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Opportunities in Magnetic Materials

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Magnetic materials are an integral part of modern industrial society. They play a key role in power distribution, enable the conversion between electrical and mechanical energy, underlie microwave communication, and provide the transducers and the active storage material for data storage. The properties of magnetic materials have been continuously improving, and there seems to be no end to their applications. For example, although semiconductor technology has displaced ferrite cores in computer memory, the appearance of microcomputers has generated a need for switched-mode power supplies based on ferrite transformers and for low-cost magnetic storage of data.

Summary. Recent discoveries of new magnetic materials may greatly improve the performance of devices containing such materials and may lead to entirely new applications. For example, boron-based ternary compounds for permanent magnets make new compact motor designs practical; amorphous transformer materials show greatly reduced losses at high frequencies; and thin magnetic alloy films offer increased data storage densities. The major technical issues associated with the new magnetic materials are identified.

The role of the United States in magnetic technology appears to be declining rapidly. There are two reasons for this. The first is that American manufacturers of systems with magnetic devices are relying more heavily on foreign sources of the devices. For example, the ferrites for the switched-mode power supplies and for magnetic recording heads increasingly come from Japan. The second reason is the current lack of basic research on magnetism. In the late 1950's and early 1960's, many distinguished American scientists, including John Van Vleck, Charles Kittel, and Philip Anderson, were working on magnetism. This is no longer the case.

Because of the importance of magnetic components in modern society, the Department of Defense asked the National Materials Advisory Board of the National Academy of Sciences–National Research Council to establish a Committee on Magnetic Materials in January 1984 (*1*). The committee was charged to assess the status of research and development (R&D) in magnetic materials in the United States, to identify issues that may limit future development of magnetic materials, and to recommend R&D areas with high potential for scientific and technological dividends. This article summarizes the findings of the committee (*2*).

The committee chose to categorize magnetic materials by their traditional applications, as determined largely by coercivity, H_c. Other properties, such as remanent induction and permeability, define the specific application. There are still other magnetic properties, such as the magneto-optic coefficient and magnetoresistance, that enable additional applications.

If there is a U.S. dependence on foreign sources for magnetic technology, then how do we reverse this trend? There are various political or economic options. However, the committee asserts that the most effective response is to develop and maintain a technological advantage by selective R&D investment by industry and government. The strategy recommended is to increase R&D in technologies that (i) represent large markets or have a large leverage in the final product, (ii) are still far from their fundamental limits, and (iii) possess rich scientific content. Several major classes of materials satisfy these conditions.

Permanent Magnets

Permanent magnets are one of the oldest and largest applications of magnetic materials. The usual measure of quality for permanent magnets is the maximum energy product, defined as the largest inscribed rectangle in the second quadrant of the hysteresis loop plotted as magnetic induction, B, versus magnetic field, H. The maximum energy product is usually expressed in megagauss-oersteds (MGOe). An ideal permanent magnet would have a constant magnetization equal to the saturation magnetization M_s in any practical applied field. Since $B = H + 4\pi M$, then, if $M = M_s$ and is constant a plot of B versus H is a straight line intersecting the B axis at $B_r = 4\pi M_s$ and the H axis at $H_c = -B_r$. The maximum energy product is then $(4\pi M_s)^2/4$. If pure iron could be made into an ideal permanent magnet with 100 percent density, it would have an energy product of 107 MGOe.

Figure 1 shows how the energy product of permanent magnets has changed over time. The first permanent magnets were natural oxide magnets, or lodestones; the first artificial permanent magnets were steels hardened by quenching. The fact that soft iron was easily magnetized and demagnetized while hardened steel acted as a permanent magnet led to the terminology of hard and soft magnetic materials that we use today. The permanent magnetic properties of steels were improved in the early 1900's by adding various alloying elements, nota-

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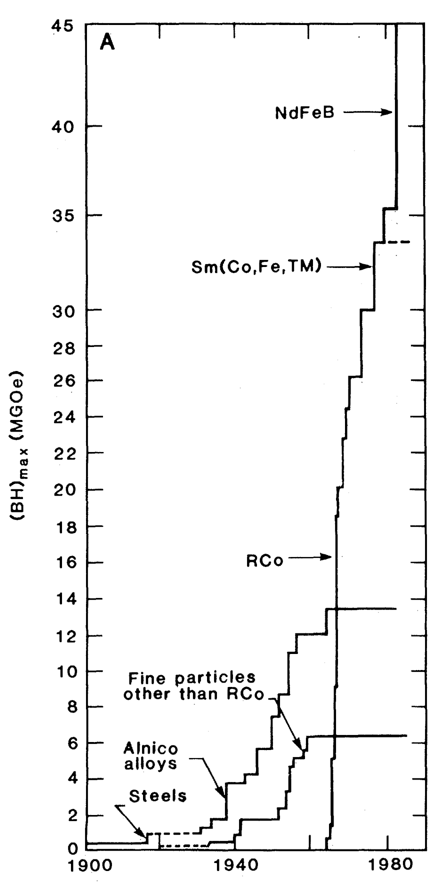
bly tungsten, but the energy product of steel does not exceed 1 MGOe. In the 1930's good permanent magnetic properties were discovered by Japanese workers in certain FeNiAl alloys. These alloys were developed into a family of alloys containing also cobalt and known collectively as Alnico, with energy products of 6 MGOe or more and produced by conventional casting technology.

Magnet steels and Alnico were developed essentially by trial and error. The major conceptual advance occurred in the 1940's, when Louis Néel, Kittel, and others introduced the idea of the single-domain particle, a single crystal so small that it is energetically unfavorable for it to contain a magnetic domain wall. Such a particle can reverse its magnetization only by a uniform or coherent rotation. The field required for this rotation depends on the magnetic anisotropy of the material. This concept has dominated subsequent R&D in permanent magnetic materials.

In the 1950's permanently magnetic ferrites were produced at Philips Industries in the Netherlands. These are iron oxides containing barium or strontium, which have a strong uniaxial magnetic anisotropy. Small single-crystal particles in the form of a loose powder are aligned by a magnetic field so that their magnetic axes are parallel, mechanically compacted, and bonded together by a high-temperature, solid-state diffusion process.

By the late 1950's it was understood that to make a superior magnet one needed to make a material with high magnetization and strong uniaxial anisotropy into single-domain particles. Strnat *et al.* (*3*) showed that a series of rare earth–cobalt compounds met the conditions. By about 1970 the first of the rare earth permanent magnets (REPM's), $SmCo_5$, was commercially available. These materials have energy products of about 20 MGOe, four times better than Alnico or hard ferrite. Although cobalt and samarium are expensive and the production process is difficult because of the strong tendency of rare earth metals to oxidize, $SmCo_5$ production was increasing rapidly until the cobalt crisis of 1977 sharply increased the price of cobalt and raised fears about the long-term stability of its supply. These events impeded growth in the REPM industry for several years.

A second generation of REPM's based on the compound Sm_2CO_{17} has become available from Japanese manufacturers within the last 5 years. Their advantage is increased magnetic induction; energy products above 25 MGOe have been achieved. These magnets are considerably off the stoichiometric 2-17 composition and contain substantial amounts of iron and copper, plus small but essential additions of zirconium, hafnium, or titanium.



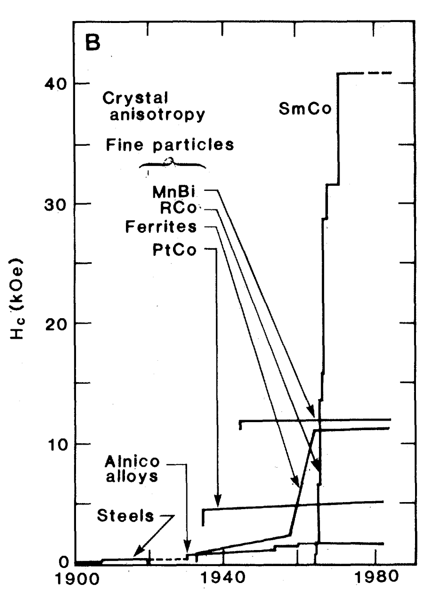


Fig. 1. Changes in energy product (A) and coercivity (B) of various permanent magnet materials, 1900 to 1980.

The latest addition to the REPM catalog is the $Fe_{14}Nd_2B$ composition, announced by Sumitomo Metal Mining Company (*4*) and General Motors Corporation (*5*) in 1983. Energy products are 30 to 45 MGOe, and the raw materials are relatively cheap. The major drawback is a low curie temperature (300°C), which causes a strong temperature dependence of magnetic properties. The curie temperature can be raised by replacing iron with cobalt. The Sumitomo magnets are made by a process very similar to that used for $SmCo_5$, so no major investment in new production facilities is required. General Motors makes a similar composition starting from a rapidly solidified ribbon sample.

Permanent magnets are used in many types of devices. The total market for permanent magnet materials is close to $1 billion. Since the volume of permanent magnet material needed to produce a given flux density in a given volume of space is inversely proportional to the energy product, as the energy product increases, new, more compact designs become practical. Such strong magnets are also finding entirely new applications. Figure 2 shows the lower half of an array of permanent magnets whose periodic magnetic field introduces wiggles in the trajectory of an electron beam, thereby producing synchrotron radiation.

Although the energy product for permanent magnets is increasing dramatically, it is nowhere near even the theoretical limit for iron (107 MGOe). This and the large market make permanent magnet materials candidates for investment. There are many opportunities for research associated with the appearance of the new ternary compounds. Their coercivities, for example, cannot be explained by the conventional single-domain particle concept. A better understanding of the temperature dependencies of the extrinsic magnetic properties could lead to improved performance at elevated temperatures. There is also the prospect that even higher energy products may be found in other ternary phases or in quaternary compounds.

Low-Frequency Soft Magnetic Materials

Soft magnetic materials are used principally in motors, generators, transformers, and related equipment. The function of the magnetic material is to produce a high magnetic flux density in some region of space. This flux density must change with time in magnitude or direction or both. The two principal materials requirements are a high working flux density and a low energy loss when the magnetic flux is changed. The highest flux density is available in FeCo alloys. The material in a device with a soft magnetic alloy usually accounts for most of the cost of the final device, effectively ruling out the use of the much more costly cobalt alloys, except for special applications. This is in contrast to permanent magnet devices, where the permanent magnet represents a small fraction of the total cost of the device. On the other hand, the relatively low electrical resistivity of iron leads to large eddy-current losses with changing flux. This problem has been addressed by electrically subdividing the iron into thin sheets or laminations and by adding alloy elements to increase the instrinsic resistivity. Energy losses can also be lowered by removing sources of domain wall pinning, primarily second-phase particles and regions of elastic or plastic deformation.

A high working flux density is attained by increasing the permeability, that is, by approaching the saturation flux density at relatively small fields. In most materials the approach to saturation is limited by the field needed to rotate the local magnetization against crystal anisotropy forces. Improved performance can be achieved by using a single crystal or a textured polycrystal with the working flux direction parallel to an easy direction of magnetization, or by choosing a composition or structure for which the anisotropy is small. The sensitivity to stress can be minimized by choosing a composition with zero magnetostriction.

These general principles have led to the use of three major classes of metallic materials. In order of increasing price and quality, these are nonoriented electrical steels, grain-oriented electrical steels, and NiFe alloys. A new class of materials, amorphous alloys, shows promise of replacing the latter two.

Ferromagnetic amorphous alloys are made by very rapidly freezing liquid alloys on a metal surface. The method was devised by Duwez and collaborators at the California Institute of Technology (*6*) in 1958 and was later developed as a manufacturing technique by Allied Corporation. The manufacturing process produces ribbon with a maximum thickness of about 0.035 mm, and only certain compositions can be made amorphous. The usual magnetic alloys are FeBSi, FeNiBSi, and CoFeNiBSi, with boron and silicon contributing 15 to 25 percent of the atomic mass. The cobalt alloy has near-zero magnetostriction. The absence of microstructure plus the small macroscopic anisotropy, high electrical resistivity (150 ohm-centimeters), thin gauge, and high elastic limit make amorphous alloys excellent soft magnetic materials. Properly annealed, they have high permeability, low losses, and saturation flux densities of 1.6 teslas or above. Since thin sheet is made from the melt in one high-speed operation and high levels of purity are generally not required, production costs can be low.

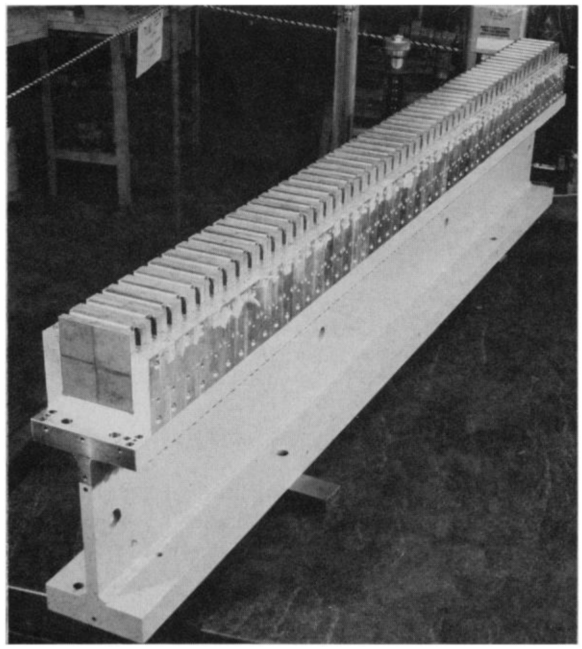


Fig. 2. Lower half of the 54-pole permanent magnet wiggler designed and constructed as a joint project of Exxon, Lawrence Berkeley Laboratory (LBL), and Stanford Synchrotron Radiation Laboratory (SSRL) and now in use at SSRL. The design is based on a concept developed by Klaus Halbach of LBL. There are four SmCo blocks in the front of the assembly; these are cemented to a vanadium Permendur pole, on the other side of which are another four SmCo blocks. This basic unit is repeated 54 times to make up the entire half-magnet. In use on the Stanford Proton Electron Asymmetric Ring at Stanford University, this magnet produces 1.5 kW of synchrotron radiation x-rays in a very narrow forward cone. [LBL photograph by Steve Adams]

Amorphous alloys will be used where their unique properties make them competitive with NiFe alloys, grain-oriented electrical steels, or ferrites. They are superior to NiFe in having higher resistivity, higher mechanical hardness, lower losses, and lower costs; superior to oriented steels in having higher resistivity, thinner gauge, and much lower losses at potentially similar cost; and superior to ferrites in having much higher flux density and permeability and sometimes lower cost.

The fact that the present world market for grain-oriented electrical steel is over $340 million indicates an enormous opportunity for amorphous alloys. Commercialization is being hindered, however, by complex patent and licensing requirements.

There is a reasonably large effort in the United States on R&D on amorphous alloys. For example, researchers are attempting to prepare and characterize new alloys and are studying the relation between structure and properties. Development activities have focused on large-scale production of wide ribbons. Much remains to be learned about this new class of materials before they can be fully exploited. For example, the effects of precipitate size, morphology, orientation, and magnetic properties on wall nucleation and pinning need to be understood. Other techniques for preparing such amorphous materials, such as solidification by atomization, should be investigated, as should the mechanism for magnetostriction.

High-Frequency Soft Magnetic Materials

Above a frequency of about 10 kHz, soft magnetic alloys such as FeNi Permalloy become degraded by eddy current losses. The preferred materials in the high-frequency range are the soft ferrites, whose electrical resistivity is more than six orders of magnitude greater than that of the metals.

The term ferrite has come to mean the whole class of magnetic oxides. Three crystal classes of commercial ferrites are in use today. One class has the hexagonal structure of the magnetoplumbite type such as $BaFe_{12}O_{19}$; it is the basis of permanent magnet ferrites. The second class has the garnet structure; compounds of this class, such as $Gd_3Fe_5O_{12}$, are used in microwave devices and bubble memory technology. The third class, with the general formula MFe_2O_4, where M is a divalent metal ion, has the spinel structure. The most common spinel ferrites in use are the MnZn and NiZn ferrites in transformers, inductors, and recording heads. Other spinel ferrites, such as MgMn, NiZn, and lithium ferrites, are used in microwave devices.

The world market for high-frequency

ferrites is about $400 million, with one-fourth in the United States. Applications include telecommunications, power supplies, deflecting yokes and flyback transformers for television receivers, and recording heads.

In the case of magnetic recording heads the material requirements are becoming more severe with increasing recording densities. Currently there are three main types of materials for recording heads. For general-purpose audio recording the recording medium is γ-Fe_2O_3, with a coercivity of about 240 A/cm (300 Oe). In this case the head material is usually laminated FeNi (Permalloy), sometimes precipitation-hardened through the use of alloying elements to reduce head wear. For high-quality audio and video recording the medium is CrO_2 or cobalt-impregnated γ-Fe_2O_3, with a coercivity of about 480 A/cm (600 Oe). Here both Sendust (85 percent iron, 9.6 percent silicon, and 5.4 percent aluminum) and spinel ferrites are used as head materials. Compared with Permalloy, Sendust has similar electrical resistivity, high saturation induction, and superior wear resistance. The last two characteristics make it attractive for use with high-coercivity media. Ferrites are characterized by extremely high electrical resistivity and wear resistance but low saturation induction. Both MnZn and NiZn ferrites are used, commonly in video and high-frequency recording where the eddy current effect is minimized by the high resistivity relative to metals.

A technical challenge associated with ferrite heads is the so-called dead layer, a thin layer of high coercivity induced by mechanical contact with the tape. This dead layer effectively increases the head-to-medium separation and hence reduces the efficiency of high-density recording systems. The problem is more severe with NiZn ferrite than with MnZn ferrite, even though the former is harder.

Related to the problem of the dead layer is wear and corrosion in the gap area, which again increases the head-to-medium separation. Furthermore, in composite structures wear of the thin pole tip material limits the head life. Here again there appears to be no direct relation between mechanical hardness and wear. The new amorphous alloys have twice the hardness of Sendust, yet the rate of head wear is three to four times higher. Other studies have shown that, in single crystals, the wear rate is highly dependent on crystallographic orientation. Presumably there are complex interactions involving friction, elastic and plastic deformation, fracture, and corrosion.

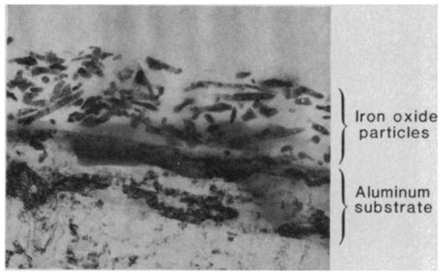


Fig. 3. Electron micrograph of a cross section of magnetic recording medium consisting of iron oxide particles suspended in a binder and coated on an aluminum substrate. [Courtesy of P. Narayan]

The trend toward high recording density has led to the need for high-coercivity recording media and high operating frequencies. Metallic recording particles with a coercivity of 1200 A/cm (1500 Oe) are now available, and the design frequency is up to 10 MHz. This combination demands head materials with high saturation induction, such as Sendust, and high electrical resistivity, such as NiZn ferrite. No single known material has this combination of properties.

The Japanese have begun to exploit the amorphous alloys described above for recording head applications. A useful composition for head applications is $Co_{70}Fe_5Si_{15}B_{10}$, whose near-zero magnetostriction helps to minimize stress-induced noise and degradation of permeability. Compositional modifications have resulted in high saturation induction ($\sim$1.3 T) suitable for the new metal particle media with very high coercivity (914 to 1200 A/cm, or 1150 to 1500 Oe).

Magnetic Recording Media

There are two modes of recording: longitudinal, in which the direction of magnetization is parallel to the plane of the recording medium, and perpendicular, in which the magnetization is normal to the plane. There are also two distinct kinds of recording media: particulate, in which the magnetic ingredient consists of submicroscopic, single-domain particles of oxides or metals immersed in a polymeric binder that separates the particles and binds them to the substrate, and thin-film, involving ferromagnetic metals and alloys. The advantages of particulate media are independent magnetic and mechanical properties, high roll-coating speeds, uniform properties within the roll, high yields, and low costs. The advantages of thin-film media are readily achievable thin coatings, high saturation magnetization, and continuously variable magnetic properties.

The substrates used in tapes, flexible disks, and magnetic cards almost always consist of polyethylene terephthalate. The substrates used in rigid disks are made of an AlMg alloy, but other materials have been proposed, such as glass and titanium.

Particles of γ-Fe_2O_3 were developed in 1934 and were first used in tapes by BASFAG in Germany. The particles were acicular, with a length-to-width ratio of about 5 to 1 and a length (less than 1 μm) that suggested single-domain behavior. Their coercivity exceeded 200 Oe and they gave a recording performance superior to that of earlier tapes made of natural magnetite (Fe_3O_4), which has a coercivity of less than 100 Oe. γ-Fe_2O_3 is still the most widely used magnetic recording material, but considerable refinements have been made over the last 50 years, with the greatest improvements occurring in the last 10 years. Figure 3 shows a cross section of a typical digital data medium.

Increasingly, however, modern applications call for higher coercivity than can be obtained from pure iron oxides. As the wavelength or the bit length of the recorded signals becomes shorter, demagnetizing fields become larger and must be resisted by higher coercivities. Early attempts to increase the coercivity of γ-Fe_2O_3 particles by incorporating 2 to 3 percent cobalt in the lattice resulted in particles having desirably high coercivities (600 to 800 Oe) but undesirably high sensitivity of the coercivity to changes in temperature. A solution to this problem, found by TDK Corporation (Japan) in 1974, consisted of impregnating only the surface of iron oxide particles with cobalt. Particles made by this method and having coercivities in the range 550 to 750 Oe are now widely used in high-performance audio and video tapes and in high-capacity flexible disks.

The total market for magnetic particles is approximately $235 million; the market for the finished media—tapes and disks—is $8 billion. Despite the ubiquitousness of these brown particles, we still do not understand (i) the relation between particle size distribution, switching fields, and the erasure and overwrite performance of tapes and disks; (ii) how cobalt, impregnating the surface of iron oxide particles, enhances coercivity almost independently of temperature; (iii) how the application of sodium metabisulfite to the surface of iron oxide particles can cause a reversible threefold increase in coercivity, and (iv) the properties of mixed anisotropies within a particle or the properties of mixed assemblies of particles.

In addition to having a high coercivity, a high-density recording medium (in which the magnetization is in the plane of the coating) should also be thin. It is difficult to make defect-free particulate coatings thinner than about 0.25 μm, so for at least 20 years the possibility of depositing continuous metallic films on rigid and on flexible substrates has been explored. Practical recording applications included electroplated drums in the 1960's and, more recently, vacuum-deposited tapes, disks, and autocatalytically plated rigid disks. In the last 5 years a great deal of study has been devoted to the preparation and properties of uniaxial thin films of CoCr alloy, in which the direction of magnetization is perpendicular to that of the substrate, in the hope that recording densities higher than those achieved in longitudinally magnetized films might be achieved.

The four general approaches to obtaining thin films are electroplating, electroless deposition, vacuum deposition, and sputtering. All these techniques are being actively developed. Confidence in this class of media would be increased if we understood the mechanism of magnetization reversal in thin films of high coercivity (greater than 500 Oe) and the fundamental magnetic units in thin films and the interactions between them.

Magneto-optic Materials

The breakdown of time reversal in magnetically ordered materials leads to the situation in which optical electric fields generate currents at right angles. These currents become the source of an electric field at right angles to the incident field which may be in phase or out of phase with that field. This creates a wealth of magneto-optic phenomena. In the Faraday configuration the light is transmitted through the material; in the Kerr configuration the light is reflected from the surface. The magnitude of these magneto-optic effects is largest when the magnetization and the propagation direction are parallel. This generally means that we are interested in planar media in which the magnetization is perpendicular to the plane, just as in perpendicular recording.

The magneto-optic effect has been the basis for optical devices since it was first discovered. In many applications the effect is used to produce optical switching for display devices or printers. The figure of merit for such materials is the rotation per unit of absorption. For a low-loss isolator, this would require a 45° rotation with an absorption of about 1 dB. But no material has these properties in the visible at room temperature. The ferrimagnetic garnets, however, can have rotation-to-loss ratios of approximately 40° per decibel in the infrared, which gives an overall optical contrast of 10 percent. Philips Industries recently combined this effect with electrophotography to give a line printer with a resolution of 300 spots per inch.

The other major application of magneto-optic materials is in data storage. If the magnetization in a small region of a magnetic film, typically on the order of the diffraction limit, is reversed relative to its environment, then the contrast provided by the magneto-optic effect may be used for readout. Writing is generally accomplished by heating. In one scheme, the heating reduces the coercivity to the point at which a small bias field is sufficient to switch the spot. This application has been extant for over 20 years, but is only now becoming practical as a result of the availability of low-cost, high-power solid-state lasers and the discovery of low-noise media. The media consist of amorphous rare earth–transition metal films. A reasonable magneto-optic effect arises through the presence of the transition metal components, and the absence of grain boundaries is responsible for the low noise.

Magneto-optic recording combines the advantages of magnetic and optical recording: erasability, high areal density (120 megabits per square centimeter), no contact between head and medium, can be overcoated for protection, removable and exchangeable media, and use of pregrooving for efficient tracking. Estimates of the market for magneto-optic media range as high as $400 million in 1990, with the drive market close to $1 billion. The enormous growth potential has been recognized by the recording industry: NHK Teleflex-Morse Company (Japan) and Sony Corporation have demonstrated video disks for TV editing, and Sharp Corporation a digital system.

This emerging technology will require a great deal of supportive research, some of it very fundamental. For example, it will be necessary to determine the origin of the anisotropy in these films, whether the magneto-optic effect can be dramatically enhanced, and what governs the stability of these amorphous structures.

In addition to these promising areas, there are classes of materials that have strategic military value but less economic potential at present. For example, two decades ago the Department of Defense supported the development of microwave ferrites, and today 85 percent of that market is still military. Magnetostrictive sensors for sonar devices are a more recent example. Certain rare earth elements and alloys have extraordinarily large values of magnetostriction. If the resistivity of these materials could be increased significantly without affecting the magnetostriction, their frequency range could be greatly extended by suppressing eddy currents. Magnetic bubbles are yet another example. Although they have not been able to compete economically with semiconductor random access memories in most applications, their nonvolatility and ruggedness make them attractive for military and space applications. Bubble devices also have the potential for much higher storage densities utilizing domain walls.

The Committee on Magnetic Materials also considered semihard magnetic materials, microwave materials, and magnetic particles for marking. In all cases the markets are small and, except for microwave materials (which would provide a larger saturation magnetization and improved microstructure), existing materials appear to be adequate.

Conclusion

The committee identified several magnetic technologies with bright prospects. The generally promising outlook is attributable largely to the development of the new materials described in this article. These materials are also raising many fundamental questions, the answers to which may require entirely new techniques.

The committee has recommended that industry and government increase their investments in magnetics research. The manufacturers of permanent magnets, for example, might consider pooling their investments, as the major recording companies have done in establishing centers for recording at the University of California, San Diego, Carnegie-Mellon University, and the University of Santa Clara. We hope that the government will encourage more joint industry-university activities. The National Science Foundation, with its materials research laboratories and the National Magnet Laboratory, is in a strong position to influence the national effort.

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