatic.
For instance, in going from a 60-Hz power supply to 100 kHz
supply, the factor is 1666. This, coupled with a 4:1 reduc-
tion in going from high-B metals to low-B ferrite still leaves
at least a 400:1 advantage. This permits a great reduction in
the size and weight of the transformer, which again reduces
wire losses.

3.9.2 Frequency-Loss Considerations

As pointed out earlier, the increase in frequency of a transformer pro-
duces the desired voltage requirement at a greatly increased efficiency.
However, we have neglected one consideration, that is, the increased
losses occurring when the frequency of operation is increased. The
losses are mainly eddy current losses due to the internal circular cur-
rent loops formed under AC excitation. The eddy current loss of a
material can be represented by the equation

$$P_e = K \frac{B^2 f^2 d^2}{\rho}$$

where:

 P_e = eddy current losses, watts
 K = constant depending on the shape of the component
 B = maximum induction, gauss
 f = frequency, hertz
 D = thickness of the narrowest dimension perpendicular to the
   flux, centimeters
 ρ = resistivity, ohm-centimeters

Again there is a trade-off for lower P_e. B can be lowered, meaning
larger A to get the same voltage. Frequency f can be lowered, which
again means larger components. The thickness D can be made small-
er as in thin metallic tapes, wire, or powder. There is a physical lim-
itation to this variable. The resistivity may also be increased (see
Table 4). A comparison demonstrates the advantage of ferrites. The
resistivity of metals, such as permalloy or Si-Fe, is about 50×10^{-6} Ω-
cm. The resistivity of even the lowest resistivity ferrite is about 100
Ω-cm. The difference then is about 2 million to 1. Since the effect of
the frequency on the losses is a square dependence and ρ only linear,
the effect on frequency is about 1400:1 so that, instead of 60 Hz, equiv-
alent losses for the same size core extend to 84,000 Hz, close to the

TABLE 4 Resistivities of Various Magnetic Materials

Material	Resistivity (ohm-cm)
Iron	9.6×10^{-6}
Silicon iron	50×10^{-6}
Nickel iron	45×10^{-6}
Amorphous metal alloy	120×10^{-6}
Manganese zinc ferrite	$10^2\text{-}10^3$
Nickel zinc ferrite	$10^6\text{-}10^8$
Yttrium iron garnet	10^{12}

100 kHz we postulated for the voltage calculation. Granted this is a simplified calculation, omitting wire losses and loss differences due to B variations, but the order of magnitude is probably reasonable. In actual cases, 60-Hz power supplies operate at efficiencies of about 50%, but the ferrite high-frequency switching power supplies operate at 70-80%. Figure 12 shows typical ferrite cores for power applications along with the mounting and winding accessories.

We must include another consideration in the comparison. We have mentioned the poor thermal conductivity of a ferrite in common with most other ceramics. Aside from the difficulty of making very large parts without flaws, there is also the previously mentioned problem of heat transfer. Because of this limitation, ferrite switching power supplies have not been made larger than about 1 kW. This is in comparison with the over 100 kW supplies that are made of metallic materials. However, since the large market in power supplies is for home computers or microprocessors and since these are well within the operational size of ferrites, there is no real size problem here.

3.9.3 Ceramic Consideration for a Ferrite Power Material

There are special requirements for a material slated for a power application. Although ferrites in general have low saturations, we must at least provide the highest available saturation consistent with loss considerations. This is mostly a matter of chemistry. Along with this consideration is the need for a high Curie point. This generally means maintaining a high saturation at some temperature above ambient that approaches actual operational temperature. Since power losses will
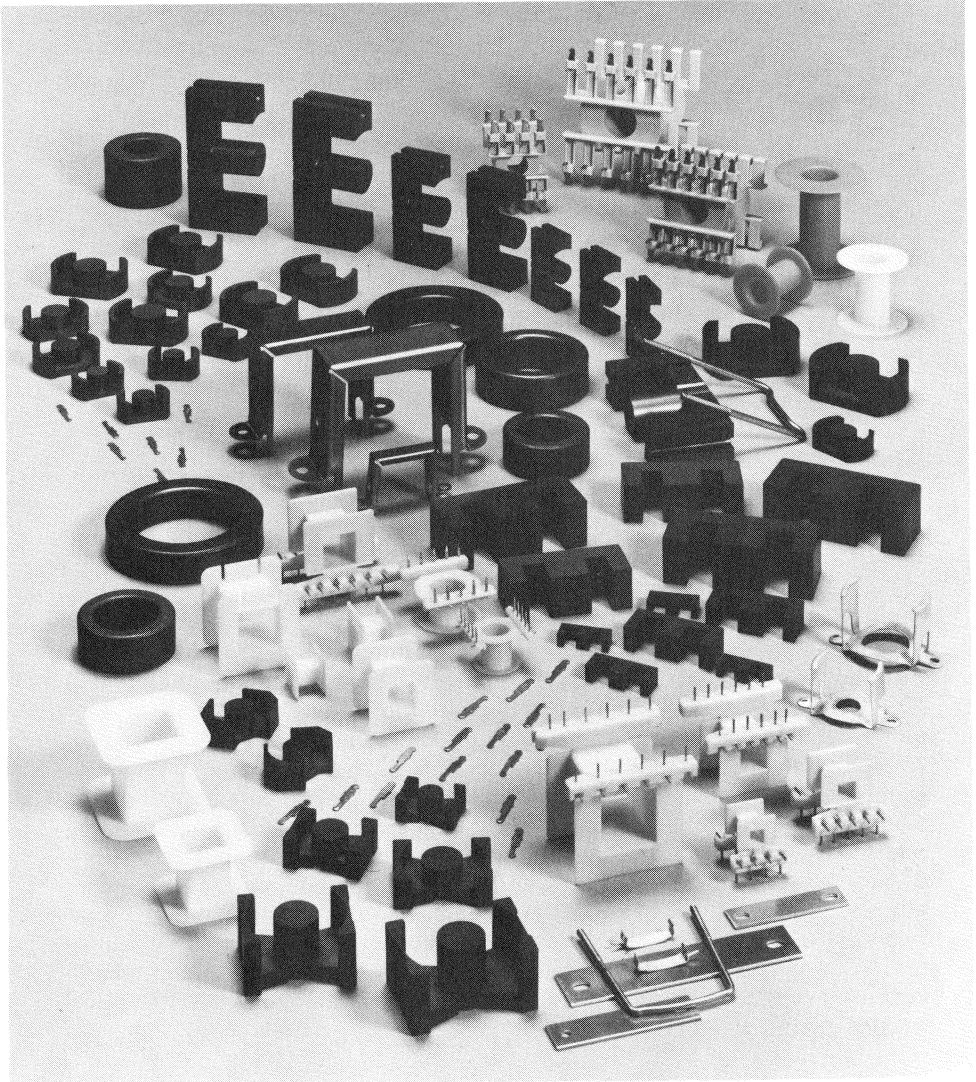
FIGURE 12 Power ferrite cores and accessories. These include E cores, toroids, and PQ cores. (Photo courtesy of Magnetics, Division of Spang & Co., Butler, PA.)

heat the ferrite and reduce the room temperature saturation, many ferrite suppliers have redesigned their materials such that the core losses actually minimize at higher operating temperatures, preventing

further heating of the cores. If this is not done, a runaway heating situation could develop leading to catastrophic failure.

To minimize losses as the frequency is raised, several ceramic modifications may be made, some of which have already been mentioned.

1. Resistivity may be raised by lower Fe^{2+} content (sometimes at the expense of other parameters, such as initial permeability). This can be done by lowering iron in the original mix and by raising oxygen in the firing process.
2. Use CaO to increase grain boundary resistivity.
3. Use a smaller grain size to reduce eddy current losses.
4. Use such additives such as TiO_2 and SnO_2 to increase resistivity.

3.10 INDUCTORS FOR LOW-POWER APPLICATIONS

3.10.1 Magnetic Consideration: Channel Filters

We have discussed the use of ferrites at high drive levels for power applications in which certain magnetic parameters were optimized. For low-level applications, such as channel filter applications, the course of the hysteresis loop is said to be in the "Rayleigh" or linear region where the permeability is described as the initial permeability. The induction change is usually not more than about 0.05 (50 gauss). The criteria we used earlier for high-power applications may not be important here. For example, the saturation induction does not have to be high. The losses at high induction levels do not necessarily have to be low. However, there are other requirements for low-level inductors or transformers. They include high initial permeability, high Q, high temperature stability, high stability to DC bias or to AC level, and low disaccommodation (a decrease of permeability with time).

3.10.2 LC: Tuned Circuits and Channel Filters

These are used to pass certain frequency bands while rejecting others. A major application is in telephone transmission circuits.

The Q of a magnetic component is defined by the equation

$$Q = \frac{X_L}{R_S} = \frac{2\pi f L}{R_S}$$

The selectivity of a specific frequency (or bandwidth) is given by
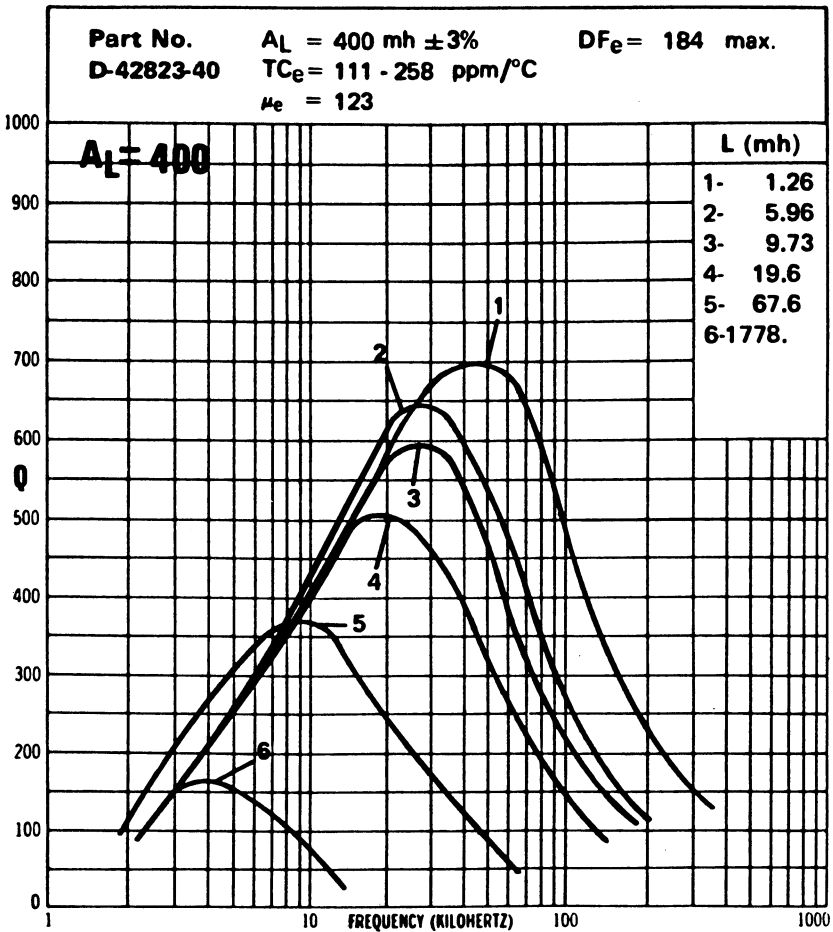
$$\frac{\Delta f}{f} \sim \frac{1}{Q}$$

FIGURE 13 Q curves for a ferrite pot core. This family of curves shows the variation of Q with frequency and induction. Note that the position of peak Q can be varied by changing the inductance (by variation of the number of turns). The inductances corresponding to the curves are shown in the upper box.

That is, the higher Q of the component, the narrower will be the frequency bandwidth or the more useful a component will be to filter out frequencies above or below a specific band (see Fig. 13). When many transmissions or messages are sent on the same line with only frequency bands to separate them, it is necessary to have this selectivity to avoid overlap of the bands, leading to "cross talk."
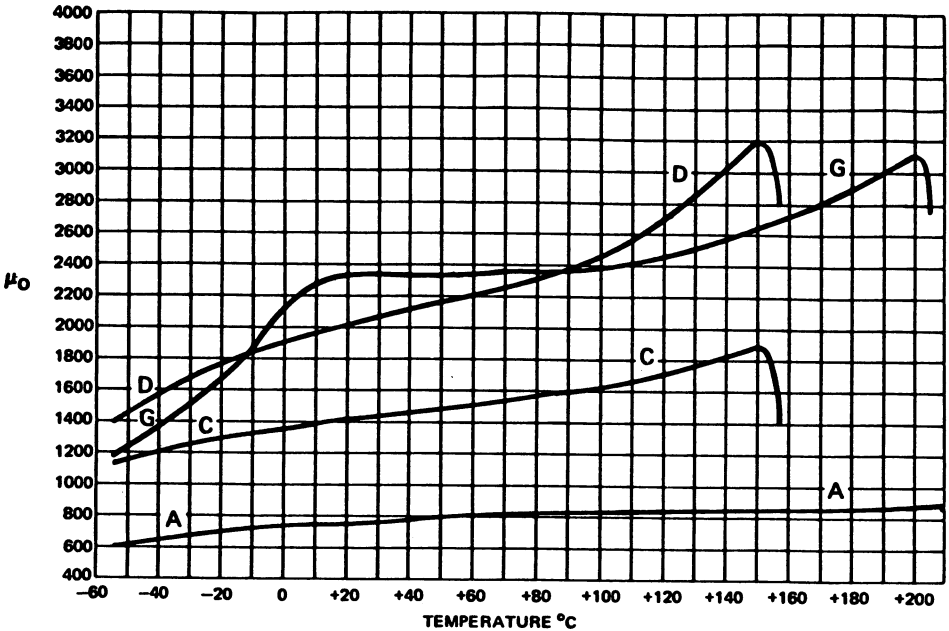
FIGURE 14 Temperature variation of permeability for ferrite materials. Three of these materials (A, C, and D) are linear materials with a positive slope. Material G has a rather flat temperature coefficient.

For the same reasons, it is important that the inductance (or permeability) of a material not vary significantly with changes in temperature, drive level, superimposed DC, or time. Magnetic components, such as telephone and transmission lines, can be subject to extreme temperatures. Most telephones have superimposed direct current at times for ringing purposes. Some components are expected to operate for about 20 years without great differences in properties. Figures 14 and 15 show the variations of some ferrite material with temperature and frequency. These variations are obtained by chemistry and processing control. Note that in Fig. 14 there are materials in which the permeability slopes are positive with respect to temperature and one in which it is flat. The resonant frequency of an LC circuit is obtained when the effects of inductance and capacitance cancel. At that frequency, the following condition exists:

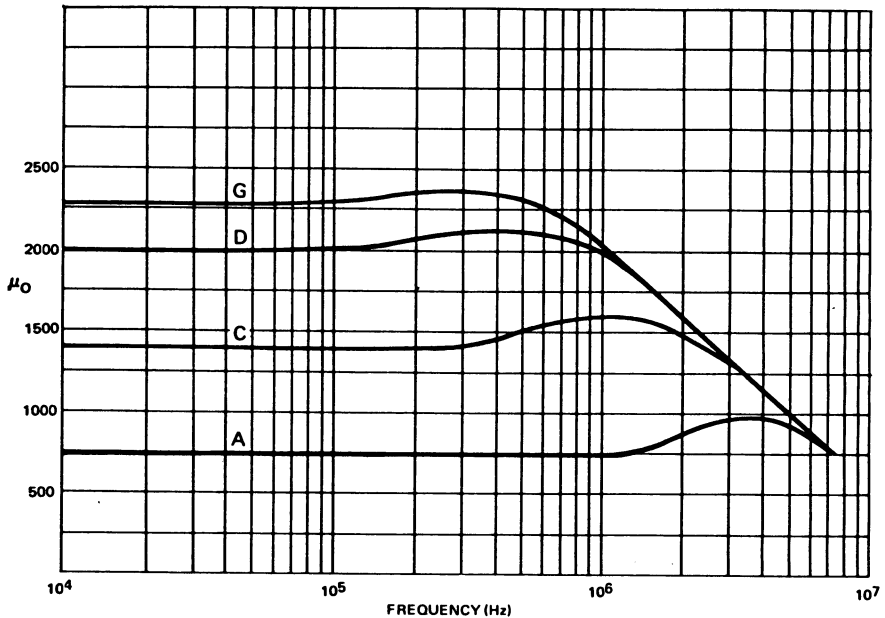$$f_{res} = \frac{1}{2\pi \sqrt{LC}}$$

FIGURE 15 Frequency variation of permeability. Note that the high-
er the permeability, the lower is the frequency of roll-off of the per-
meability.

where

f_{res} = resonant frequency, hertz
L   = inductance, henrys
C   = capacitance, farads

To maintain the resonant frequency constancy, the LC product must
be constant. Many capacitors, such as the polystyrene types, have
temperature coefficients in the usable range that are slightly negative.
If the inductor (TC) has the same but opposite (positive) slope, the
net effect will be cancellation or no variation. If the capacitor is a sil-
ver mica capacitor that has a flat TC, then a flat TC inductor is used.
The TC can be adjusted either by movement of the secondary permea-
bility maximum by chemistry control, as shown in Fig. 16, or by addi-
tions, such as TiO_2 or CoO. Figure 17 shows a typical ferrite pot core
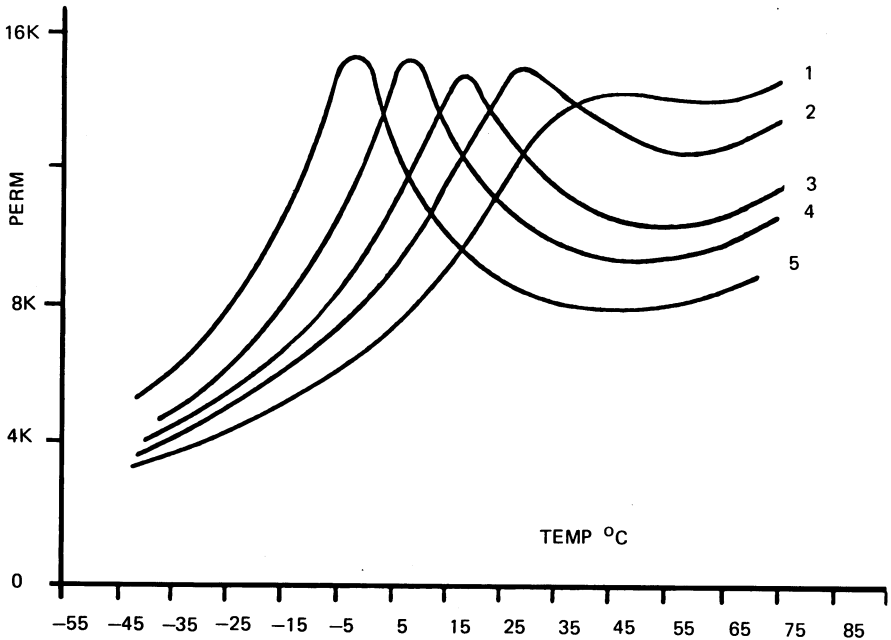used as a telecommunications inductor.

FIGURE 16   Variation of secondary permeability maximum by chem-
istry control.   In these curves the iron content has been increased
about 0.15 mol% for each material, starting with sample 1 and in-
creasing through 5.   Note the shift of the SPM to lower tempera-
tures as the iron is increased.   (From Ref. 3.)

3.10.3 Loading Coils

Loading coils are used in transmission lines to add inductance, off-
setting the increase in capacitance that occurs over long distances.
The "loading coils" are placed about every half mile. In the United
States, where transmission lines are mainly aboveground and tem-
perature variation and lightning may change the inductance of a
material, moly permalloy powder cores are used extensively since
ferrites cannot yield that stability. In most of the rest of the world,
where transmission lines are below ground, ferrite is the material
used for cost considerations. The Q and stability needed can be
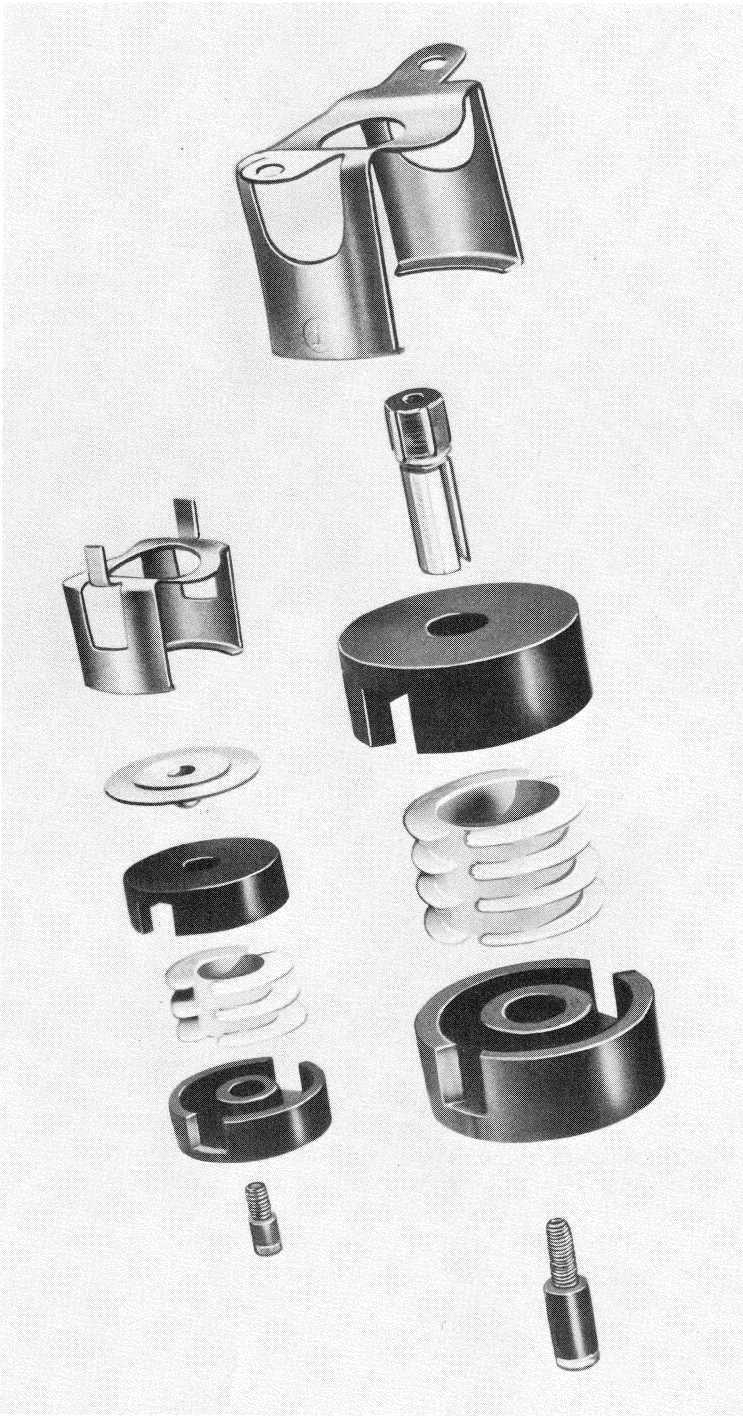accomplished by insertion of an air gap into the magnetic circuit.

FIGURE 17 A typical pot core assembly. (Photo courtesy of Magnetics, Division of Spang & Co., Butler, PA.)

3.10.4 Recording Head Ferrites

Ferrites for recording heads are used to write or read (interpret) information impressed on a recording medium (tape, disc, or wire) by setting (write) or detecting (read) the state of magnetization of that medium. As such, the head material must have sufficient permeability over a wide band of frequencies. In addition, since the medium may be quite abrasive, the ferrite must have good wear resistance. This means high hardness and a grain structure that is less likely to pull out or, if a grain is pulled out, will leave only a small void. A fine-grain structure is less likely to pull out. For this reason, dense ferrites are employed, preferably the hot-pressed variety. Hot pressing, preferably hot isostatic pressing (HIP), allows high density without the usual large grain size that comes with conventional pressed and sintered parts.

The other approach is to use single-crystal ferrites, which of course are more costly than other varieties.

Recording head ferrites are either of the Mn-Zn or Ni-Zn variety. Originally, when glass bonding as a means of assembling and fastening the ferrite head was first introduced, Ni-Zn ferrites were the only ferrites used because of the high temperatures required for melting and fusing the glass. The Mn-Zn ferrite materials would have changed properties because of the sensitive oxygen equilibrium, which does not affect the Ni-Zn ferrite as much. However, recently, by tailoring the glass and changing the atmosphere under which the glass bonding was done, Mn-Zn ferrite is also used as a recording head material with glass bonding. The future of ferrites for recording head materials is somewhat clouded now because of alternative head techniques, such as thin film and magneto-optic recording.

3.11 HARD FERRITES

There are a great many applications for hard ferrites. Some are strictly mechanical and are used only for attraction or repulsion. One use that comes to mind is as a gasket for refrigerator doors. This is actually accomplished by taking the fired ferrite powder and incorporating it into a rubber material. In this case, the usefulness of the ferrite is its formability, and no use is made of the high-resistivity ceramic properties. Other uses are aimed toward AC application.

3.11.1 Speaker Magnets

Here the purpose of the magnet is to convert the higher frequency electrical signals representing sound transmission back to sound again. This is accomplished by sending the electrical signals through a coil

in the speaker cone. The varying attraction of the coil for the permanent magnet will vibrate the speaker, producing sound. In contrast to the metallic magnets used for the same purpose, advantage is taken of high coercive force Hc (see Fig. 1) of Ba ferrite compared with Alnico, for example. The high coercive force permits thinner magnets since this property prevents demagnetization. On the other hand, because the remanent induction B_r (see Fig. 11) is much lower than Alnico, to obtain the same magnetic flux the cross-sectional area of the magnet must be increased. The total flux ϕ is given by

$$\phi = BA$$

where

    ϕ = total magnetic flux, maxwells
    B = induction, gauss
    A = area, square centimeters

Since for ferrite, $B_r \simeq 3000$ for Alnico 15,000, the cross-sectional area of the ferrite magnet must be five times as large to have the equivalent flux. Therefore, a ferrite speaker magnet will be disc shaped, stubby, and short, and the Alnico magnet will be long and thin. When Co was in very tight supply, therefore, costly Alnico magnets were switched over to other systems, including Ba ferrite. The situation has somewhat returned with the lower price of Co.

3.11.2 Motor Segments

This application is a replacement for the field coils to form the alternating field in motors. The main use has been in the cordless portable electric appliances, such as electric knives. Another even wider application is in the automotive industry, where many electric motors are used for windshield wipers, windshield washers, window openers, seat adjustors, fans, and so on.

3.12 MICROWAVE APPLICATIONS: GARNETS AND OTHER MICROWAVE FERRITES

At a microwave frequency that extends from the gigahertz (10^9 Hz) region, the only bulk magnetic materials available are ferrites. The applications are somewhat different, as one cannot talk about electric voltages and currents in wires with discrete components affecting these currents and voltages. With microwaves, we are mainly dealing

with electromagnetic fields, which are not confined to wires and are affected somewhat differently.

Microwave fields are usually contained in waveguides and then propagated into the atmosphere. Microwave components, such as Faraday rotators, circulators, and phase shifters, make use of these fields to transmit signals over very large distances, as in satellite transmission. Here, the use is in telecommunications. Other uses are in navigation, such as instrument landing systems for aircraft and early warning radar systems.

Microwave frequencies demand high-resistivity ferrites, as one can infer from our previous discussion of the frequency dependence of losses. Mn-Zn ferrites are not used here for that purpose. Nickel ferrites, Mg-Mn ferrites, and, more recently, the garnets have been used for microwave applications. The original material for garnets was YIG (yttrium-iron-garnet, $Y_3Fe_5O_{12}$). Many substituted garnets have been used, such as Al^{3+} substitution to lower the saturation for lower microwave frequencies. The rare earths used have been extended to Sm and many others. As in recording heads, hot-pressed and single-crystal ferrites have been produced. To keep the resistivity high in microwave ferrites, excess Fe is avoided to eliminate Fe^{2+}. In many instances, the Fe_2O_3 mole percentage is lower than 50%. Recently, garnets have also been used as a matrix for magnetic bubbles, which we will describe later.

3.13 MAGNETIC RECORDING

3.13.1 Recording Media

In recording media, we are attempting to impress on the material bits of information, either analog as in music and speech recording or digital for computer and information processing. The material must be capable of being permanently magnetized locally but must be capable of being read or demagnetized without much difficulty. Therefore, the material is somewhat magnetically hard, but not as much as the conventional permanent magnet materials. The most widely used material is γ-Fe_2O_3, which has the spinel structure and is technically a ferrite (a defect structure). A third of the octahedral sites normally occupied by Fe^{3+} ions are vacancies. Also, the Fe^{2+} ion on the tetrahedral site are oxidized to Fe^{3+}. The spins on the two different lattice sites are oriented antiparallel, but the difference in the number of ions and therefore unpaired spins creates a net moment. Part of the permanent magnet properties of a recording media material, such as γ-Fe_2O_3, is due to what is known as shape anisotropy, which means the influence of ratio of length to cross-sectional area of the particles. In γ-Fe_2O_3, crystallite ratios of 5:1 to 10:1 help achieve better performance. A

typical way of manufacturing the Fe_2O_3 is to grow elongated crystallites of a $\gamma\text{-}Fe_2O_3$ hydrate from solution on previously precipitated seed crystals. This hydrate cannot be directly converted to the unhydrated crystal. Instead, it must be reduced to the magnetite or Fe_3O_4 form, retaining the acicular structure. The magnetite is then oxidized controllably to the Fe_2O_3. Recently, the addition of small amounts of Co^{2+} ion absorbed on the surface of the Fe_2O_3 dramatically improved the performance.

Magnetite (Fe_3O_4 or ferrous ferrite) is sometimes also used as a medium. However, this is not as good as the $\gamma\text{-}Fe_2O_3$.

Another ferromagnetic medium is CrO_2 (chromium dioxide), which can be produced in acicular form. It is produced by decomposing CrO_3 and is a costly material.

3.13.2 Magnetic Bubbles

Magnetic bubbles are reverse domains in a uniformly magnetized matrix. They can be generated, moved, stored, and detected, and this represents a memory system.

The original bubbles were generated from orthoferrites having the formula $MFeO_3$. The matrix is a plate that can be magnetized (by a direct current or a permanent magnet) to be essentially one domain. By a small loop with opposing current, a small cylindrical reverse domain can be generated and moved along a thin film deposited Ni-Fe path and stored at various locations. These can then be recalled, and the presence or absence of a bubble gives rise to the digital logic necessary for storage. It has been found more advantageous to employ special substituted anisotropic garnets at present. These garnets are formed as films on substrates on nonmagnetic garnets (gadolinium gallium garnet, GGG) by liquid-phase epitaxy. The thinner the garnet film, the smaller are the bubbles and the denser is the packing. Bubble memories remain a potentially useful memory technique.

3.13.3 Ferrite Memory Cores

In the earlier days of digital computers, before semiconductor memories were as prevalent, small ferrite toroids were used as individual storage elements in a memory matrix system that could be addressed in the matrix of memory cores made of a square loop magnesium manganese ferrite material. By pulsing in one direction the core could be reset to a 0 state. By pulsing in the other direction it could be set to a 1 state. The cores could then be read by resetting all back to 0. Those with an imprinted 1 would show an output but the 0 would not. Memory cores that were as small as 0.010 inch in diameter have all but disappeared.

3.14 FUTURE DEVELOPMENTS

3.14.1 New Power Materials

Since the largest increase in ferrite use has come in the area of power magnetics, this is the area that seems the most receptive to improvement. It would appear that frequencies of power supplies should be increasing, placing a greater emphasis on the ferrite. New raw materials and the use of additives should allow this goal to be met, as will improved firing schedules in kilns of special design. The use of nonconventional processing, such as coprecipitation, activated sintering, and cospray roasting, should also contribute to an improved product. Lower cost raw materials and rapid firing schedules would keep ferrites competitive with other materials.

3.14.2 High-Permeability Materials

Permeabilities have reached 10,000 in most ferrite shapes and 15,000-18,000 in some shapes, such as small toroids. Higher purity raw materials and improved high-temperature firing techniques could raise these to the 20,000 permeability mark. The problem will then be to reduce the large temperature dependence of these materials.

3.14.3 New Recording Media

Codoped γ-Fe_2O_3 will take over as the premiere material in recording media but will be pushed by thin film and fine metallic media. Better particle shape control will also improve properties.

3.14.4 Miniaturization-Chip Inductors

Along with the increase in frequency, the size of inductors can be made quite small and susceptible to being formed as chips mounted on the printed-circuit boards. Power supplies of this type are already being used at frequencies up to 1 MHz. This on-board type of supply and digital control may be expected to increase in importance.

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