FERROMAGNETISM

By ***S. B. Batdorf***

While ferromagnetic materials have been used for centuries, little has been known of the reasons for their behavior. New advances in ferromagnetic research have done much to explain why these substances act as they do.

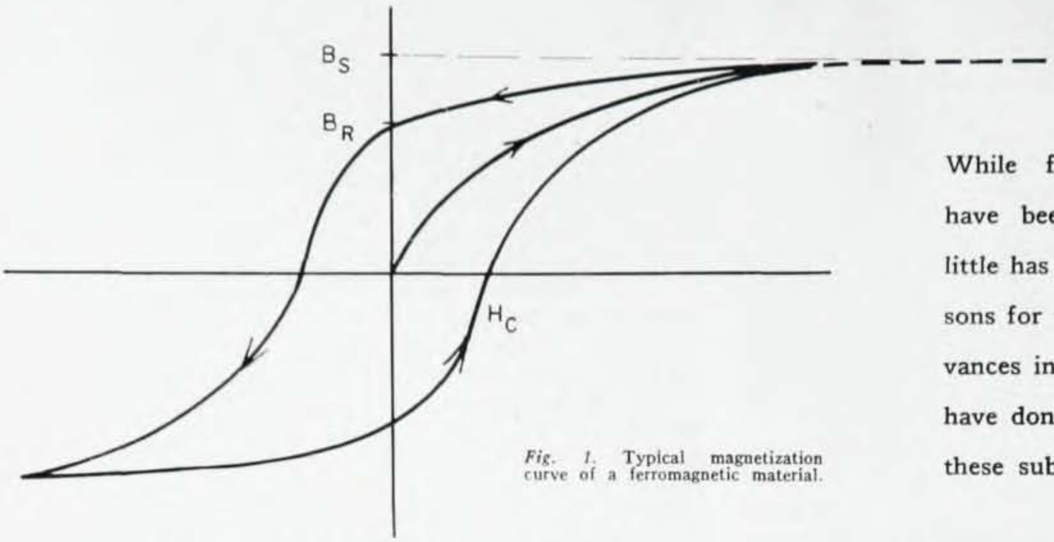

Fig. 1. Typical magnetization curve of a ferromagnetic material.

ALL SUBSTANCES react in some degree to a magnetic field, but only iron and those substances designated ferromagnetic by virtue of their similarity to iron become strongly enough magnetized in ordinary magnetic fields to be popularly regarded as magnetic. Ferromagnetic materials are generally characterized by (a) saturation in readily obtainable magnetic fields, (b) a magnetization curve exhibiting a hysteresis loop (see Fig. 1), and (c) a temperature, known as the Curie temperature, above which ferromagnetic effects disappear.

Classical Magnetism

The simplest concept of a magnetic material is that of a collection of small elementary magnets which are aligned into a single large magnet by the action of an applied magnetic field. If these elementary magnets are identified with atoms, a qualitatively satisfactory picture emerges. The saturation magnetization seems about right, having an order of magnitude of one Bohr magneton per atom (a Bohr magneton is defined as the magnetic moment associated with the smallest circular orbit of a hydrogen atom; it is also the magnetic moment of an electron due to spin). The Curie temperature may be thought of as the temperature above which the disordering effects of thermal agitation predominate over the aligning influences of the interaction between atoms. Below this temperature, the atoms tend to be in magnetic alignment and to assume the direction of any applied magnetic field; the retention of this magnetization after removal of the field can then account for the residual induction or remanence, B_r.

There is, however, a serious difficulty with this picture. Calculations using the known magnetic moments and separations of the atoms lead to Curie temperatures within less than a degree of absolute zero. Weiss pointed out some forty years ago that this difficulty could be avoided by assuming the existence of a strong "inner field" which could keep the atoms in alignment up to the required temperatures. Aside from the fact that the origin of this inner field was a complete mystery, an explanation now had to be given for the existence of ferromagnetic materials in a demagnetized state. Weiss did this by assuming that the material normally consists of a large number of small saturated domains magnetized in a variety of directions so that the net magnetization can take any value between positive and negative saturation. The two concepts of an inner field and a domain structure set the stage for most of the subsequent progress in ferromagnetic research.

Domain Behavior

The domain concept was soon confirmed by experiments showing that the magnetization process was not really smooth as shown in Fig. 1, but that the magnetization normally increases in tiny jumps. These "Barkhausen jumps" were originally attributed to domains suddenly reversing their direction of magnetization, but have more recently been identified with discontinuities in the motions of domain walls, concerning which more will be said later.

The experimental study of domain behavior was greatly enhanced by Bitter's discovery that domain boundaries on the surface of a magnetic material could be delineated with the aid of magnetic powders. The powder patterns observed on the surface of a mechanically polished specimen are distorted and unintelligible, but Williams and his co-workers have shown that when the cold-worked layer is removed by electropolishing,

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the powder patterns observed are susceptible to ready interpretation and much can be inferred about the domain structure of the interior, especially in the case of single crystals.

The domain structure can be accounted for theoretically as the minimum energy state of the material. In the absence of an applied field, the energy involved comes from the following sources: (a) crystalline anisotropy energy, minimization of which tends to keep the magnetization parallel to one of several crystallographically determined "easy" directions of magnetization, (b) magnetic energy, minimization of which tends to prevent the formation of free magnetic poles either at the crystal surface or at domain boundaries, (c) domain wall energy which gives rise to effects somewhat like surface tension, (d) magnetoelastic energy, which comes into the picture because changes in magnetization are associated with small changes in the dimensions of the material. A very simple domain structure in a picture-frame specimen cut from a single crystal of silicon iron at the Bell Telephone Laboratories is shown in Fig. 2.

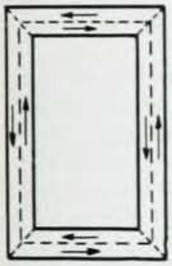


Fig. 2. Domain structure in a picture frame specimen cut from a single crystal.

In the domain structure illustrated, the magnetization is everywhere in an easy direction and there are no free magnetic poles.

The domain structure changes when a magnetic field is applied because the energy of interaction of the field and the material is added to the energies already considered. Becker has shown that two independent processes occur during magnetization. In the first, which generally predominates in the initial stages of magnetization, the domain walls move in such a way that favorably oriented domains grow at the expense of unfavorably oriented domains. In the second, which generally predominates in the approach to saturation, the direction of magnetization is rotated from the most favorable easy direction of magnetization toward the direction of the applied field. This situation is shown schematically in Fig. 3.

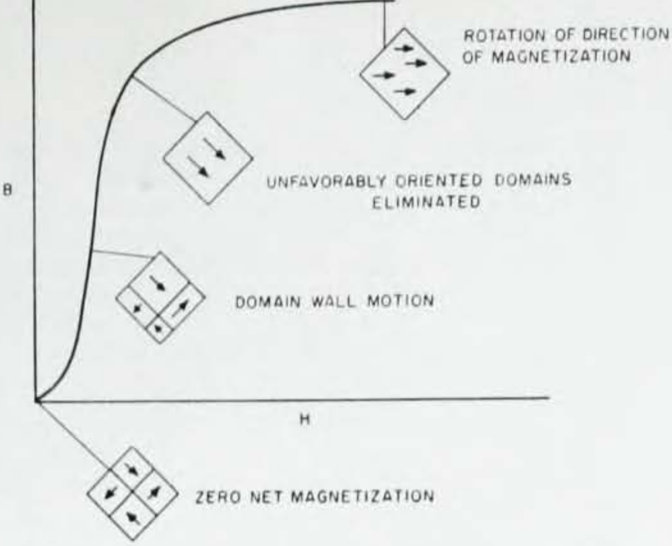


Fig. 3. Processes occurring during magnetization.

The inclination of the direction of magnetization away from the most favorable easy direction and toward the applied field is a reversible process so that the magnetic losses represented by the area of the hysteresis loop must be attributed to domain wall motion. The motion of the domain walls is impeded by the presence of inclusions, impurities, and lattice distortions. A portion of the wall may be held back temporarily by such an impediment, while the rest of the wall continues to advance (Fig. 4). The arrested portion eventually snaps forward into alignment with the wall as a whole, and the associated sudden change in magnetization gives rise to Barkhausen noises and also to local eddy currents which are responsible for the magnetic losses. The coercive force is a measure of the field necessary to force the domain wall past such obstacles.

Nature of Ferromagnetic Coupling

So far, our consideration of ferromagnetism has been in terms of macroscopic concepts, such as crystalline anisotropy and magnetostriction. To go beyond a purely empirical basis for these phenomena, or to understand the magnitude of the saturation magnetization and the nature of Weiss's inner field which is responsible for ferromagnetism, one must consider the situation from an atomic point of view.

The magnetic moment of a free atom is due in part to the orbital motion of electrons, and in part to electron spin. In ferromagnetic crystals with cubic symmetry, the contributions of the orbital motion are "quenched" and the magnetization is almost entirely due to electron spin. This has been shown by measurements of the ratio of magnetic moment to angular momentum, which is twice as large for electron spin as for orbital motion.

The magnetic moment of any filled shell of electrons is zero, so that any net magnetic moment must arise from an unfilled shell. If only the outer shell is incomplete, however, ferromagnetism does not usually occur because the disposition of outer electrons in the various types of binding in solids is generally such that the net spin and angular momentum are zero. Ferromagnet-

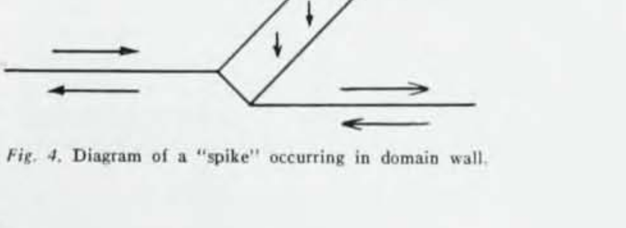
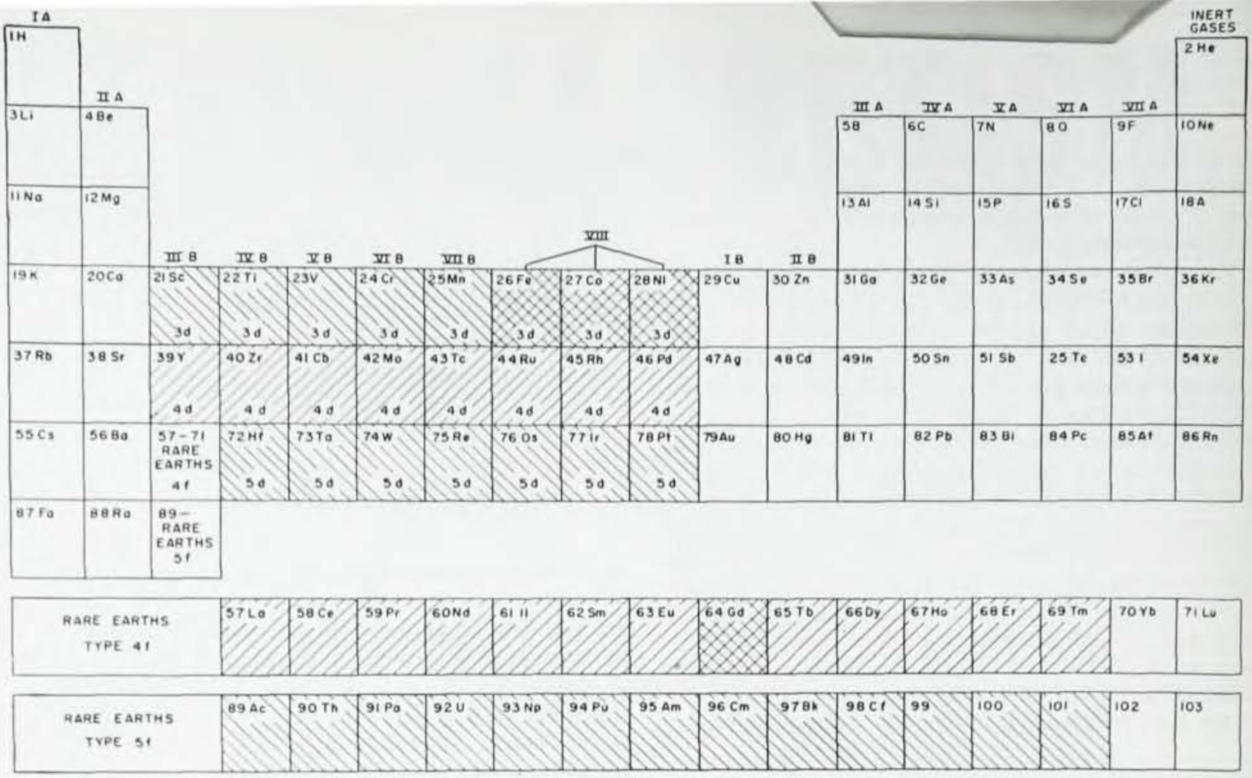


Fig. 4. Diagram of a "spike" occurring in domain wall.



IA	IIA	III B	IV B	V B	VI B	VII B	VIII	VIII	VIII	I B	II B	III A	IV A	V A	VI A	VII A	INERT GASES
1H																	2He
3Li	4Be											5B	6C	7N	8O	9F	10Ne
11Na	12Mg											13Al	14Si	15P	16S	17Cl	18A
19K	20Ca	21Sc 3d	22Ti 3d	23V 3d	24Cr 3d	25Mn 3d	26Fe 3d	27Co 3d	28Ni 3d	29Cu	30Zn	31Ga	32Ge	33As	34Se	35Br	36Kr
37Rb	38Sr	39Y 4d	40Zr 4d	41Cb 4d	42Mo 4d	43Tc 4d	44Ru 4d	45Rh 4d	46Pd 4d	47Ag	48Cd	49In	50Sn	51Sb	25Te	53I	54Xe
55Cs	56Ba	57–71 RARE EARTHS 4f	72Hf 5d	73Ta 5d	74W 5d	75Re 5d	76Os 5d	77Ir 5d	78Pt 5d	79Au	80Hg	81Tl	82Pb	83Bi	84Pc	85At	86Rn
87Fa	88Ra	89— RARE EARTHS 5f															

RARE EARTHS TYPE 4f	57La	58Ce	59Pr	60Nd	61 Il	62Sm	63Eu	64Gd	65Tb	66Dy	67Ho	68Er	69Tm	70Yb	71Lu
RARE EARTHS TYPE 5f	89Ac	90Th	91Pa	92U	93Np	94Pu	95Am	96Cm	97Bk	98Cf	99	100	101	102	103

Fig. 5. Periodic Table. Transition elements are indicated by shading. The unfilled shell is shown in each case.

ism then is normally associated with unfilled inner shells and then only under quite restricted conditions. Unfilled inner shells occur in several groups of transition elements (Fig. 5); however, only iron, cobalt, nickel and gadolinium are known to be ferromagnetic, while dysprosium is suspected of being so also. In the first three of these elements, the 3-*d* shell is incomplete, while in the last two, the 4-*f* and 5-*d* shells are both incomplete.

The magnetic interaction energy of neighboring atoms is very small as has already been mentioned; however, the electrostatic energy, which is very much larger, depends strongly on the electron spin, and thus on the magnetic moment. This comes about as a result of the Pauli exclusion principle which states that two electrons can occupy the same orbit (or have the same space wave function) only if they have opposing spins. In practice, the exclusion principle prevents electrons of like spin from coming close together, thus reducing the electrostatic energy of repulsion below what it would otherwise be. The reduction in energy arising in this manner is generally called the "exchange" energy. Exchange forces are responsible for the binding of the atoms in the hydrogen molecule, and early in the development of wave mechanics, Heisenberg suggested that Weiss's inner field might be accounted for in a related fashion.

This approach has led to the concept of ferromagnetism illustrated in Fig. 6. According to the Heisenberg viewpoint, the exchange energy between two atoms is a function of the ratio of atomic separation to the diameter of the unfilled shell. It is zero at large atomic separations, increases rapidly, and causes parallel coupling as the separation diminishes, passes through a maximum and then decreases. At still closer spacing, the exchange energy becomes negative, resulting in antiparallel coupling of the unfilled shells. In Fig. 6, the Curie temperature is used as a convenient measure of the exchange energy, to which it is proportional. Two curves for Curie temperature versus atomic spacing are shown corresponding to the fact that, depending on the crystal structure, an atom may have 8 or 12 nearest neighbors. Except for the rare earths, the ratio of atomic spacing to unfilled shell diameter is largest for the ferromagnetic elements iron, cobalt, and nickel. Cobalt has the highest Curie temperature, while gadolinium has a Curie temperature of only 16° C. The diagram suggests that manganese might be made ferromagnetic by increasing its atomic separation; this proves to be the case in a number of alloys, among them the Heusler alloys, the best known of which is Cu_2MnAl. It should be mentioned that the curves as drawn are empirical. A qualitatively similar curve for

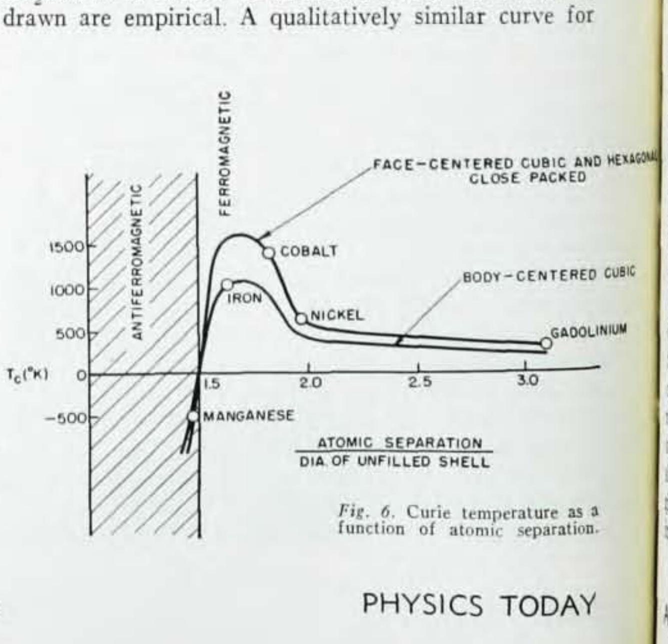


Fig. 6. Curie temperature as a function of atomic separation.

the interaction between two atoms has been derived theoretically by Bethe on the Heisenberg model, but the approximations involved were so rough that the calculation is generally considered to suggest, rather than demonstrate, the theoretical existence of a positive exchange energy over part of the curve.

The Heisenberg approach is the equivalent in magnetic theory of the Heitler-London method in molecular theory. Since its inception, it has been applied to the interpretation of many of the phenomena of ferromagnetism. For example, Van Vleck has used it to investigate the macroscopic characteristics of antiferromagnetism. In Fig. 7 the temperature dependences of the magnetic susceptibilities of ferromagnetic, antiferromagnetic, and paramagnetic substances are compared. Above the ordering, or Curie temperature, all the materials are paramagnetic, that is, they have a susceptibility χ given by

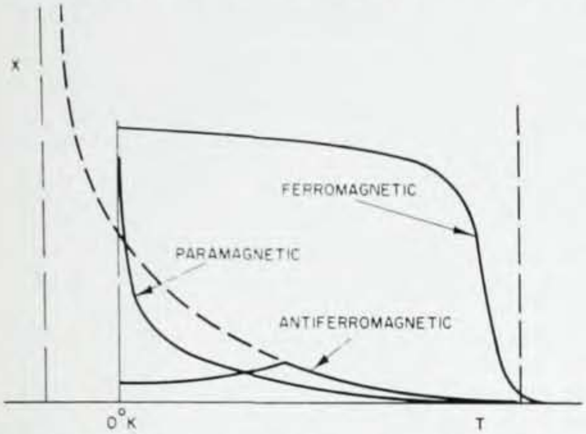


Fig. 7. Temperature dependences of magnetic susceptibility.

$$\chi=\frac{c}{T-\theta}.$$

A plot of χ against T is a rectangular hyperbola with a vertical asymptote at θ. The vertical asymptote occurs at a positive absolute temperature for a ferromagnetic, a negative absolute temperature for an antiferromagnetic (see also Fig. 6), and at 0° K for an ideal paramagnetic substance. In the neighborhood of the Curie temperature, the hyperbolic behavior breaks down. A ferromagnetic substance approaches its saturation magnetization slowly as the temperature continues to diminish, while the magnetization of an antiferromagnetic substance decreases below the Curie temperature, reaching approximately two-thirds of its Curie value at 0° K.

Another interpretation of ferromagnetism has been developed by Slater and others by means of energy band considerations. One can think of assembling a crystal by starting with discrete atoms in the proper relative position but with a very large atomic spacing, or lattice constant, then allowing the lattice constant to shrink to normal size. As the various electron shells begin to overlap, the corresponding energy levels broaden into bands; this is somewhat analogous to obtaining two frequencies by loosely coupling two identical oscillators. The electrons are thought of in first approximation as distributed uniformly through the solid rather than congregated about individual atoms. When energy bands corresponding to the unfilled inner shells are comparatively narrow, the (negative) exchange energy associated with having as many electrons as possible with parallel spin outweighs the energy penalty in taking electrons from the lower energy positions of one spin orientation and placing them in higher energy positions of opposite orientation. Thus, at large atomic spacing we get ferromagnetism. At small atomic spacing, on the other hand, the energy band widens and the minimum energy requirement leads to an equal division of electrons between the two possible orientations. Thus, the simplest form of band theory, often called the collective electron theory, leads to results somewhat similar to those shown in Fig. 6; however, in this theory close atomic spacing leads to a kind of paramagnetism and, as recently emphasized by Slater, the theory does not lead to the proper diminution of coupling with increasing atomic spacing. In spite of the latter limitation, Stoner and others have used it to correlate many magnetic phenomena.

The two approaches just described are based on an atomic and on a collective electron point of view, respectively. Zener has recently proposed a theory of intermediate type. In this theory the electrons in incomplete inner shells (hereafter called d shells for brevity) have an atomic or localized character. On the other hand, the outer s or conduction electrons are collective and, in contrast to the situation in the previously described theories, play an essential role in ferromagnetism.

Zener considered three types of atomic interaction: The interaction between d shells (assumed always antiferromagnetic), the interaction between conduction electrons, and the interaction between conduction electrons and d shells. Considering the first two alone, the lowest energy state in the absence of an external field would be that in which the d shell spins are antiferromagnetically arranged and the conduction electron spins (for the relatively low density of conduction electrons occurring in metals) are half positive and half negative, giving an over-all zero magnetization. Considering the interaction of conduction electrons with d shells alone, the minimum energy state is that in which all conduction electrons and all d shells have spins pointing in the same direction. Thus, in this theory, it is the conduction electrons which are responsible for ferromagnetic alignment through their interaction with the d shells. At close atomic spacing, the d-d interaction is predominant and the material behaves antiferromagnetically. At larger separations, the s-d interaction predominates and ferromagnetism occurs with all d shells in parallel alignment and a majority (but not all) of the conduction electrons parallel to the d shells. As the separation becomes still larger, the ferromagnetic coupling drops off because the s electrons gradually lose the capacity to conduct and cause parallel alignment. Like the Heisenberg theory, this theory also leads to the situation depicted in Fig. 6 but without use of the rather arbitrary assumption of a change of sign of the exchange interaction as a function of atomic separation inherent in the earlier approach.

In varying degrees, the theories just discussed lack rigor and contain empirical elements. For this reason, Slater has urged the desirability of carrying out accurate calculations which will indicate unambiguously what quantum theory really has to say about ferromagnetism and has indicated a feasible method to attack the problem. Following this approach, and with the assistance of the MIT Whirlwind Computer, Meckler has worked out the energy of the oxygen molecule as a function of atomic separation in both the ground and the first excited state. The success of the calculations for the oxygen molecule, the two atoms of which have parallel spins, and which is therefore in a sense the simplest ferromagnetic, encourages the view that some more representative ferromagnetic problems may prove not too arduous a task.

Saturation Magnetization

In first approximation, one might assume that in the solid state the transition elements from calcium to copper each have one conduction electron. Then our considerations so far would lead to the intrinsic magnetization per atom of these elements shown by line *A B* in Fig. 8. This figure indicates zero magnetization for copper, which has a complete *d* shell, one Bohr magneton per atom for nickel, which is one electron short of a closed shell, two for cobalt, and three for iron. As previously indicated, the rest of the elements shown are too closely spaced relative to their *d* shell radii to be ferromagnetic, but *B C D* shows approximately what magnetization per atom might be expected to occur under favorable circumstances in alloys or compounds.

On the same diagram is a skeletalized version of a plot due to Bozorth showing the actual magnetization of a number of two-component alloys. The discrepancy between the lines *A B* and *E F* can be accounted for by assuming that the number of conduction electrons per atom is 0.6 rather than 1.0. On the collective electron theory, the linear variation of saturation magnetization with electrons per atom in alloys, as represented by the line *E F*, follows immediately, while the explanation for the line *F G* is a little more involved. The curves falling below the triangle *E F G* can presumably be interpreted in terms of a more complex version of the band theory but such an interpretation has not yet come to the attention of the writer.

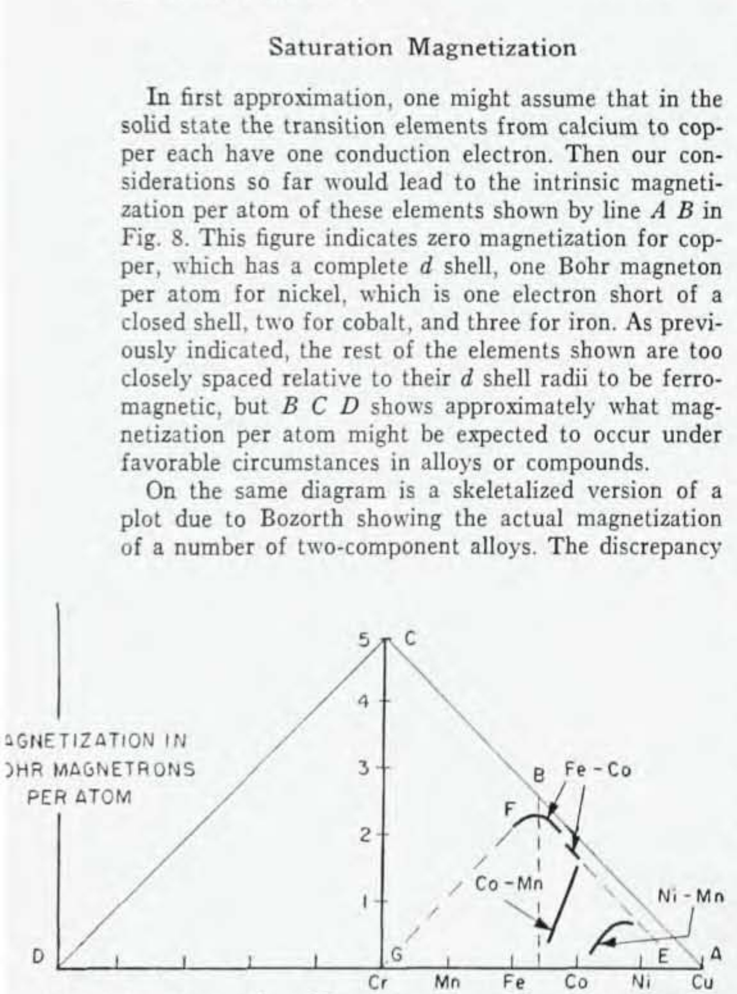


Fig. 8. Magnetization of metals and 2 component alloys as a function of the number of electrons per atom.

A quantitative treatment of all of the experimental curves of Fig. 8 has, however, been given by Carr in terms of the Zener theory. According to this explanation, the curves for various alloys break away from line *E F* and form lines of positive slope as the number of electrons per atom decreases because of the increasing density of antiferromagnetically coupled atoms.

The location of iron to the left of the peak magnetization on such a line of positive slope suggests the presence in iron itself of some antiferromagnetic atoms. Zener has, in fact, suggested that the body-centered cubic iron crystal may be regarded as two interpenetrating cubic lattices composed of atoms having spins of $+5$ and -1, respectively. Shull and his collaborators have not found any evidence for such a structure from neutron diffraction experiments. However, the wide discrepancy between the Curie temperature measured magnetically and by neutron diffraction in the case of chromium gives a basis for the suspicion that antiferromagnetic coupling may in some cases escape detection by current neutron diffraction techniques. Because of this, no definite conclusions can be drawn at present from the negative result in the case of iron.

Of the materials included in Fig. 8, only iron, cobalt, nickel, and some of their alloys have been discussed up to this point. As suggested by the figure, manganese exhibits four Bohr magnetons per atom in the Heusler alloy Cu_2MnAl. Chromium becomes ferromagnetic in some combinations but appears generally to exhibit half or less than half of the potential moment given in the figure. This does not imply that four Bohr magnetons per atom is the maximum attainable, however, for gadolinium exhibits seven.

Although we have been talking of magnetizations per atom far in excess of that in iron, it is the magnetization per unit volume which is the quantity of interest in engineering applications. In the case of gadolinium, the atom is so large that even at absolute zero, the saturation induction is only about 25,000 gauss and the Curie point is so low that B_s for gadolinium exceeds that for iron only below the temperature of dry ice. In the case of chromium and manganese, the atomic spacing would have to be considerably increased to obtain ferromagnetism with a reasonably high Curie point, with a consequent reduction in magnetization per unit volume. All in all, the outlook for obtaining a material with a saturation induction substantially in excess of the iron cobalt alloy corresponding to point *F* of Fig. 8 is not too hopeful.

Nonmetallic Ferromagnetism

One of the most recent and active areas of ferromagnetic research is that of nonmetallic ferromagnetic materials, which are chemical compounds of the transition elements. In compounds, the atoms with incomplete shells may be isolated from each other, in which case the material is paramagnetic, or they may interact. If an interaction exists, it may be due to direct exchange, as already discussed, or to either of two types of indirect exchange in which two atoms with incomplete inner shells interact through an ordinary nonmagnetic atom as intermediary. More commonly, a combination of these three types of interaction occurs and the net coupling may be either ferromagnetic or antiferromagnetic.

Among the nonmetallic ferromagnetics, the "ferrites" constitute the most completely investigated and understood system. These are variants of magnetite, the oldest ferromagnetic material. In magnetite, $FeOFe_2O_3$, one iron atom is divalent and two are trivalent in each molecule, and the crystal structure is that of spinel, $MgOAl_2O_3$. The ferrites comprise the general class of magnetic oxides of type $MOFe_2O_3$, where M may be any divalent metal. Mixed ferrites and solid solutions of ferrites with MO and Fe_2O_3 have also been studied. The chromites, with the composition $MOCr_2O_3$, constitute a class of materials similar to ferrites.

Néel has developed a theory according to which the magnetism of the ferrites arises from the incomplete cancellation of two interpenetrating lattices of atoms with oppositely oriented spins. The difference between the magnetic behavior of ferrites and metallic ferromagnetic behavior has led to the use of the term "ferromagnetism" to designate the former. Generally speaking, the ferrites have relatively low saturation induction (usually less than 5000 gauss), a low Curie point, and very high electrical resistivity compared to ferromagnetic alloys.

Applications

The ferromagnetics of technical interest are generally classified as hard or soft according to whether they are permanent magnet materials or are readily magnetized by induction. Soft magnetic materials are characterized by a low coercive force, H_c. Iron, with a few percent of silicon added, is widely used in power applications, such as transformers and motors, because it has the high saturation induction of iron combined with greatly increased electrical resistivity, which decreases eddy current losses. In many cases losses are further reduced by the use of material in which the grains have been oriented parallel to the direction of magnetization. For some specialized applications, sheet material has recently become available in thicknesses as low as 0.0001 inch. However, as the material is made very thin, the coercive force tends to increase.

The coercive force can be minimized by such measures as making the magnetostriction and crystalline anisotropy zero and eliminating impurities and residual stresses. The crystalline anisotropy is of opposite sign in iron and nickel, and the same is true of magnetostriction. Both become very small in a nickel-iron alloy which is approximately 78 percent nickel. Improvement of this composition by small additions of other constituents and suitable heat treatments has resulted in materials that approach saturation at fields of only a few hundredths of an oersted and are thus well suited to the requirements of telephony and other applications involving feeble magnetizing currents. There is, however, a penalty for such low H_c, for the saturation induction of these alloys is less than half that of silicon iron.

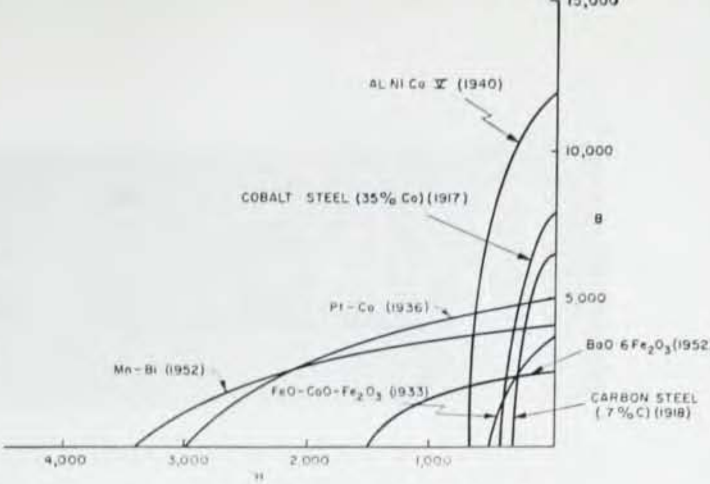


Fig. 9. Demagnetization curves of permanent magnet materials.

For high frequency applications, ferrites are of interest because of their high resistivity. They are used in television sweep circuit transformers, for example.

In hard, or permanent, magnet materials, the coercive force, H_c, is a rough measure of the stability of a magnet against demagnetizing influences, and the product $H_c B_r$ is an upper limit to the field energy a unit of volume of the magnet can produce. It is thus desirable to have both of these quantities as large as possible. The coercive force is increased by having large magnetostriction, anisotropy, and residual stresses, or lattice distortions.

A permanent magnet normally operates in the second quadrant, or demagnetizing portion of the hysteresis loop. Fig. 9 gives these portions of the loop for several permanent magnet materials together with the dates when they appeared.

As may be inferred from the preceding discussion, ferromagnetism continues to be a very active field of research both as regards theory and material development. To the classical listing of ferromagnetism, paramagnetism, and diamagnetism there must now be added antiferromagnetism and ferrimagnetism. The recent rapid advances in nonmetallic ferromagnetics are providing many useful products as well as resulting in much new insight into the nature of magnetic coupling. It appears reasonable to expect that the insight now being generated will make possible the preparation of a wealth of new magnetic materials during the coming decade.