Figure 20.8 Schematic representation of antiparallel alignment of spin magnetic moments for antiferromagnetic manganese oxide.

Mn^{2+}

0^{2-}

20.5 ANTIFERROMAGNETISM AND FERRIMAGNETISM

Antiferromagnetism

antiferromagnetism

This phenomenon of magnetic moment coupling between adjacent atoms or ions occurs in materials other than those that are ferromagnetic. In one such group, this coupling results in an antiparallel alignment; the alignment of the spin moments of neighboring atoms or ions in exactly opposite directions is termed **antiferromagnetism.** Manganese oxide (MnO) is one material that displays this behavior. Manganese oxide is a ceramic material that is ionic in character, having both Mn^{2+} and O^{2-} ions. No net magnetic moment is associated with the O^{2-} ions, because there is a total cancellation of both spin and orbital moments. However, the Mn^{2+} ions possess a net magnetic moment that is predominantly of spin origin. These Mn^{2+} ions are arrayed in the crystal structure such that the moments of adjacent ions are antiparallel. This arrangement is represented schematically in Figure 20.8. Obviously, the opposing magnetic moments cancel one another, and, as a consequence, the solid as a whole possesses no net magnetic moment.

Ferrimagnetism

ferrimagnetism

Some ceramics also exhibit a permanent magnetization, termed **ferrimagnetism.** The macroscopic magnetic characteristics of ferromagnets and ferrimagnets are similar; the distinction lies in the source of the net magnetic moments. The principles of ferrimagnetism are illustrated with the cubic ferrites.[2] These ionic materials may be represented by the chemical formula MFe_2O_4, in which M represents any one of several metallic elements. The prototype ferrite is Fe_3O_4, the mineral magnetite, sometimes called lodestone.

The formula for Fe_3O_4 may be written as $Fe^{2+}O^{2-}–(Fe^{3+})_2 (O^{2-})_3$, in which the Fe ions exist in both +2 and +3 valence states in the ratio of 1:2. A net spin magnetic moment exists for each Fe^{2+} and Fe^{3+} ion, which corresponds to 4 and 5 Bohr magnetons, respectively, for the two ion types. Furthermore, the O^{2-} ions are magnetically neutral. There are antiparallel spin-coupling interactions between the Fe ions, similar in character to antiferromagnetism. However, the net ferrimagnetic moment arises from the incomplete cancellation of spin moments.

Cubic ferrites have the inverse spinel crystal structure, which is cubic in symmetry, and similar to the spinel structure (Section 12.2). (A unit cell for this inverse spinel structure is shown on the front cover of the book. Red spheres represent

ferrite

[2] Ferrite in the magnetic sense should not be confused with the ferrite α-iron discussed in Section 9.18; in the remainder of this chapter, the term **ferrite** implies the magnetic ceramic.
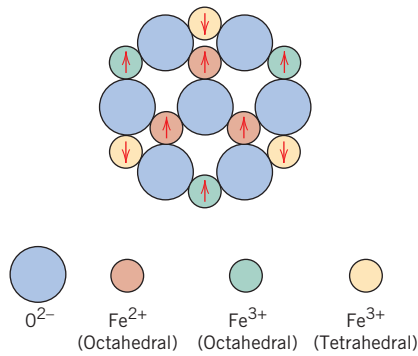
Figure 20.9 Schematic diagram showing the spin magnetic moment configuration for Fe^{2+} and Fe^{3+} ions in Fe_3O_4. (From Richard A. Flinn and Paul K. Trojan, *Engineering Materials and Their Applications,* 4th edition. Copyright © 1990 by John Wiley & Sons, Inc. Adapted by permission of John Wiley & Sons, Inc.)

0^{2-} Fe^{2+} (Octahedral) Fe^{3+} (Octahedral) Fe^{3+} (Tetrahedral)

VMSE

Spinel/Inverse Spinel

O^{2-} ions whereas dark blue and light blue spheres denote Fe^{2+} and Fe^{3+} ions, respectively.) The inverse spinel crystal structure might be thought of as having been generated by the stacking of close-packed planes of O^{2-} ions. Again, there are two types of positions that may be occupied by the iron cations, as illustrated in Figure 12.7. For one, the coordination number is 4 (tetrahedral coordination); that is, each Fe ion is surrounded by four oxygen nearest neighbors. For the other, the coordination number is 6 (octahedral coordination). With this inverse spinel structure, half the trivalent (Fe^{3+}) ions are situated in octahedral positions, and the other half in tetrahedral positions. The divalent Fe^{2+} ions are all located in octahedral positions. (The occupancy of tetrahedral and octahedral positions by Fe^{2+} and Fe^{3+} ions within close-packed planes of O^{2-} ions, as well as their relationship to the inverse spinel unit cell are represented on the book's back cover.) The critical factor is the arrangement of the spin moments of the Fe ions, as represented in Figure 20.9 and Table 20.3. The spin moments of all the Fe^{3+} ions in the octahedral positions are aligned parallel to one another; however, they are directed oppositely to the Fe^{3+} ions disposed in the tetrahedral positions, which are also aligned. This results from the antiparallel coupling of adjacent iron ions. Thus, the spin moments of all Fe^{3+} ions cancel one another and make no net contribution to the magnetization of the solid. All the Fe^{2+} ions have their moments aligned in the same direction; this total moment is responsible for the net magnetization (see Table 20.3). Thus, the saturation magnetization of a ferrimagnetic solid may be computed from the product of the net spin magnetic moment for each Fe^{2+} ion and the number of Fe^{2+} ions; this would correspond to the mutual alignment of all the Fe^{2+} ion magnetic moments in the Fe_3O_4 specimen.

Table 20.3 **The Distribution of Spin Magnetic Moments for Fe^{2+} and Fe^{3+} Ions in a Unit Cell Fe_3O_4[a]**

Cation	Octahedral Lattice Site	Tetrahedral Lattice Site	Net Magnetic Moment
Fe^{3+}	↑↑↑↑ ↑↑↑↑	↓↓↓↓ ↓↓↓↓	Complete cancellation
Fe^{2+}	↑↑↑↑ ↑↑↑↑	—	↑↑↑↑ ↑↑↑↑

[a] Each arrow represents the magnetic moment orientation for one of the cations.

Table 20.4 Net Magnetic Moments for Six Cations

Cation	Net Spin Magnetic Moment (Bohr magnetons)
Fe^{3+}	5
Fe^{2+}	4
Mn^{2+}	5
Co^{2+}	3
Ni^{2+}	2
Cu^{2+}	1

Cubic ferrites having other compositions may be produced by adding metallic ions that substitute for some of the iron in the crystal structure. Again, from the ferrite chemical formula, $M^{2+}O^{2-}$–$(Fe^{3+})_2(O^{2-})_3$, in addition to Fe^{2+}, M^{2+} may represent divalent ions such as Ni^{2+}, Mn^{2+}, Co^{2+}, and Cu^{2+}, each of which possesses a net spin magnetic moment different from 4; several are listed in Table 20.4. Thus, by adjustment of composition, ferrite compounds having a range of magnetic properties may be produced. For example, nickel ferrite has the formula $NiFe_2O_4$. Other compounds may also be produced containing mixtures of two divalent metal ions such as $(Mn,Mg)Fe_2O_4$, in which the $Mn^{2+}:Mg^{2+}$ ratio may be varied; these are called *mixed ferrites*.

Ceramic materials other than the cubic ferrites are also ferrimagnetic; these include the hexagonal ferrites and garnets. Hexagonal ferrites have a crystal structure similar to the inverse spinel, with hexagonal symmetry rather than cubic. The chemical formula for these materials may be represented by $AB_{12}O_{19}$, in which A is a divalent metal such as barium, lead, or strontium, and B is a trivalent metal such as aluminum, gallium, chromium, or iron. The two most common examples of the hexagonal ferrites are $PbFe_{12}O_{19}$ and $BaFe_{12}O_{19}$.

The garnets have a very complicated crystal structure, which may be represented by the general formula $M_3Fe_5O_{12}$; here, M represents a rare earth ion such as samarium, europium, gadolinium, or yttrium. Yttrium iron garnet ($Y_3Fe_5O_{12}$), sometimes denoted YIG, is the most common material of this type.

The saturation magnetizations for ferrimagnetic materials are not as high as for ferromagnets. On the other hand, ferrites, being ceramic materials, are good electrical insulators. For some magnetic applications, such as high-frequency transformers, a low electrical conductivity is most desirable.

✓ *Concept Check 20.1*

Cite the major similarities and differences between ferromagnetic and ferrimagnetic materials.

[*The answer may be found at www.wiley.com/college/callister (Student Companion Site.)*]

✓ *Concept Check 20.2*

What is the difference between the spinel and inverse spinel crystal structures? *Hint:* you may want to consult Section 12.2.

[*The answer may be found at www.wiley.com/college/callister (Student Companion Site.)*]

EXAMPLE PROBLEM 20.2

Saturation Magnetization Determination for Fe_3O_4

Calculate the saturation magnetization for Fe_3O_4 given that each cubic unit cell contains 8 Fe^{2+} and 16 Fe^{3+} ions, and that the unit cell edge length is 0.839 nm.

Solution

This problem is solved in a manner similar to Example Problem 20.1, except that the computational basis is per unit cell as opposed to per atom or ion.

The saturation magnetization will be equal to the product of the number N' of Bohr magnetons per cubic meter of Fe_3O_4, and the magnetic moment per Bohr magneton μ_B,

Saturation magnetization for a ferrimagnetic material (Fe_3O_4)

$$M_s = N'\mu_B \tag{20.11}$$

Now, N' is just the number of Bohr magnetons per unit cell n_B divided by the unit cell volume V_C, or

Computation of the number of Bohr magnetons per unit cell

$$N' = \frac{n_B}{V_C} \tag{20.12}$$

Again, the net magnetization results from the Fe^{2+} ions only. Because there are 8 Fe^{2+} ions per unit cell and 4 Bohr magnetons per Fe^{2+} ion, n_B is 32. Furthermore, the unit cell is a cube, and $V_C = a^3$, a being the unit cell edge length. Therefore.

$$M_s = \frac{n_B\mu_B}{a^3} \tag{20.13}$$

$$= \frac{(32 \text{ Bohr magnetons/unit cell})(9.27 \times 10^{-24} \text{ A·m}^2/\text{Bohr magneton})}{(0.839 \times 10^{-9} \text{ m})^3/\text{unit cell}}$$

$$= 5.0 \times 10^5 \text{ A/m}$$

DESIGN EXAMPLE 20.1

Design of a Mixed Ferrite Magnetic Material

Design a cubic mixed-ferrite magnetic material that has a saturation magnetization of 5.25×10^5 A/m.

Solution

According to Example Problem 20.2, the saturation magnetization for Fe_3O_4 is 5.0×10^5 A/m. In order to increase the magnitude of M_s it is necessary to replace some fraction of the Fe^{2+} with a divalent metal ion that has a greater magnetic moment—for example Mn^{2+}; from Table 20.4, note that there are 5 Bohr magnetons/Mn^{2+} ion as compared to 4 Bohr magnetons/Fe^{2+}. Let us first employ Equation 20.13 to compute the number of Bohr magnetons per unit cell (n_B),

assuming that the Mn^{2+} addition does not change the unit cell edge length (0.839 nm). Thus,

$$n_B = \frac{M_s a^3}{\mu_B}$$

$$= \frac{(5.25 \times 10^5 \, A/m)(0.839 \times 10^{-9} \, m)^3/\text{unit cell}}{9.27 \times 10^{-24} \, A \cdot m^2/\text{Bohr magneton}}$$

$$= 33.45 \text{ Bohr magnetons/unit cell}$$

If we let x represent the fraction of Mn^{2+} that have substituted for Fe^{2+}, then the remaining unsubstituted Fe^{2+} fraction is equal to $(1 - x)$. Furthermore, inasmuch as there are 8 divalent ions per unit cell, we may write the following expression:

$$8[5x + 4(1 - x)] = 33.45$$

which leads to $x = 0.181$. Thus, if 18.1 at% of the Fe^{2+} in Fe_3O_4 are replaced with Mn^{2+}, the saturation magnetization will be increased to 5.25×10^5 A/m.

20.6 THE INFLUENCE OF TEMPERATURE ON MAGNETIC BEHAVIOR

Temperature can also influence the magnetic characteristics of materials. Recall that raising the temperature of a solid results in an increase in the magnitude of the thermal vibrations of atoms. The atomic magnetic moments are free to rotate; hence, with rising temperature, the increased thermal motion of the atoms tends to randomize the directions of any moments that may be aligned.

For ferromagnetic, antiferromagnetic, and ferrimagnetic materials, the atomic thermal motions counteract the coupling forces between the adjacent atomic dipole moments, causing some dipole misalignment, regardless of whether an external field is present. This results in a decrease in the saturation magnetization for both ferro- and ferrimagnets. The saturation magnetization is a maximum at 0 K, at which temperature the thermal vibrations are a minimum. With increasing temperature, the saturation magnetization diminishes gradually and then abruptly drops to zero at what is called the **Curie temperature** T_c. The magnetization-temperature behavior for iron and Fe_3O_4 is represented in Figure 20.10. At T_c the mutual spin-coupling forces are completely destroyed, such that for temperatures above T_c both ferromagnetic and ferrimagnetic materials are paramagnetic. The magnitude of the Curie temperature varies from material to material; for example, for iron, cobalt, nickel, and Fe_3O_4, the respective values are 768, 1120, 335, and 585°C.

Curie temperature

Antiferromagnetism is also affected by temperature; this behavior vanishes at what is called the *Néel temperature*. At temperatures above this point, antiferromagnetic materials also become paramagnetic.

✓ Concept Check 20.3

Explain why repeatedly dropping a permanent magnet on the floor will cause it to become demagnetized.

[*The answer may be found at* www.wiley.com/college/callister *(Student Companion Site.)*]
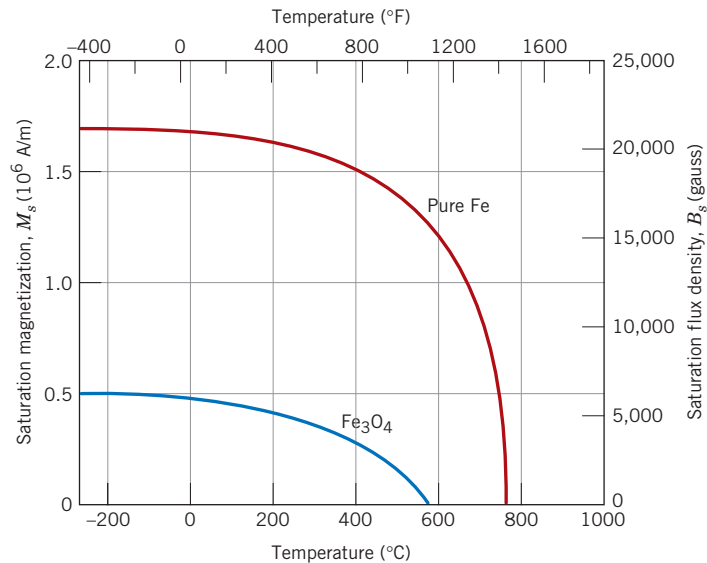
Figure 20.10 Plot of saturation magnetization as a function of temperature for iron and Fe_3O_4. [Adapted from J. Smit and H. P. J. Wijn, *Ferrites.* Copyright © 1959 by N. V. Philips Gloeilampenfabrieken, Eindhoven (Holland). Reprinted by permission.]

20.7 DOMAINS AND HYSTERESIS

Any ferromagnetic or ferrimagnetic material that is at a temperature below T_c is composed of small-volume regions in which there is a mutual alignment in the same direction of all magnetic dipole moments, as illustrated in Figure 20.11. Such a region is called a *domain,* and each one is magnetized to its saturation magnetization. Adjacent domains are separated by domain boundaries or walls, across which the direction of magnetization gradually changes (Figure 20.12). Normally, domains are microscopic in size, and for a polycrystalline specimen, each grain may consist of more than a single domain. Thus, in a macroscopic piece of material, there will be a large number of domains, and all may have different magnetization orientations. The magnitude of the M field for the entire solid is the vector sum of the magnetizations of all the domains, each domain contribution being weighted by its volume fraction. For an unmagnetized specimen, the appropriately weighted vector sum of the magnetizations of all the domains is zero.
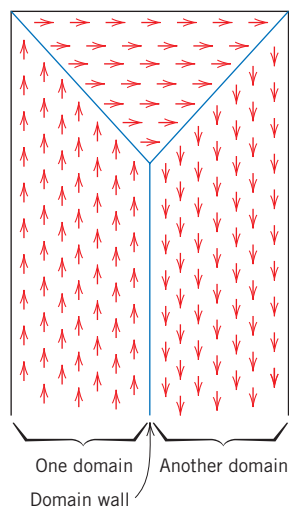

Figure 20.11 Schematic depiction of domains in a ferromagnetic or ferrimagnetic material; arrows represent atomic magnetic dipoles. Within each domain, all dipoles are aligned, whereas the direction of alignment varies from one domain to another.
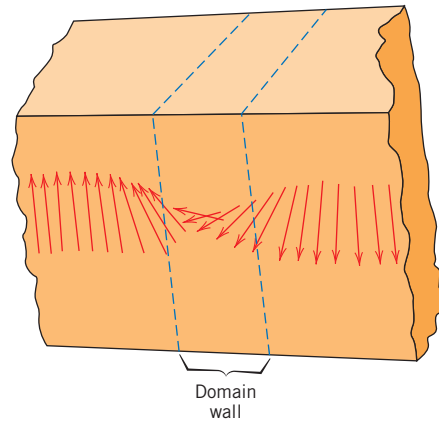
Figure 20.12 The gradual change in magnetic dipole orientation across a domain wall. (From W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics,* 2nd edition. Copyright © 1976 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

Domain wall

Flux density B and field intensity H are not proportional for ferromagnets and ferrimagnets. If the material is initially unmagnetized, then B varies as a function of H, as shown in Figure 20.13. The curve begins at the origin, and as H is increased, the B field begins to increase slowly, then more rapidly, finally leveling off and becoming independent of H. This maximum value of B is the saturation flux density B_s, and the corresponding magnetization is the saturation magnetization M_s, mentioned previously. Because the permeability μ from Equation 20.2 is the slope of the B-versus-H curve, note from Figure 20.13 that the permeability changes with and is dependent on H. On occasion, the slope of the B-versus-H curve at $H = 0$ is specified as a material property, which is termed the *initial permeability* μ_i, as indicated in Figure 20.13.

As an H field is applied, the domains change shape and size by the movement of domain boundaries. Schematic domain structures are represented in the insets (labeled U through Z) at several points along the B-versus-H curve in Figure 20.13. Initially, the moments of the constituent domains are randomly oriented such that there is no net B (or M) field (inset U). As the external field is applied, the domains that are oriented in directions favorable to (or nearly aligned with) the applied field
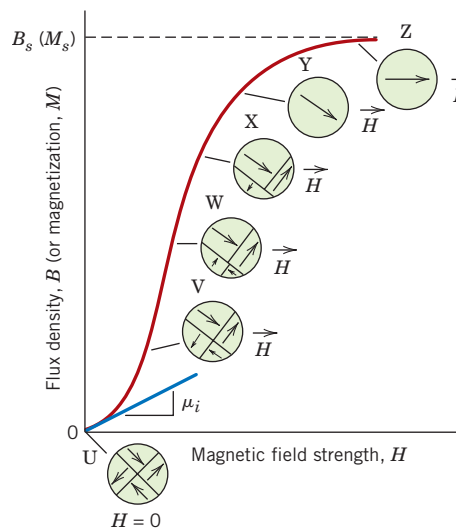

Figure 20.13 The B-versus-H behavior for a ferromagnetic or ferrimagnetic material that was initially unmagnetized. Domain configurations during several stages of magnetization are represented. Saturation flux density B_s, magnetization M_s, and initial permeability μ_i are also indicated. (Adapted from O. H. Wyatt and D. Dew-Hughes, *Metals, Ceramics and Polymers,* Cambridge University Press, 1974.)
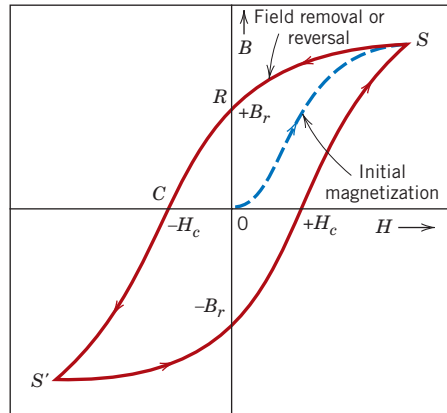
Figure 20.14 Magnetic flux density versus the magnetic field strength for a ferromagnetic material that is subjected to forward and reverse saturations (points S and S'). The hysteresis loop is represented by the solid curve; the dashed curve indicates the initial magnetization. The remanence B_r and the coercive force H_c are also shown.

grow at the expense of those that are unfavorably oriented (insets V through X). This process continues with increasing field strength until the macroscopic specimen becomes a single domain, which is nearly aligned with the field (inset Y). Saturation is achieved when this domain, by means of rotation, becomes oriented with the H field (inset Z).

From saturation, point S in Figure 20.14, as the H field is reduced by reversal of field direction, the curve does not retrace its original path. A **hysteresis** effect is produced in which the B field lags behind the applied H field, or decreases at a lower rate. At zero H field (point R on the curve), there exists a residual B field that is called the **remanence,** or *remanent flux density, B_r,* the material remains magnetized in the absence of an external H field.

hysteresis

remanence

Hysteresis behavior and permanent magnetization may be explained by the motion of domain walls. Upon reversal of the field direction from saturation (point S in Figure 20.14), the process by which the domain structure changes is reversed. First, there is a rotation of the single domain with the reversed field. Next, domains having magnetic moments aligned with the new field form and grow at the expense of the former domains. Critical to this explanation is the resistance to movement of domain walls that occurs in response to the increase of the magnetic field in the opposite direction; this accounts for the lag of B with H, or the hysteresis. When the applied field reaches zero, there is still some net volume fraction of domains oriented in the former direction, which explains the existence of the remanence B_r.

To reduce the B field within the specimen to zero (point C on Figure 20.14), an H field of magnitude $-H_c$ must be applied in a direction opposite to that of the original field; H_c is called the **coercivity,** or sometimes the *coercive force.* Upon continuation of the applied field in this reverse direction, as indicated in the figure, saturation is ultimately achieved in the opposite sense, corresponding to point S'. A second reversal of the field to the point of the initial saturation (point S) completes the symmetrical hysteresis loop and also yields both a negative remanence $(-B_r)$ and a positive coercivity $(+H_c)$.

coercivity

The B-versus-H curve in Figure 20.14 represents a hysteresis loop taken to saturation. Of course, it is not necessary to increase the H field to saturation before reversing the field direction; in Figure 20.15, loop NP is a hysteresis curve corresponding to less than saturation. Furthermore, it is possible to reverse the direction
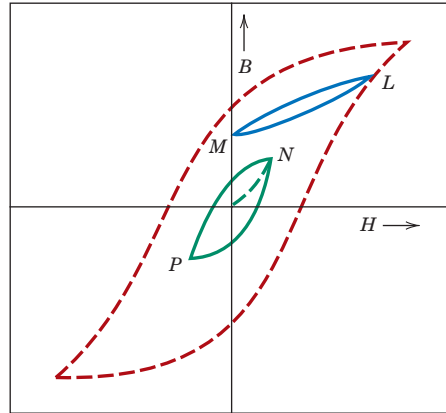
Figure 20.15 A hysteresis curve at less than saturation (curve *NP*) within the saturation loop for a ferromagnetic material. The *B–H* behavior for field reversal at other than saturation is indicated by curve *LM*.

of the field at any point along the curve and generate other hysteresis loops. One such loop is indicated on the saturation curve in Figure 20.15: for loop *LM*, the *H* field is reversed to zero. One method of demagnetizing a ferromagnet or ferrimagnet is to repeatedly cycle it in an *H* field that alternates direction and decreases in magnitude.

At this point it is instructive to compare the *B*-versus-*H* behaviors of paramagnetic, diamagnetic, and ferromagnetic/ferrimagnetic materials; such a comparison is shown in Figure 20.16. The linearity of paramagnetic and diamagnetic materials may be noted in the small inset plot, whereas the behavior of a typical ferromagnetic/ferrimagnetic is nonlinear. Furthermore, the rationale for labeling paramagnetics and diamagnetics as nonmagnetic materials is verified by comparing the *B* scales on the vertical axes of the two plots—at an *H* field strength of
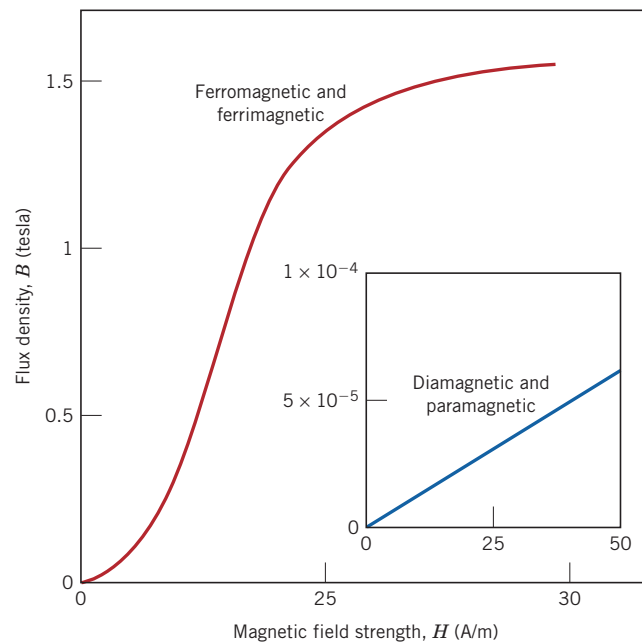

Figure 20.16 Comparison of *B*-versus-*H* behaviors for ferromagnetic/ferrimagnetic and diamagnetic/paramagnetic materials (inset plot). Here it may be noted that extremely small *B* fields are generated in materials that experience only diamagnetic/paramagnetic behavior, which is why they are considered nonmagnetics.