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Perspectives on Permanent Magnetic Materials for Energy Conversion and Power Generation

LAURA H. LEWIS and FÉLIX JIMÉNEZ-VILLACORTA

Permanent magnet development has historically been driven by the need to supply larger magnetic energy in ever smaller volumes for incorporation in an enormous variety of applications that include consumer products, transportation components, military hardware, and clean energy technologies such as wind turbine generators and hybrid vehicle regenerative motors. Since the 1960s, the so-called rare-earth “supermagnets,” composed of iron, cobalt, and rare-earth elements such as Nd, Pr, and Sm, have accounted for the majority of global sales of high-energy-product permanent magnets for advanced applications. In rare-earth magnets, the transition-metal components provide high magnetization, and the rare-earth components contribute a very large magnetocrystalline anisotropy that donates high resistance to demagnetization. However, at the end of 2009, geopolitical influences created a worldwide strategic shortage of rare-earth elements that may be addressed, among other actions, through the development of rare-earth-free magnetic materials harnessing sources of magnetic anisotropy other than that provided by the rare-earth components. Materials engineering at the micron scale, nanoscale, and Angstrom scales, accompanied by improvements in the understanding and characterization of nanoscale magnetic phenomena, is anticipated to result in new types of permanent magnetic materials with superior performance.

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I. INTRODUCTION

MAGNETIC materials play a key role in modern life and are present in advanced devices and motors of every kind. Their unique ability to (1) enable the conversion of electrical to mechanical energy, (2) transmit and distribute electric power, (3) facilitate microwave communications, and (4) provide the basis for data storage systems make them indispensable to modern life. In particular, advanced permanent magnets—which maintain a large magnetic flux in the absence of a magnetizing field—underlie the operation of generators, alternators, eddy current brakes, motors, and relays. Among many applications, permanent magnets are found in computers, automobiles, motor scooters, consumer electronic products, medical products, and speakers/headphones. In particular, they are of vital importance to military applications as they add functionality to jet fighter engines, electronic countermeasure systems, missile systems, and satellite communication systems. Advanced permanent magnets are also integral parts of alternative energy technologies, such as those that harvest wind, wave, and tidal power. In this review article, a summary of the magnetism and materials science underlying historic, current, and future permanent magnets will

be provided and presented in the 21st-century context of global strategic materials supply and world demand.

II. TERMINOLOGY, MATERIALS REQUIREMENTS, AND HISTORICAL DEVELOPMENT OF PERMANENT MAGNETIC MATERIALS

While the optimal attributes of permanent magnets for advanced applications are easy to articulate, it is very challenging to engineer these properties into a material. “Technical,” or extrinsic, magnetic properties refer to those properties that are dependent on the magnetic materials’ microstructure and are defined at the temperature of interest. Specifically, in an ideal permanent magnet, a large remanent magnetic flux (“remanence” or B_r) must be maintained in the absence of a magnetic field and be matched with a large resistance to demagnetization (“coercivity” or H_c or intrinsic coercivity H_{ci}). The strength of a permanent magnet is quantified by the maximum energy product $(BH)_{max}$, a figure of merit calculated as the optimal product of the remanence B_r and the coercivity H_c manifest in the second quadrant of the $(B-H)$ hysteresis loop (Figure 1). In contrast, “intrinsic” magnetic properties are those determined by the crystal structure and composition of the material, and ideally are insensitive to the microstructure of the material. Important intrinsic properties are the saturation magnetization M_s and the magnetic ordering temperatures: the ferromagnetic Curie temperature T_C and its antiferromagnetic counterpart, the Néel temperature T_N . These parameters

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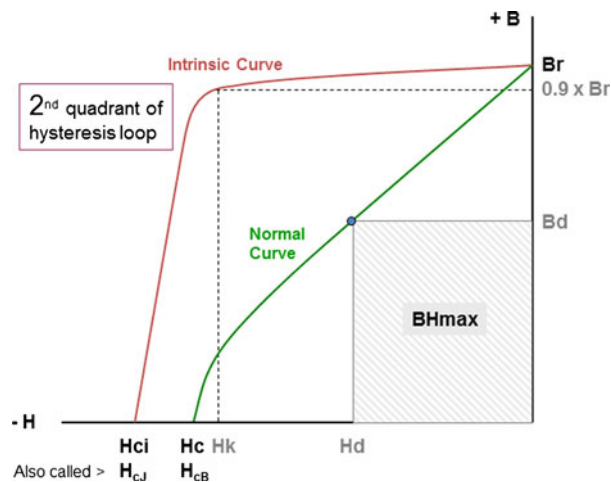


Fig. 1—The second quadrant of the intrinsic magnetic (B - H) hysteresis loop, identifying important parameters such as magnetic remanence (B_r), intrinsic coercivity (H_{ci}), and maximum energy product (BH)_{max} that quantifies the energy stored, or the strength, of a permanent magnet. (Figure courtesy of Arnold Magnetic Technologies.).

define the temperature at which the ambient thermal energy becomes sufficiently large to destroy the effective magnetic ordering within the material. The magnetic anisotropy field H_K defines the strength of magnetic field necessary to direct magnetization in a unit cell from a low-energy direction (the magnetically “easy” axis) to a high-energy direction (the magnetically “hard” axis). The magnetocrystalline anisotropy energy E_A , which is determined by the local interatomic bonding environment surrounding a magnetic atom, specifies the energy per unit volume necessary to direct the magnetization from the easy axis to the hard axis in a crystal. The magnetocrystalline anisotropy energy is approximated in a uniaxial system as a power series of the form:

$$E_A = \sum_n K_n \cdot \sin^{2n}(\theta) \quad [1]$$

where K_n is the uniaxial anisotropy constant for the n th direction in the crystal and θ is the angle between the magnetization vector $\vec{M}$ and the easy axis. Typically, it is appropriate to use only the first term of the expansion:

$$E_A = K_1 \sin^2(\theta) \quad [2]$$

where K_1 is the first anisotropy constant. If magnetic reversal of the material occurs only through rotation of the magnetic vector from one easy axis to another against the magnetocrystalline anisotropy, then a maximum coercivity is realized, and is given by

$$H_{C,max} = \frac{2K_1}{M_S} \quad [3]$$

Incorporating these ideal circumstances provides an expression for the maximum theoretical energy product (BH)_{max}, in cgs units (MGOe), for a permanent magnet as

$$(BH)_{max} = \frac{(4\pi M_S)^2}{4} \quad [4]$$

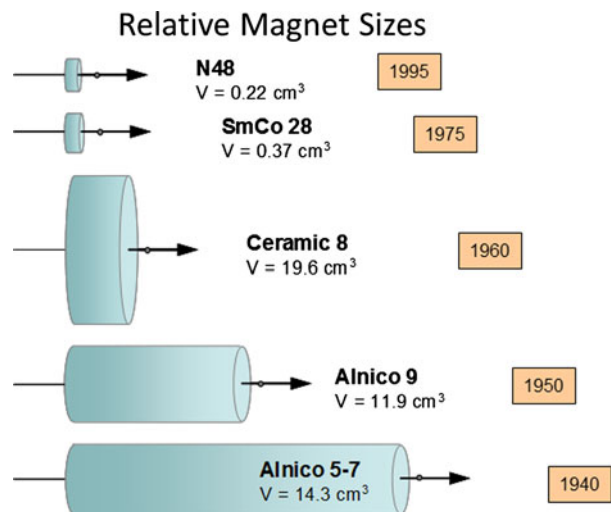


Fig. 2—Relative magnet size and shape of various permanent magnet materials to generate 1000 G at 5 mm from the pole face of the magnet. (Figure courtesy of Arnold Magnetic Technologies.).

Thorough discussions of these magnetic parameters and of magnetic units are provided in textbooks covering the subject.^[1–3] Ideally, in a high-performance permanent magnet, all of these parameters should be insensitive to temperature so as to maintain their integrity in the elevated-temperature operating environments of motors and generators. Thus technologically relevant magnetic materials should have a Curie temperature T_C well above room temperature. Furthermore, the constituent materials should ultimately be inexpensive, easy to process, lightweight, nontoxic, and corrosion resistant. Currently, the world’s strongest “supermagnets,” based on the rare-earth (RE)-based intermetallic compounds $Nd_2Fe_{14}B$ and $SmCo_5$, can exhibit maximum energy products on the order of 56 MGOe (445.7 kJ/m³) with remanences $B_r \sim 14$ kG (1.4 T) and typical intrinsic coercivities $H_{Ci} \sim 10$ kOe (796 kA/m), in cgs (SI) units.^[3] For comparison, rather bonded weak magnets, such as novelty or souvenir magnets that are commonly displayed on refrigerators, possess a typical energy product of less than 1 MGOe (8 kJ/m³).^[4]

Through the centuries, the perpetual technological objectives of reduced device size and increased efficiency dictates that incorporated magnets be as small, and therefore as strong, as possible. Stronger magnets with higher energy products can furnish the same energy density, but in a much smaller package, than weaker magnets, as illustrated in Figure 2. A brief historical overview of the chronological development of permanent magnets is furnished in the following sections. Many excellent overviews of the history of permanent magnets are available for interested readers.^[5]

A. Early Permanent Magnets

Magnet development has its origins in lodestones, which are magnetic rocks that consist of the iron-oxide mineral magnetite (Fe_3O_4). These naturally derived magnets are found in many places on the Earth’s surface and were initially employed to attract metallic iron ore, which

became available around 1200 B.C. through the metallurgical extraction process of smelting.^[5] Archaeologists determined that the Chinese employed lodestones for ceremonial or navigational purposes around 1000 A.D., 200 or 300 years earlier than their first appearance in Western civilization records around 1300 A.D.^[6]

B. Alnico Magnets

An invigorated drive for stronger and, thus more efficient, magnetic materials was launched in 1917 with cobalt steel magnets that provided enhanced coercivity values relative to those of the earlier magnetic workhorse, quench-hardened carbon steels.^[7] An important advance was announced in 1930 with the introduction of metallic Alnico magnets (so-called by their majority composition of iron, aluminum, nickel and cobalt, with minority additions of Cu, Ti, and/or Si) with a coercivity double that of the best magnet steels of the era.^[8–10] The Alnico magnets were one of the first so-called “fine-particle” magnets, possessing a microstructure consisting of micron- or submicron-scale ferromagnetic particles dispersed in a weakly magnetic matrix. The basic Alnico alloys derive their magnetic strength by virtue of a phase separation in the cast alloy into ferromagnetic FeCo-rich and weakly magnetic NiAl-rich phases precipitated from the high-temperature homogeneous composition. The decomposition rate is sufficiently high only at elevated temperature, and these two phases develop by a gradual fluctuation and periodicity in composition—spinodal decomposition—rather than by more typical nucleation and growth processes.^[11] In addition to the formation of isotropic microstructures in Alnico alloys, an anisotropic microstructure containing elongated particles may be attained by the application of a magnetic field during the annealing processes, resulting in the formation of elongated FeCo precipitates in the $\langle 001 \rangle$ directions, aligned parallel to the direction of the applied magnetic field.^[12,13] This processing procedure creates superior Alnico alloys with maximum energy products in the range of 5 to 7 MGOe (40 to 56 kJ/m³).^[14,15]

The significance of Alnico magnet development was that it marked the beginning of a new way of thinking about magnetic materials, in which multiple phases were combined, according to fundamental physical principles, to yield a new composite magnetic material with attributes superior to those of the individual components taken alone. In this manner, development of the Alnico magnets was coincident with the development of materials science as an interdisciplinary field of study, extending beyond the historical field of metallurgy in that relationships among synthesis, structure, function, and properties could be engineered to defined parameters. As discussed in Section VI, future generation supermagnets have their origins in the science and technology of these pre-World War II magnets. Today, Alnico remains a leading material in the permanent magnet industry for lower-value applications by virtue of its reliable performance and outstanding technical magnetic characteristics, such as a low-temperature coefficient of coercivity and high flux density, accompanied by desirable low cost.^[16,17]

C. Hexaferrites

In response to the need for nonmetallic, electrically insulating magnetic materials, the Philips Company (Eindhoven, the Netherlands) announced the first commercial ceramic magnets in 1952.^[18] These magnetic iron-oxide compounds possess a rich compositional spectrum with prototypical composition $\text{MO} \cdot 6\text{Fe}_2\text{O}_3$ or, equivalently, $\text{MFe}_{12}\text{O}_{19}$, where M represents the divalent metals Ba, Sr, or Pb. The barium-containing composition became the highly successful permanent magnetic material known as barium ferrite or barium hexaferrite. These ferrite magnets possess a rather low $(BH)_{\text{max}}$, but they are inexpensive, chemically inert, easy to process, and are very important commercially.

The hexaferrites are ferrimagnetic, with both ferromagnetic (FM) and antiferromagnetic (AF) coupling between atomic moments. The magnetic coupling depends on the specific crystallographic position of Fe ions, through oxygen-mediated indirect superexchange interactions. Such FM or AF coupling is strongly determined by the arrangement, in terms of distance and angle, of Fe-O-Fe bonds, yielding a resultant net moment of $40 \mu_B$ per unit cell (at 4.2 K), assuming an atomic moment of $5 \mu_B/\text{Fe}$ atom. However, one main drawback is the evolution of magnetization with temperature of this class of magnets; magnetization values decrease with increasing temperature much faster than the classic Brillouin evolution, and thus, these magnets exhibit relatively low magnetization values at room temperature. This disadvantage is offset by relatively high Curie temperatures ($T_C \sim 950 \text{ K}$ to 975 K [1223°C to 1248°C]) obtained in these compounds. The magnetocrystalline anisotropy in hard ferrites produces an easy magnetization direction along the hexagonal c -axis of the unit cell. Additionally, since the saturation magnetization M_S decreases more rapidly than does the overall anisotropy constant K with increasing temperature, an unusual dependence of coercivity upon temperature is obtained. This property results in a gradual increase of the anisotropy field H_A with increasing temperature, even above room temperature, fostering good performance and enhanced properties for high-temperature applications. Broadly speaking, this family of magnetic oxide materials may be considered as the original ancestors of the class of materials known as the “complex oxides,” in which the interplay of variety of electronic, magnetic, and structural attributes in transition-metal oxide compositions gives rise to unusual properties. Complex oxides remain an area of intense research activity today with both fundamental and applied interest as battery cathode materials, spintronic materials, microwave communication materials, and high- T_C superconductors.^[19–23]

III. THE GOLDEN AGE OF RARE-EARTH MAGNETS

A. SmCo Magnets

Permanent magnet development accelerated and took an unexpected turn in the mid-1960s, under the direction

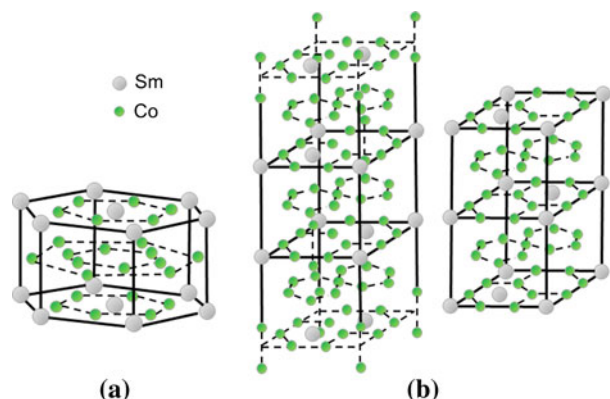


Fig. 3—Basic crystal structures of RE-TM compounds (a) near the 1-5 stoichiometry (CaCu₅-type) and (b) 2-17 stoichiometry: rhombohedral Th₂Zn₁₇-type structure (left) and hexagonal Th₂Ni₁₇-type structure (right).

of Dr. Karl J. Strnat at the U.S. Air Force Materials Laboratory at Wright-Patterson Air Force Base, later at the University of Dayton in Dayton, Ohio. Inarguably, this occurrence marked the beginning of the reign of the rare-earth “supermagnets.” Strnat’s team of researchers reported high energy products in ferromagnetic intermetallic phases of the types RE(TM)₅ with the hexagonal CaCu₅-type crystal structure (space group *P6₃/mmm*). Here RE is a rare-earth element or mixture, in particular containing Y, Ce, Pr, Sm, and (TM) is a transition metal, namely cobalt^[24,25]; see Section V. At the time, special attention was paid to the extremely large magnetic noted in these compounds donated by the rare-earth components; in particular, initial characterization of the compound SmCo₅ yielded an energy product of 5.1 MGOe (40.6 kJ/m³), later optimized to approximately 18 MGOe (143.2 kJ/m³), with higher energy products reported in laboratory tests.

Continued exploration of the rare-earth/transition-metal alloys resulted in the introduction in 1972 of a new rare-earth-based intermetallic compound RE₂(TM)₁₇. These so-called “2-17” compounds are crystallographically related to the CaCu₅-type “1-5” compounds but offer a higher transition-metal content and, thus, a higher magnetization per unit weight (Figure 3). The compound Sm₂(Co,Fe)₁₇ was reported to possess a theoretical maximum energy product up to 60 MGOe (477.5 kJ/m³).^[26] Equilibrium RE₂Co₁₇ intermetallic compounds, known as the 2-17 compounds, can exist in the hexagonal Th₂Ni₁₇-type structure (for heavy RE, space group *P6₃/mmc*) adopted by the Sm₂Co₁₇ family of compounds or in the rhombohedral Th₂Zn₁₇-type structure (for light RE, space group *R-3m*). Eventually the SmCo magnets were commercialized with energy products in the range 22 MGOe to 32 MGOe (175 to 255 kJ/m³), depending upon precise composition. This attribute of high energy product combined with a favorable Curie temperature (~1000 K [~750 °C])^[27] makes them the premium choice for high-temperature applications today.^[28] The Th₂Ni₁₇-type crystal structure, adopted by Sm₂Co₁₇, may be derived from the CaCu₅-type structure by a chemically ordered

replacement of one rare-earth atom by a pair (“dumbbell”) of two smaller Co atoms in every three formula units.^[29] Unfortunately, the only intermetallic equilibrium phase that forms with iron in this family of compounds is RE₂Fe₁₇, with RE = Pr or Nd.^[30,31] The general composition (Pr,Nd)₂Fe₁₇ has a low Curie temperature and a low magnetocrystalline anisotropy, so it is not viable as a permanent magnet material.^[32] However, in 1990, Coey and Sun^[33] reported that introduction of interstitial nitrogen to form Sm₂Fe₁₇N₃ fostered a substantial enhancement of the technical magnetic properties of such compounds. This modification resulted in an increased Curie temperature (*T_C* ~ 750 K (~477 °C)) and a transition of the magnetocrystalline anisotropy from easy planar to uniaxial^[34] associated with nitrogen incorporation occupying the 9e interstitial sites around the Sm atoms in the rhombohedral structure.^[35] A theoretical energy product of approximately 59 MGOe (470 kJ/m³) is anticipated for this interstitially-modified compound,^[31] although experimental values are smaller, ~20 MGOe (~160 kJ/m³).^[36,37] Other RE-TM compounds based on the CaCu₅-type structure may be constructed by systematically replacing portions of the RE atoms residing in the Ca sites by dumbbell pairs of TM atoms. This process induces a lattice distortion (typically an *a*-parameter contraction and a *c*-parameter expansion) and produces the following compounds: the RE(TM)₁₂ (“1-12”) compound *via* TM dumbbell substitution for one RE atom in every two formula units^[38] and the RE₃(TM)₂₉ (“3-29”) compound *via* TM dumbbell substitution for two RE atoms in every five formula units, or by alternate stacking of the “2-17” and “1-12”^[39] structures. The “1-12” compound exhibits a ThMn₁₂-type tetragonal structure (space group *I4/mmm*),^[40] whereas the “3-29” compound, first reported in its precise stoichiometry, crystal symmetry, and magnetic properties by Kalogirou *et al.*,^[41] is monoclinic (space group *A2/m*).^[42] In both cases, substitution of a TM atom by a second TM (such as Ti, V, or Mn) stabilizes the phase.^[43]

Finally, the intermediate chemically disordered SmCo₇ (TbCu₇-type structure) phase has a large homogeneity region and may be attained^[28] though continual replacement of RE atoms by dumbbell pairs of Co atoms to create a series of compounds that span the Co:RE compositional range from Co:RE = 5 to 8.5. These magnets are synthesized by liquid phase sintering techniques^[44] and are subjected to a series of isothermal annealing steps to optimize the microstructures.

B. Nd₂Fe₁₄B Magnets

As impressive as the technical magnetic properties of the RE(Co)₅ or RE₂(Co)₁₇ magnets were, geopolitical events in the late 1970s forced the development of permanent magnets to take a new direction. According to the U.S. Geological Survey (USGS), the Democratic Republic of Congo, known as Zaire prior to 1997, produces 60 pct of the world supply of cobalt.^[45] Political instabilities in the region around 1978 severely

jeopardized the global supply of cobalt and greatly increased its cost, prompting the U.S. Congressional Budget Office in 1982 to publish an analysis of policy options for this strategic mineral,^[46] with the recommendation to “reduce significantly U.S. vulnerability to cobalt shortfalls, both by expanding supply and improving the performance of cobalt substitutes.” Against this backdrop, a new iron-based supermagnet—Nd₂Fe₁₄B (also known as NdFeB, “Neo” and/or 2-14-1)—was quasi-simultaneously developed by General Motors (GM), Sumitomo Special Metals Co., Ltd. (Sumitomo), and by the U.S. Naval Research Laboratory (NRL). These three groups each took a separate developmental path to this important intermetallic compound, and a review of the patent positions filed around that time shows that the intellectual property environment was, and still remains, very complex.^[47–49] It is interesting to note that the addition of boron, a well-known glass-forming element, to the NdFe composition was key to the discovery of this important compound. Researchers at the NRL and General Motors chose to rapidly solidify the NdFeB composition, with the hopes of achieving a fully amorphous precursor that could be carefully annealed to a fine particle state, much like the Alnico microstructure. Instead of creating an amorphous material, the addition of boron led to the new ternary intermetallic compound, Nd₂Fe₁₄B. Indeed, the 29th Magnetism and Magnetic Materials Conference held in Pittsburgh, PA in 1983 featured talks on intermetallic RE-Fe-(B,Si) compounds with near-record energy products from no less than four independent research groups.

The discovery of the crucial class of RE₂Fe₁₄B materials not only launched more than three decades of focused research to tailor intermetallic magnetic materials through understanding structure–property relationships but also furnished a continually growing number and variety of applications incorporating this material. The RE₂Fe₁₄B compound can be formed from almost all the lanthanides as a line compound, with a rather narrow compositional homogeneity range. The compound forms in an elegant and very complex tetragonal crystal structure (space group $P4_2/mnm$) with 68 atoms and 6 crystallographically distinct iron sites per unit cell.^[50] It can be noted that the 2-14-1 structure, shown in Figure 4, features staggered, canted hexagonal nets of iron atoms, spaced by planes containing rare-earth and boron atoms.

NdFeB magnets were first produced in the mid-1980s using the rapidly solidified synthesis method at GM and the sintered synthesis method at Sumitomo (later merged with Hitachi Metals in 2007). The rapid solidification method of melt spinning rapidly cools liquid metals at rates in the range 10^4 to 10^7 K/s,^[51,52] to attain nanocrystalline or largely amorphous NdFeB ribbons that, upon annealing, devitrify to a high-coercivity nanocrystalline structure with energy products in the range 5 to 50 MGOe (40 to 400 kJ/m³),^[53] depending upon detailed composition and postsolidification processing. In order of increased performance and cost, these powders may be mixed with epoxy to form bonded magnets (isotropic “MQ-1”-type

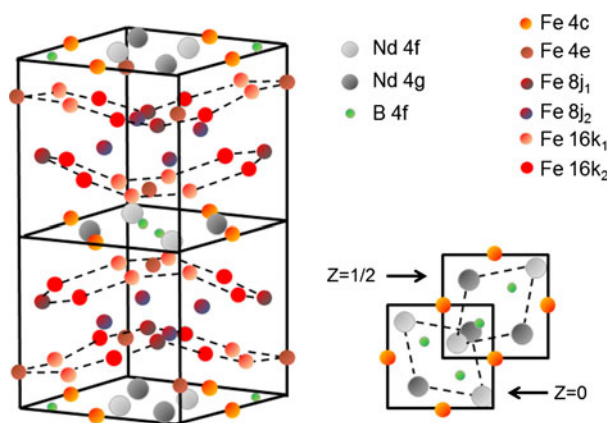


Fig. 4—The crystal structure of Nd₂Fe₁₄B. A view looking down the tetragonal *c*-axis is shown on the right.

magnets), hot-pressed to form dense compacts (isotropic “MQ-2”-type magnets), or thermomechanically deformed (aligned “die-upset” or “MQ-3”-type magnets).^[54] Sumitomo, on the other hand, focused on NdFeB magnet production using a sintering process applied to micron-scale powder derived from pulverized ingots that are magnetically aligned and liquid-phase sintered into dense compacts. As the structural scales of these two types of 2-14-1 magnets are very different, materials design and engineering strategies to optimize the structure-sensitive (technical) magnetic properties to create ultra-strong magnets is likewise very different. An overview of control of structure-property relationships is beyond the scope of this article; interested readers are referred to the excellent review article by Herbst.^[50] While these magnets could achieve close to the theoretical energy product, they have only a marginal Curie temperature in the vicinity of 600 K to 700 K (300 °C to 400 °C), with operating temperatures typically restricted to 400 K (~150 °C). Furthermore, NdFeB magnets are plagued by both brittleness and a large propensity for corrosion.

IV. ADVANCED PERMANENT MAGNETS: THE 21ST-CENTURY CONTEXT

The unbeatable combination of low price and spectacular technical magnet properties made NdFeB the enabling magnet of choice for higher end applications. Table I, adapted from Reference 55, shows a listing of products and applications that contain NdFeB magnets. Applications that are anticipated to show accelerated growth over the next decade, started in Table I, are hard disk-drive/CD/DVD components, the so-called “electric bicycles” or motor scooters that are currently very prevalent in Asia, hybrid vehicles/electric vehicles, and wind power generators.

By the mid-1990s, there was a general consensus that the vigorous research efforts in the United States’ industrial, governmental, and university laboratories to improve the magnetic properties of the “Neo” magnets were yielding only incremental advances; no major

Table I. A Selection of Applications Utilizing Advanced Permanent Magnets, Typically Nd₂Fe₁₄B (Adapted from Ref. 45)

Category	Application Examples
Computer and office automation	*disk drive spindle motors and voice coil motors (computer hard drives) CD-ROM spindle motors and pick-up motors printer and fax stepper motors printer hammer copy machine rollers
Automotive & transportation	starter motors electric steering sensors electric fuel pumps instrumentation gauges brushless DC motors *electric bicycles
Consumer electronics	VCRs and camcorders cameras speakers, headsets microphones pagers DVD players watches cell phones
Appliances & systems	portable power tools household appliance motors scales air conditioners water pumps security systems
Factory automation	magnetic couplings pumps motors servo motors generators bearings
Medical industry	magnetic resonance imaging equipment surgical tools medical implants
Alternative energy	*hybrid/ electric vehicles *wind power systems wave, tidal power systems power generation systems energy storage systems
Military	weapons systems vehicles, watercraft, avionics precision-guided munitions, communications systems, radar satellites

*Technologies that are anticipated to experience continued rapid growth and expansion.

breakthrough advances were expected in the magnetic performance because technologists were able to harness almost all of the theoretically predicted magnetic power of the NdFeB family of magnets. This conclusion, combined with the low price and low profit margin of the raw materials, prompted General Motors management to sell off all of its magnet and motor operations, including all their automotive components businesses by the year 2000. In particular, GM's Magnequench-Delco

Remy Division, created in 1986 to commercialize the Nd₂Fe₁₄B-family of magnetic materials, was acquired in 1995 by a trio of Chinese-based entities who opened a magnetic production facility in Tienjin, P.R. China, in 1998.^[56] Other magnet producers such as Crucible Magnetics, Hitachi Magnetics, and Ugimag also closed their U.S. operations during this time. Aside from a few smaller specialty magnet producers, all capability for U.S. rare-earth magnet manufacture was transferred to China. Accompanying this exodus was an atrophy of U.S.-based research on rare-earth magnets and an effective "brain drain" of scientists and engineers in the field of high-energy product permanent magnet materials.

Today, the choice of permanent magnet material for a given application is based on a balanced consideration of price and performance. While the hexaferrite magnets are much weaker than the rare-earth-based magnets, they dominate global sales by virtue of their much lower price, representing 85 pct (by weight) of all permanent magnets sold. Nonetheless, the design goal of lower device weight and smaller size makes the NdFeB family of magnets the advanced magnet of choice, representing over 50 pct of total magnet sales, on a dollar basis.^[57] Figure 5(a) illustrates the quasi-exponential growth of permanent magnet sales, in dollars as a function of time from 1985 projected to 2020 for four classes of magnet type: Alnico, SmCo, ferrite, and NdFeB. The fastest growth is noted for NdFeB magnets, with a projection of NdFeB magnet sales to over \$17 billion by 2020.^[57]

The sales trend illustrated in Figure 5(a) is complemented by the data in Figure 5(b) that show the price trend of neodymium metal from January 2010 to the mid-February 2012. A surprising and alarming spike in the price per kg of Nd metal during the second half of 2011 by over 800 pct is noted. The origin of this unprecedented price increase for neodymium metal, combined with the increasing demand for NdFeB magnets, is known popularly in the press as the "rare earth crisis".^[58,59] Put simply, the demand for rare-earth elements for many applications, including materials for military applications and alternative energy technologies, is currently outstripping supply. The subsequent partial reduction in the price of Nd noted in the first quarter of 2012 emphasizes the price volatility of this strategic element. Distributed according to global geological patterns, rare-earth ores of relevance to the permanent magnet market are located primarily in China, with China possessing 95 pct of the world rare-earth oxide production in 2008.^[60] As of 2010, most of the global REE production remains in China, with estimates ranging from 93 to 97 pct.

It is projected that as the demand for permanent magnet ores grows, rare-earth oxide prices overall will continue to climb by as much as 200 pct.^[60] In late August 2009, it was revealed that China's Ministry of Industry and Information Technology will likely exercise tighter restrictions on rare-earth ore exports and institute strict curbs on rare-earth mines.^[61] These price increases are attributed to the goal of the Chinese government to control its reserves of rare earths in response to domestic economic priorities as well as its intention to clean up existing environmental issues

Table II. Rare Earth Elements: 2010 World Production and Reserves*

Country	Mine Production	Pct of total	Reserves (Million Metric Tons)	Pct of Total
United States	none	—	13.0	13
China	130,000	97.3	55.0	50
Russia and former Soviet Union countries	not reported	not reported	19.0	17
Australia	not reported	not reported	1.6	1.5
India	2700	2	3.1	2.8
Brazil	550	0.42	small	—
Malaysia	350	0.27	small	—
Other	N/A	22	—	20
Total	133,600	—	1100	

*Adapted from Ref. 65.

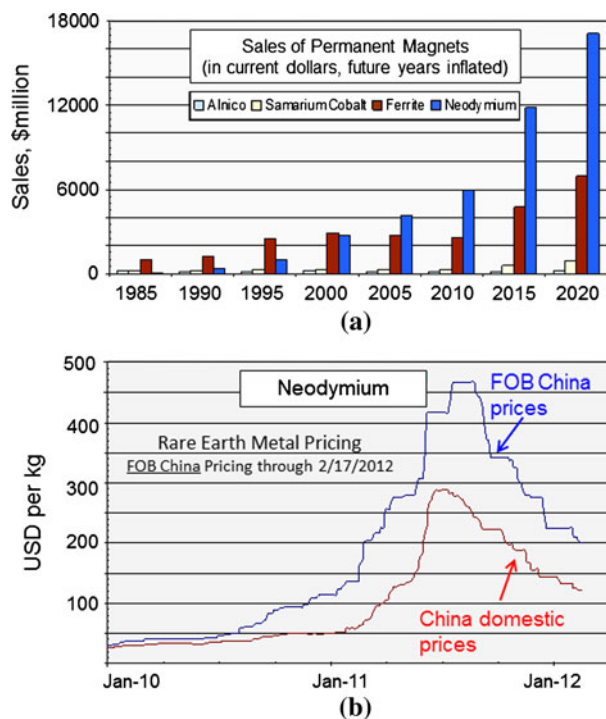


Fig. 5—(a). Growth of permanent magnet sales, in dollars as a function of time from 1985 projected to 2020 for four classes of magnet type: Alnico, SmCo, ferrite, and NdFeB. (b) Evolution of Neodymium metal price in the last 2 years. (Figure courtesy of Arnold Magnetic Technologies.).

related to past mining practices and preventing new environmental issues. Quotas have been put in place for the existing Chinese mines, but their impact going forward is not clear.^[62] In this context, the need to develop new high-energy product magnets that are free of rare-earth elements is realized.

V. THE RARE-EARTH ELEMENTS

The so-called rare-earth “supermagnets” derive their superior properties from the high magnetization provided by the 3*d* transition metal crystalline sublattice, composed of Fe and Co, and the extremely strong

magnetocrystalline anisotropy field H_K provided by the rare earth 4*f* electrons. The rare-earth elements (REEs) encompass a family of 17 chemical elements in the periodic table: scandium (Sc), yttrium (Y), and the 15 lanthanides. The “light” rare earth elements are composed of elements with atomic numbers $Z = 57$ (lanthanum, La) through 61 (promethium, Pm), the “medium” REEs range from $Z = 62$ (samarium, Sm) to $Z = 64$ (gadolinium, Gd), and the “heavy” REEs encompass $Z = 65$ (terbium, Tb) through $Z = 71$ (lutetium, Lu). Despite their appellation, most rare-earth elements are not particularly rare in the Earth’s crust; according to the USGS, cerium is the 25th most abundant element of the 78 common elements in the Earth’s crust (60 parts per million), with the elements thulium and lutetium as the least abundant rare-earth elements (0.5 part per million) but are still much more plentiful than gold.^[63] The rare-earth elements are distributed in the Earth’s crust according to global geological patterns and are found in specialized deposits as ore that contains subsets of these elements. Their global distribution is very uneven, with most of the world’s geologic supply originating from only a handful of sources as illustrated in Table II. Figure 6 shows the geological distribution of the rare-earth elements.^[64,65] Estimates of global rare-earth reserves vary from source to source and are difficult to quantify.

The rare-earth metals are all quite chemically similar and are thus very difficult to separate from the ore as pure elements. Of particular importance to advanced permanent magnet production are the elements Pr ($Z = 59$), Nd ($Z = 60$), Sm ($Z = 62$), and Gd (for specialized applications; $Z = 64$); extremely important REEs are Tb ($Z = 65$) and Dy ($Z = 66$). Overall, rare-earth elements are distinguished by a unique arrangement of electrons that lends special properties to materials containing REEs. Across the rare-earth, or lanthanide, series in the periodic table, electrons are added to the 4*f* electronic shell that is very localized near the atomic nucleus and resides within, and at a lower energy, the full 5*s* and 5*p* orbitals. Due to their spatial localization, 4*f* electrons do not participate to an appreciable extent in chemical bonding; however, they do possess a very strong quantum-mechanical spin-orbit interaction between the various electronic angular momenta in the

Table III. Sources of Magnetic Anisotropy

Phenomenon	Source or Definition	Magnetic Example
Magnetocrystalline anisotropy	spin-orbit interaction intrinsic to the specific crystal structure	$\text{Nd}_2\text{Fe}_{14}\text{B}$
Pinning of domain walls	obstruction of the motion of the boundary between magnetic domains by inclusions	alnico permanent magnets of iron-aluminum-based matrix and cobalt-rich precipitates
Shape anisotropy	minimization of stray fields through alignment of magnetization with acicular axes in macroscopic particles.	CrO_2 -based recording media; CoCr-based metallic recording media.
Stress anisotropy or magnetostriction	arises from the strain dependence of the anisotropy constants; also a product of the spin-orbit interaction	terfenol-D, used in magnetomechanical sensors and actuators
Exchange anisotropy	quantum mechanical exchange at the ferro/antiferromagnetic interface.	oxidized cobalt particles: ferromagnetic cobalt core with an antiferromagnetic CoO shell.

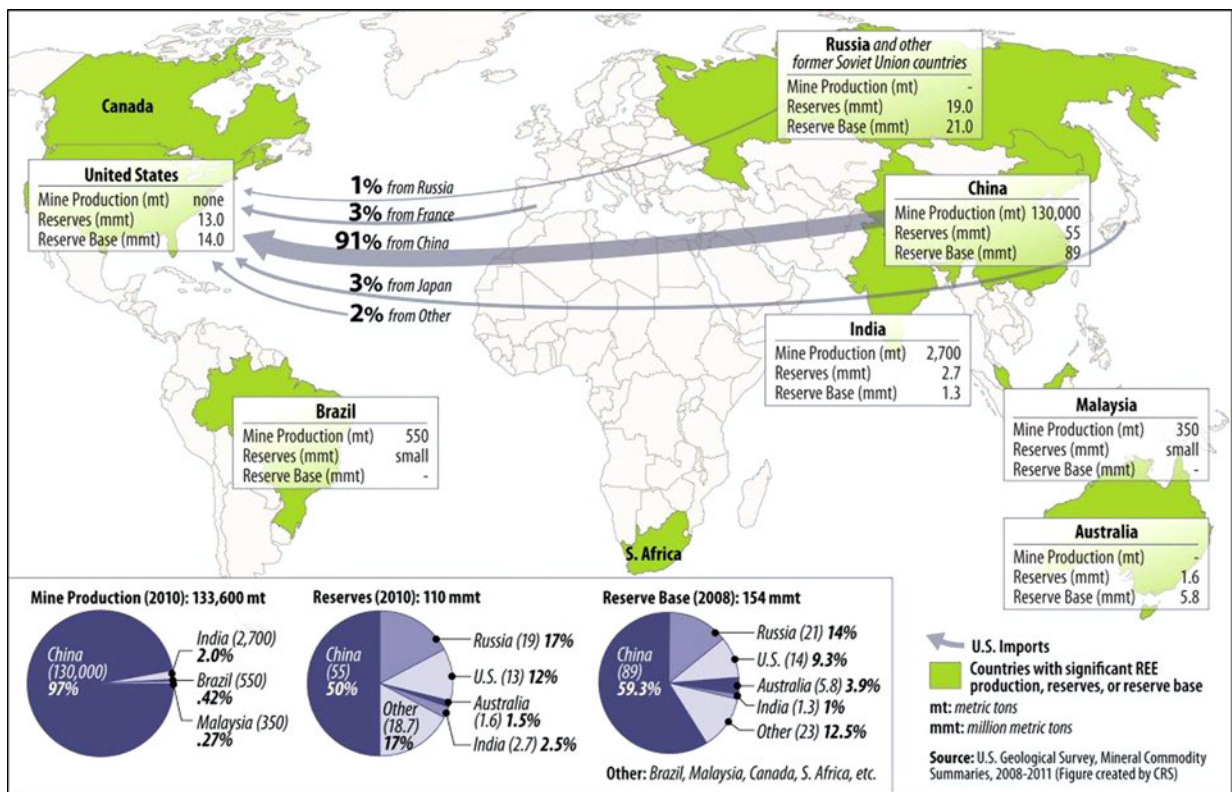


Fig. 6—World production, reserves and U.S. imports of rare-earth elements. (from Ref. 65).

atomic environment surrounding magnetic ions in a permanent magnet system.^[66,67] This property lends incredible magnetocrystalline anisotropy magnets made with REEs. The spin-orbit interaction is a relativistic effect and is particularly large in heavier elements, such as the rare-earth elements, where the energy of the orbiting electrons is a significant fraction of their rest-mass energy. This interaction results in a so-called single-ion anisotropy that describes the tendency for the magnetic moment to lay along specific crystal axes in the system, donating strong magnetocrystalline anisotropy.^[66,68–72]

VI. FUTURE SUPERMAGNETS

It is noted that REEs are essential ingredients for the synthesis of today's best high-energy product permanent magnets. However, in order for the United States to satisfy its demand for advanced permanent magnets to power the technology underlying its strategic military, alternative energy, and consumer product demands, it is clear that new materials design paradigms for the creation of high-energy-product magnets with low or zero rare-earth content must be developed.^[58–60] Partially due to the exodus of the rare earth-magnet

processing industry in the mid-1990s to China, little rare-earth expertise remains in the United States.^[61] Thus, it will be necessary to train future scientists and engineers in the field of advanced magnetic materials. Additionally, it is anticipated that new rare-earth mining operations will be developed, and existing operations will be optimized^[64] to address this situation.

From a materials engineering standpoint, the goal of achieving rare-earth-free permanent magnetic materials with high-energy products $(BH)_{\max}$ means that the principal source of the exceptional anisotropy, the magnetocrystalline anisotropy arising from the $4f$ electronic state,^[73] is no longer available for exploitation. While it is not possible to find or create elemental replacements for rare earth elements, it is anticipated that materials scientists may be able to engineer the magnetic signature of REEs—a very large magnetic anisotropy—into other magnetic materials systems by control of the crystal structure, the nanostructure and/or the microstructure of alloys and compounds composed of common and plentiful elements.^[74]

A. Magnetic Anisotropy Options

To account for the loss of robust magnetocrystalline anisotropy conveyed by rare-earth components, it is necessary to harness all other known forms of magnetic anisotropy to confer a high coercivity H_C and yield a high energy product $(BH)_{\max}$ magnet. It is clear that other anisotropy sources, in addition to that furnished by magnetocrystalline anisotropy, must be exploited to provide coercivity to the rare-earth-free alloys. In many cases, through careful metallurgical manipulation of a microstructure or nanostructure, it is indeed possible to tailor the coercivity of an alloy *via* the introduction of other forms of anisotropy.^[75] In addition to the previously introduced magnetocrystalline anisotropy, other types of anisotropy and/or coercivity sources include domain wall pinning,^[76] shape anisotropy,^[77] stress anisotropy,^[1] and exchange anisotropy.^[78] These magnetic anisotropy sources, along with illustrative examples, are described in Table III; general details regarding these phenomena may be found in References 1 through 3.

Iron and its ferromagnetic alloys are an important place to start: The alloy $\text{Fe}_{65}\text{Co}_{35}$ possesses the largest magnetic moment ($\sim 2.5 \mu_B/\text{atom}$) among the transition metal alloys and has a Curie temperature in excess of 1200 K (900 °C).^[79] Thus, from a permanent magnetic alloy design point of view, iron must be a main constituent in these proposed next-generation permanent magnets. However, the high-symmetry (Fe,Co) cubic crystal structure provides in an intrinsically low magnetocrystalline anisotropy. With an anisotropy field H_K of ~ 400 Oe (31.8 kA/m) and in the absence of inclusions to pin domain walls, the coercivity of pure Fe is only a few oersteds. Larger coercivities can be generated in iron-based alloys by the introduction of a second, nonmagnetic phase to pin magnetic domain walls in the material, as examined analytically by Kittel.^[80] Inclusion-hardened magnets, typically martensitic steels, have maximum coercivities in the range of

a few hundred oersteds. The introduction of shape anisotropy raises the maximum coercivity to close to 1000 Oe (79.6 kA/m) in the Alnico materials previously introduced in Section II.

A selection of six novel magnetic materials systems is described in the following sections that hold potential for the development of rare-earth-free magnets with a high energy product, high Curie temperature, and good chemical and thermal stability. These six systems, identified as i) through vi) below, are under current exploration in various research laboratories around the world and are divided below into two categories that describe the inherent materials development challenge to engineer magnetic anisotropy. These two categories are category I: nanostructural and microstructural development, and category II: crystal structure development. Successful synthesis and transition of a promising rare-earth-free, high $(BH)_{\max}$ permanent magnetic nanocomposite system from the lab to the production line and out to the world will require successful attainment of both of the engineering challenges in categories I and II.

Category I: Nanostructural and microstructural development in permanent magnetic nanocomposites with i) exchange spring or ii) exchange bias behavior.

Category II: Crystal structure development to realize high-anisotropy magnetic compounds: iii) α'' - Fe_{16}N_2 ; iv) L_{10} -type FeNi, v) L_{10} -type MnAl(C,B), and vi) $\text{Co}_3\text{C}/\text{Co}_2\text{C}$ nanophases.

It is to be emphasized that advancement of the above materials systems as rare-earth-free permanent magnets is an extraordinarily difficult challenge, requiring dedicated, focused, and concerted interdisciplinary research and development carried out by experienced teams of metallurgists, computational experts, solid-state physicists, solid-state chemists, and materials engineers—this quest is truly a high-risk/high pay-off endeavor and, in the absence of disruptive breakthroughs, will likely take many years to achieve.^[81]

Category I: Nanostructural and Microstructural Development of Permanent Magnetic Nanocomposites.

Permanent magnet nanocomposites are magnetic materials composed of at least two magnetic phases of complementary magnetic character that are combined at the nanoscale to exploit the best properties of each phase; in this manner, the magnetic behavior of the composite is superior to that of either component taken separately.^[82] This synthesis strategy is a direct extension of the materials development strategy employed for the Alnico magnets over 80 years ago but using 21st-century tools and new understanding of nanoscience and nanotechnology to engineer magnetism at the nanoscale. The operative important force at the nanoscale in magnetic materials is the quantum mechanical exchange force (exchange interaction) that describes the expectation value of the energy between two or more identical electrons when their wave functions overlap. Thus, these types of magnets are also known as “exchange-spring” magnets or “exchange-bias” magnets, emphasizing the quantum-mechanical origins of their functionality (Figure 7). The optimal structural

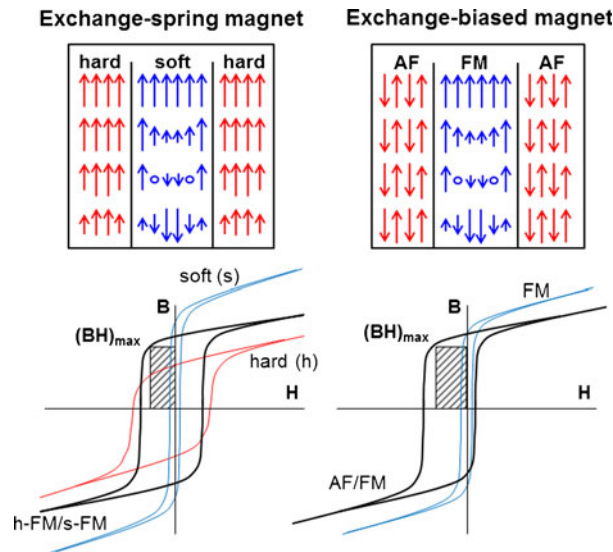


Fig. 7—Schematic representation of the demagnetization mechanism (2nd quadrant) in exchange-coupled nanocomposite structures, for the case of hard-soft magnetic phases (exchange spring magnets) and antiferromagnetic-ferromagnetic phases (exchange-biased magnets).

scale of magnetic nanocomposites may be determined from physical principles, described as follows. The relationship between the nanocrystalline grain size and the magnetic exchange force is communicated by the magnetic exchange length L_{ex}^0 as given below

$$L_{ex}^0 \approx \sqrt{\frac{A}{K_1}} \quad [5]$$

where A is the exchange stiffness and K_1 is the first-order anisotropy constant.^[83] The magnetic exchange length L_{ex}^0 describes the thickness of the magnetization transition existing near an interface, where the magnetization direction can deviate from the direction defined by the magnetocrystalline anisotropy in the bulk region of a given grain. In the absence of a perpendicular magnetization component across the interface, L_{ex}^0 may be related to the domain wall width δ_{DW} as^[2]

$$L_{ex}^0 \approx \frac{\delta_{DW}}{\pi} \quad [6]$$

In this manner, it can be seen that the magnetic exchange length controls the magnetic behavior in nanocrystalline magnets. Ideally, for optimal performance, the components of the nanocomposite should be combined uniformly on the nanoscale such that the diameter of the magnetically soft phase is twice the domain wall width of the magnetically hard phase in the system. When the average grain size of a ferromagnet is much larger than the magnetic exchange length (or, equivalently, the domain wall), the magnetization deviation at the grain perimeters does not significantly affect the reversal of the system. In such cases, the coercivity of the system is largely controlled by lattice imperfections and grain boundary defects that furnish regions more susceptible to magnetic reversal relative to the bulk. However, when the grain size descends to the nanoscale, the exchange length becomes important;

under its influence, spins at the peripheries of neighboring nanograins become strongly exchange coupled. The exchange coupling effectively erases the distinction between nanocrystalline grains and decreases the efficacy of the physical grain boundaries to act as barriers to domain wall motion. The peripheral spins on the edges of the nanocrystalline grains constitute a large volume fraction of the total number of spins in the grain; this situation results in magnetic behavior that is very different from that found in the larger-grained counterparts. Furthermore, in optimal structures, the easy axes of the constituents should be aligned in the composite to allow for maximum remanence and, thus, maximum energy product.

B. Exchange-Spring Permanent Magnets

The “nanocomposite” or “exchange-spring” magnet^[82] is composed of intimately combined nanoscaled hard and soft magnetic phases that are exchange coupled at the mutual interface (Figure 7, left). The “exchange spring” is named for the largely reversible—“springy”—magnetic interaction that takes place between the constituent magnetic components under the application and removal of an applied magnetic field. The interphase interfacial magnetic exchange coupling yields a composite system that benefits from the best attributes of the constituent phases: The magnetically-hard phase furnishes high anisotropy and accompanying high coercivity, while the magnetically-soft phase donates a large saturation magnetization. Theoretical work suggests that energy products could significantly surpass those provided by conventional uncoupled magnetic materials,^[84] and experiments have verified that energy products are indeed increased.^[85–88] However, to date, the technical magnetic properties of the resultant products have not come close to their theoretical promise due to unresolved issues of phase purity, uniformity, and crystallographic alignment. While these challenges have ensured that a commercially viable rare-earth-based exchange-spring magnet remains elusive, it is believed that such extrinsic factors may be controlled in the proposed systems to yield a superior response.

One active strategy to create high-energy product magnets with reduced rare-earth content is to combine, at the nanoscale, $\text{Nd}_2\text{Fe}_{14}\text{B}$, donating high coercivity with a material, such as $\alpha\text{-Fe}$, that donates high magnetization. In this manner, the lower magnetization of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ is offset by the higher magnetization of the Fe phase, and vice versa for the intrinsic anisotropy contribution. It is a formidable challenge to synthesize high-performing nanocomposite magnets of 2-14-1 and $\alpha\text{-Fe}$, as the room-temperature value of the magnetic exchange length L_{ex}^0 in $\text{Nd}_2\text{Fe}_{14}\text{B}$ is extremely small, around 21 Å.^[73] This requirement dictates achievement of grain size below 100 Å for most exchange-spring nanocomposite magnets comprised of rare-earth-based intermetallic hard magnetic phases such as $\text{Nd}_2\text{Fe}_{14}\text{B}$ or $\text{Sm}_2\text{Co}_{17}$.^[89–93] Additionally, while straightforward in concept, attainment of a uniform, nanoscaled, and textured (aligned) composite material has not yet been achieved, although strong interphase exchange coupling,

manifest as a single-phase demagnetization curve, has been confirmed in bulk nanocomposite magnetic materials.^[94,95] The inherent requirement of creating a bulk nanostructured material calls for nonequilibrium synthesis techniques such as melt spinning or mechanical alloying.^[51,52,96] Rapid solidification processing techniques aim to retain, or “quench in,” at room temperature the metastable quasi-random atomic configuration that the material possesses when it is in its elevated temperature or liquid state. Not only are materials processed in this manner plagued by inhomogeneities, but also they can contain a large amount of strain, foreign crystallites, and other undesirable effects of this high stochastic synthesis technique. However, in principle, optimally designed NdFeB/ α -Fe exchange-spring magnets can achieve strengths that are 3 to 4 times the strength of today’s best commercial Neo magnets. This increase in strength would allow for a significant reduction in size and, hence weight, of the magnets. Moreover, permanent nanocomposite magnets made from Nd₂Fe₁₄B and iron are expected to be not only cheaper than today’s Neo magnets but also much more corrosion resistant, allowing them to be used in challenging high-temperature environments where the currently used magnets might degrade and lose their strength.

C. Exchange-Biased Permanent Magnets

The design principle of combining two magnetic materials with complementary attributes at the nanoscale, within the exchange length L_{ex}^0 (Eq. [6]) to create a magnetic material with properties superior to either component taken alone may also be applied to the creation of “exchange-bias” hard and semihard magnets. The principle of exchange biasing,^[97] whereby an AF material is exchange-coupled to a FM material at the AF-FM phase interface to produce an asymmetric major hysteresis loop, is a known route to coercivity and remanence enhancement.^[98,99] In this manner, the demagnetization curve in the second quadrant of the hysteresis loop is asymmetrically extended, effectively increasing the coercive field and the remanent magnetization of the composite and enhancing the energy product (Figure 7, right). In exchange-bias systems the Néel temperature T_N of the antiferromagnetic component must lie below the Curie temperature T_C of the ferromagnetic component so that the composite may be cooled in a ferromagnetic state through the Néel point to establish a preferred magnetic moment direction. Because the magnetic exchange interaction is an extremely short-ranged phenomenon, with exchange lengths extending only over a few lattice constants at most, it is imperative that contact between the antiferromagnetic and the ferromagnetic phase be maximized.^[100,101] These requirements are met by the creation of nanostructured materials with large surface-to-volume phase ratios. Exchange anisotropy was first reported by Meiklejohn and Bean in 1956 for Co/CoO core-shell particles^[97] and is deduced to result from atomic-level exchange coupling derived from electron

orbital overlap at the interfaces between antiferromagnetic (or ferrimagnetic) material and ferromagnetic materials. The antiferromagnetic material provides a unidirectional bias or anisotropy to the ferromagnetic phase and causes a shift in the hysteresis loop along the field axis for materials field-cooled from temperatures above the Néel temperature T_N of the antiferromagnetic phase. The exchange bias effect vanishes above a temperature called the “blocking” temperature T_B , where $T_B \leq T_N$. Details of the phenomena are reviewed in References 78, 101, and 102.

Systems exhibiting exchange bias have been studied extensively over recent years, particularly in thin film form^[103–105] where the interface between the two phases is easier to control and characterize and because current technological applications also utilize the material in thin-film form. It is interesting to note that while the exchange-bias effect has been explored thoroughly as the key enabler of the design and operation of spin-valve devices,^[106] it has not at all been widely explored as an anisotropy source for permanent magnets. Meiklejohn and Bean^[97] explicitly stated in their seminal article that the displacement of the hysteresis loop would result in a higher energy product and, therefore superior, permanent magnet. However, to date, this concept has not been widely investigated in magnetic materials in bulk form. A few authors have reported on a variety of nanocomposite magnetic materials with exchange-bias mechanism as the underlying source of coercivity. Studies performed on the bulk metallic glass system (Pr,Nd)₆₀Fe₃₀Al₁₀^[107] indicate that their appreciable room-temperature coercivity values are inconsistent with the reported amorphous structure of the bulk cast alloy and, instead, are attributed to the existence of sub-unit-cell “motifs” related to the antiferromagnetic Nd₆Fe_{13-x}Al_{1+x} phase of average diameter 1.2 nm.^[108,109] Work by Sort *et al.*^[110,111] reports an enhanced coercivity and augmented squareness ratio at room temperature in bulk composites of ferromagnetic materials (SmCo₅, Co) and antiferromagnetic materials (NiO, MnO, CoO, and FeS) synthesized by ball milling. Sort *et al.*’s work has been followed by similar efforts^[112,113] also focused on composite materials made by ball milling. In 2004, Lewis *et al.*^[114] explored metallurgical synthesis from the melt of bulk permanent magnets with coercivity conferred by the exchange bias mechanism in a two-phase materials system composed of ferromagnetic FeCo and antiferromagnetic, nominally equiatomic AuMn. Rapid solidification synthesis of composite alloys of nominal composition (Fe₆₅Co₃₅)_{100-x}(AuMn)_x was carried out with the melt-spinning technique. Magnetization measurements confirmed the exchange bias effect that is correlated with an increase in the coercivity of the composite over that of the (Fe,Co) melt-spun base alloy. However, resultant exchange bias effect was weak in this system and attributed to low magnetocrystalline anisotropy, chemical disorder of the antiferromagnetic AuMn phase, and a nonideal interfacial contact between the antiferromagnetic phase and the matrix.^[96,115] Nonetheless, in this work, an enhanced coercivity and a shifted hysteresis loop were observed in a single sample, creating a strong

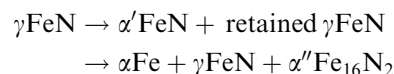
argument for coercivity enhancement conferred by the exchange bias interaction between antiferromagnetic and ferromagnetic phases in a bulk nanocomposite permanent magnetic material. Current efforts are focused on the synthesis of components with a majority Fe-based matrix phase combined with antiferromagnetic metallic nanophases of CuMn, AgMn, CoMn, and IrMn.^[116] These systems were chosen on the basis of their metallurgical compatibility with the proposed ferromagnetic matrix, potential for nanostructuring, and capacity for development of the necessary antiferromagnetic ordering and particle morphology with minimal postsynthesis manipulation. Additionally, it seems possible to tune the antiferromagnetic features of such Mn-based alloys, such as the antiferromagnetic anisotropy constant K_{AF} or the Néel temperature T_N by modifying the Mn concentration.^[116] Previous work has documented promising antiferromagnetic properties, with relatively high antiferromagnetic ordering temperatures T_N (above room temperature), for the metallic alloys $\text{Cu}_{10}\text{Mn}_{90}$,^[117–119] $\text{Co}_{50}\text{Mn}_{50}$,^[120,121] and $\text{Ir}_{25}\text{Mn}_{75}$.^[122,123] Rapid solidification processing is considered to be essential in the preparation of these antiferromagnetic alloys, not only because of its capability to yield alloys containing metastable phases but also in terms of increasing the solid solubility, and thus, the incorporation of Mn, into the alloys. Recent promising results focused on optimization of the antiferromagnetic phase component of potential exchange-biased permanent magnets demonstrate the attainment of phase-separated nanostructured alloys with an enhanced T_N . In particular, melt-spun AgMn ribbons were demonstrated to exhibit a very large exchange bias at low temperatures, up to 17 kOe at 10 K (–263 °C), underlying a remarkable interfacial exchange-energy density of the order of 1 erg/cm² (~10 J/m²) estimated between nanoscaled FM regions coupled to the AF crystallites,^[124] with respect to previously reported values.^[125–128] Future efforts to combine such nanoscaled, chemically disproportionated antiferromagnetic phases with ferromagnetic phases such as Fe or FeCo are anticipated to exhibit an enhanced energy product.

Category II: Crystal Structure Development to Realize High-Anisotropy Magnetic Compounds. Among the various sources of magnetic anisotropy, magnetocrystalline anisotropy provides the largest anisotropy and is thus the favored mechanism to induce coercivity in high-energy permanent magnets. However, in the absence of rare-earth components, the magnetocrystalline anisotropy donated by REEs in permanent magnet compounds may be recovered, to various degrees, in magnetic materials that adopt a low-symmetry crystal structure, such as hexagonal or tetragonal crystal structures. In such low-symmetry crystal structures, the material's magnetic moment may align perpendicular to the basal plane direction, providing two energy minima for the magnetization that defines the uniaxial magnetic anisotropy state. In this section, aspects of ferromagnetic materials existing in one of two tetragonal crystal structures that may be suitable for permanent magnet applications will be reviewed: the high-moment ordered nitrogen martensite $\alpha''\text{-Fe}_{16}\text{N}_2$ with the

tetragonal structure, the L1_0 -type equiatomic FeNi, also known as tetrataenite, and the tetragonal L1_0 form of equiatomic $\tau\text{-MnAl}$, interstitially modified with C or B.

D. Ordered Nitrogen Martensite $\alpha''\text{-Fe}_{16}\text{N}_2$

In the mid-1990s, a flurry of activity was reactivated concerning the nature and magnitude of the large magnetic moment found in the ordered nitrogen martensite $\alpha''\text{-Fe}_{16}\text{N}_2$.^[129–131] This material was originally synthesized in thin film form in 1972^[132] with an unprecedented value reported for the magnetic moment on the order of 3.0 μ_B per iron atom. At the time, it was not possible to reproduce these results, but in 1993, researchers at Hitachi in Japan claimed to have confirmed the 1972 results and obtained an average magnetic moment of 3.2 μ_B per iron in the ordered iron martensite,^[133] which is almost 50 pct larger than the 2.2 μ_B per iron atom found in pure metallic iron. All of these studies had their origins in the work done by Jack^[134,135] in 1951 that elucidated the structural and mechanical aspects of a metastable form of iron interstitially modified with nitrogen such that a distorted body-centered tetragonal martensitic phase resulted. The material was formed in bulk by quenching face-centered-cubic (fcc) nitrogen austenite ($\gamma\text{-FeN}$). In this manner, the formation of $\alpha\text{-Fe}$ is avoided, and instead, the disordered nitrogen martensite $\alpha'\text{-FeN}$ is formed. When tempered at low temperature (400 K to 475 K [127 °C to 202 °C]) the $\alpha'\text{-FeN}$ orders to form $\alpha''\text{-Fe}_{16}\text{N}_2$. The reaction is described below:



The $\alpha''\text{-Fe}_{16}\text{N}_2$ phase is noted to be metastable and decomposes into $\alpha\text{-Fe}$ and Fe_4N around $T = 450$ K to 550 K (approximately 200 to 300 °C). There are three crystallographically unique iron sites in the $\alpha''\text{-Fe}_{16}\text{N}_2$ structure, and it has been established that the magnetic moments found on the Fe sites are very sensitive to the degree of nitrogen ordering.^[136] It is not possible to obtain pure $\alpha''\text{-Fe}_{16}\text{N}_2$ because the solubility of nitrogen in austenite is less than the required 12.5 nitrogen atoms per every 100 iron atoms per the established stoichiometry. In the mid-1990s, a good deal of controversy existed, with the scientific community divided into those that believed an elevated moment existed on the iron and those who saw no evidence for an enhanced Fe moment. However, there was almost unanimous agreement that additional efforts and techniques prepare the $\alpha''\text{-Fe}_{16}\text{N}_2$ were worth the investment. While the $\alpha''\text{-Fe}_{16}\text{N}_2$ problem still attracted limited attention in the last decade,^[137] in 2011, it received new attention through a recent report from the Graduate School of Engineering, Department of Electronic Engineering at Tohoku University^[138] announced successful and reproducible chemical synthesis of highly oriented $\alpha''\text{-Fe}_{16}\text{N}_2$ powder with a purity of 91 pct. The $\alpha''\text{-Fe}_{16}\text{N}_2$ powder was reported to have a particle diameter of several tens to several hundreds of nanometers and a saturation

magnetization of 230 emu/g (230 A·m²/kg) at 50 K (−223 °C) and 221 emu/g (221 A·m²/kg) at room temperature, which is higher than that of pure iron. While crystallographic analysis of the α'' -Fe₁₆N₂ structure confirms a tetragonal symmetry that is lower than that of the parent cubic phase, the magnetic crystalline anisotropy of this compound is still relatively low, and the promise of this compound as a permanent magnet remains under discussion.

E. L1₀-Type Magnetic Compounds

While the majority of strongly magnetic transition-metal alloys assume a high-symmetry cubic structure that displays low magnetocrystalline anisotropy, certain transition-metal alloys compounds form in the tetragonal L1₀ (space group *P4/mmm* or AuCu I structure type) structure, with an associated uniaxial magnetic character. Two magnetic compounds that adopt the L1₀-type structure—FeNi and MnAl—are anticipated to yield promising technical magnetic properties.

The L1₀ structure forms in many equiatomic compounds AB and consists of alternating layers of the two constituent elements stacked parallel to the tetragonal *c*-axis, creating a natural superlattice (Figure 8). The left structure of Figure 8 depicts a chemically disordered cubic alloy; if the unit cell is taken as the right figure, the Pearson symbol is tP4, with the space group *P4/mmm*, and the prototype CuAu I. The chemically ordered L1₀ alloys (right structure of Figure 8) form through a disorder-order transformation from a parent phase, which is often a chemically disordered, fcc solid solution of the two elements. The decrease in symmetry concurrent with the formation of the L1₀ structure leads to a tetragonal distortion, which usually, although not always, results in a contraction in the unit cell *c*-axis, [001].

In the fcc or A1 structure, the probability of occupation of a given atomic site by either of the two component elements is equal. By contrast, in the ordered structure, which is the thermodynamically stable phase below a critical temperature *T*_{CR}, each crystal lattice site has a different probability of being occupied by one of the two atom types. By symmetry arguments, it can be shown that the A1 to L1₀ phase transformation is first order in the Ehrenfest sense.^[139–142] This first-order

transformation proceeds by nucleation and growth of the L1₀ ordered regions within the disordered A1 matrix. The local atomic rearrangements necessary for ordering can be facilitated by creating point defects (vacancies) in the structure or by ternary alloying additions that enhance diffusion rates.

Magnetic compounds with the L1₀ structure such as FePt and FePd possess the high magnetization and significant magnetocrystalline anisotropy, derived from the lower symmetry crystal structure, necessary for advanced permanent magnet applications.^[143–146] Experimental energy products around $(BH)_{\max} = 14.7$ MGOe (117 kJ/m³) have been achieved in single-phase Fe₅₈Pt₄₂ nanoparticles, whereas important improved $(BH)_{\max}$ (up to 20 MGOe, *i.e.*, approximately 159 kJ/m³) was obtained in exchange spring FePt-based nanocomposite magnets.^[147,148] However, FePt and FePd are under consideration only for thin-film-based devices for applications in magnetic recording due to the costliness of Pt and Pd, which preclude their use as components in bulk permanent magnets for motors and generators. The isostructural ferromagnetic L1₀-type compositions FeNi and MnAl, on the other hand, are composed of much less expensive and more readily available constituents. While these materials are very promising, based on their reported intrinsic properties such as a large magnetization and a large magnetocrystalline anisotropy, to date no research team or commercial effort has been successful in developing them for permanent magnet applications. This technological barrier is attributed to significant challenges regarding the kinetics of the chemical order-disorder transformations to stabilize the high-anisotropy forms of the compounds. If the chemical ordering in nominally equiatomic FeNi and MnAl may be induced so that the L1₀ structure is easily formed and is retained at high temperature, a less costly, non-RE-based advanced permanent magnetic material can be achieved (Table IV).

1. L1₀-type FeNi (*a.k.a.* tetrataenite)

The L1₀ form of FeNi remains largely unknown in the magnetic materials community; in fact, most published Fe-Ni binary phase diagrams do not explicitly show the phase. Figure 9(a) displays a modern phase diagram that shows the L1₀ phase region around the 50-50 at. pct composition.^[149] Typically FeNi alloys occur in a solid-solution/chemically disordered alloy A1 (fcc) structure with cubic symmetry and low magnetocrystalline anisotropy but good magnetization and a Curie temperature in excess of 800 K (~ 500 °C), depending on the detailed composition. Fe-Ni alloys are known in the magnetic materials community as canonical soft magnetic materials. The identification of the L1₀ structure in the Fe-Ni system is extremely significant because the tetragonal distortion that accompanies the chemical ordering in this structure gives rise to appreciable anisotropy. L1₀-type FeNi has been observed under certain conditions in the laboratory^[150] as well as in many stony, stony-iron, and iron meteorites.^[151,152] This phase, known as tetrataenite, has great potential for excellent permanent magnetic behavior, provided that nonequilibrium

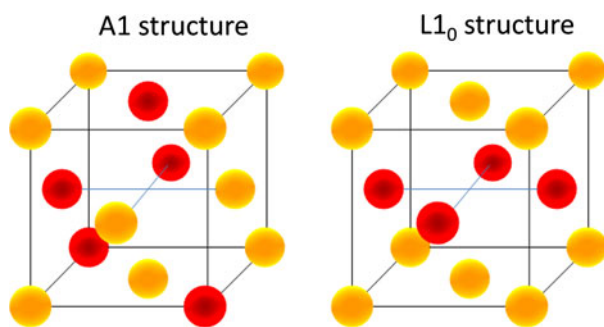


Fig. 8—Schematic representation of face-centered cubic A1 and L1₀ crystal structures.

Table IV. Room-Temperature Magnetic Properties of L1₀-Type Magnetic Materials

Composition	Saturation Magnetization $4\pi M_S$ (kG)	Anisotropy Constant K_U (ergs/cm ³)	Curie Temperature T_C	Theoretical Maximum Energy Product $(BH)_{\max}$ MGOe
L1 ₀ FeNi	16	$0.32 \times (10)^7$	~500 °C/~770 K	40*
MnAl	7.5	$1.7 \times (10)^7$	250 °C/~520 K	14

*Calculated as $(BH)_{\max} = H_C(M_S - H_C) \sim H_A * M_S$.

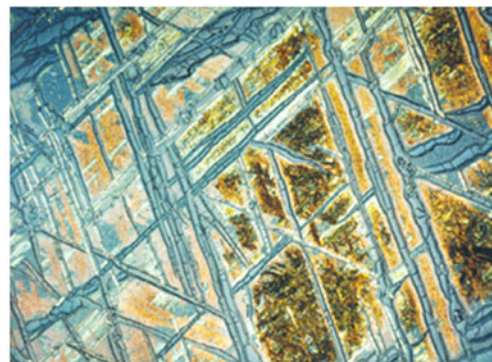
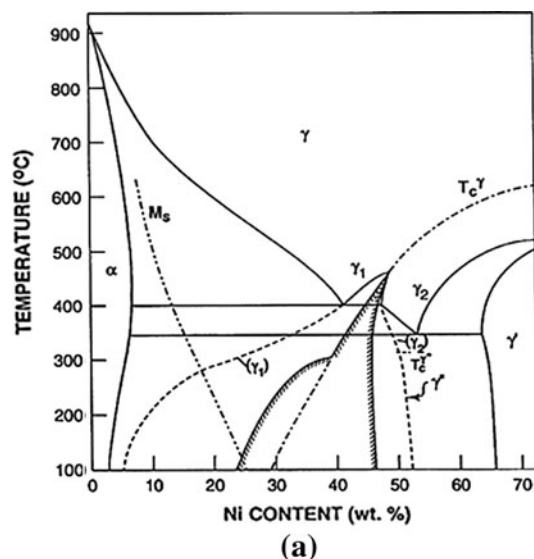


Fig. 9—(a) Fe-Ni binary phase diagram, labeled as follows: α is a low-Ni bcc phase, γ is a high-Ni fcc phase, γ_1 is a low-Ni paramagnetic fcc phase, γ_2 is a high-Ni ferromagnetic fcc phase, γ' is ordered Ni₃Fe, γ'' is ordered FeNi-tetrataenite, and M_S is the martensite starting temperature. T_C is the Curie temperature of the γ phase. T_C' is the ordering temperature of FeNi, γ'' (from Ref. 136). (b) Polished and etched slices of the Carlton IIICD iron meteorite showing Widmanstätten patterns. Kamacite plates (blue) formed on the close-packed planes of the parent taenite phase. Plessite, a fine mixture of kamacite and tetrataenite, formed in the prior taenite regions between the kamacite plates. Schreibersite precipitates are observed in the centers of some of the kamacite plates. Scale is 1 cm along the bottom (from Ref. 152). (Color figure online).

processing coupled with substitutional or interstitial alloying additions can stabilize the phase and that the stabilized alloy microstructures can be tailored by appropriate synthesis and processing techniques to allow full manifestation of their intrinsic magnetic properties. While tetrataenite possesses a high magnetization and high anisotropy, it exhibits a low chemical ordering temperature of 600 K (320 °C), potentially indicating that the disorder $\rightarrow$ order transformation in FeNi is kinetically limited on account of low atom mobilities characteristic at temperatures below the ordering temperature.

The first report on L1₀-type FeNi in 1960 by Paulevé and Dautreppe^[153] noted unique properties in an FeNi single crystal as a result of neutron bombardment under the influence of a magnetic field. This work was followed in 1962 by Paulevé *et al.*^[154] who reported attainment of the L1₀ structure and a coercivity increase in a polycrystalline sample of nominally equiatomic FeNi, as well as single-crystal FeNi L1₀-type anisotropy constants of $K_1 = 3.2 \times 10^6$ ergs/cm³ (3.2×10^5 J/m³) and $K_2 = 2.3 \times 10^6$ ergs/cm³ (2.3×10^5 J/m³).^[155] A note on these results, provided by Néel in 1977 as documented in the translation volume, *Selected Works of Louis Néel*, edited by Nicholas Kurti (1988)^[156]:

“The formation of the FeNi superlattice, described here and unknown until that time, is due to the increase in the number of vacancies in the crystal lattice and to the accompanying increase in diffusion and in ordering rate of the atoms. Irradiation with electrons produces similar effects....”

Subsequent to this above-referenced publication, scientists (known as meteoriticists) have found the L1₀ FeNi tetrataenite phase in large numbers of stony, stony-iron, and iron meteorites. Tetrataenite is a component of the famous Widmanstätten pattern consisting of long, interwoven nickel-iron crystals in which the close-packed planes of the body-centered cubic (bcc) kamacite form on the close packed planes of the fcc taenite (Figure 9(b)). The width of the kamacite in the Widmanstätten pattern is a function of the cooling rate of the meteorite in its parent asteroidal body; in slowly cooled stony-iron meteorites, the tetrataenite phase dimension can exceed 10 μ m in width. Typical meteorite cooling rates vary from 0.2 K/Myr to 2000 K/Myr and foster long-range chemical ordering at the low temperatures (<600 K [<320 °C]) where the tetrataenite phase forms. Other than the initial papers by Néel *et al.* on bulk material, very few publications of experimental efforts to date on this system have examined the material in thin film form.^[150,157] Experimental efforts to produce

the 50Fe-50Ni compound in bulk Fe-Ni alloys or Fe-Ni-S alloys have achieved limited success although the presence of ordered FeNi was not unequivocally established.^[158,159] It is anticipated that knowledge gained from engineering the structure-property relationships of the better known L1₀-type alloys of CoPt and FePt will reveal kinetic pathways to access chemically ordered L1₀-type FeNi on laboratory time scales.

2. L1₀ τ -phase MnAl(C)

Near-equiatomic L1₀-type MnAl and structurally stabilized MnAlC compounds containing interstitial carbon hold promise as an advanced permanent magnet due to their high coercivity values, moderately high energy product, large corrosion resistivity, and low cost.^[160] The magnetic properties of the L1₀ tetragonal τ -MnAl compound, identified as the only FM phase in the Al-Mn system at room temperature, have been reported extensively in the literature.^[161–163] This intermetallic compound exhibits a face-centered-tetragonal structure, with a composition range of 51 to 58 at. pct Mn. The ferromagnetic character of this compound is derived from the Mn atoms that occupy the (0, 0, 0) and ($\frac{1}{2}$, $\frac{1}{2}$, 0) positions in the unit cell, whereas the Al occupy mainly the (0, $\frac{1}{2}$, $\frac{1}{2}$) sites. The slight excess of Mn, resulting in the substitution of some Mn on the Al sites, produces a local antiferromagnetic coupling of some atomic Mn moments while at the same time stabilizing the high-anisotropy tetragonal phase and thus a large anisotropy, albeit with a slightly reduced volume magnetization.

The MnAl L1₀ phase was discovered during an investigation of the structural and magnetic properties of near equiatomic Mn-Al alloys by Kono^[164] and by Koch *et al.*^[165] in the late 1950s. Carbon was later introduced in order to stabilize the tetragonal L1₀ phase.^[166,167] The incorporation of C within interstitial sites of the crystal structure reduces the Curie temperature and likely the anisotropy field, but enhances the saturation magnetization. As shown in the phase

diagram of Figure 10(a), the chemically ordered L1₀ MnAl phase is obtained through a massive phase transformation from the high-temperature hexagonal ε -phase^[168,169] that can only be attained by cooling from high temperature at rapid cooling rates on the order of 10 to 30 K/s.^[170] It is generally accepted that this transformation is a result of an ordering reaction from this ε -phase to an intermediate orthorhombic phase (ε'), followed by a martensitic phase transition into the ferromagnetic τ -phase,^[171] without ruling out diffusion and nucleation processes.^[168] Application of nonequilibrium materials synthesis processes, such as melt spinning, may allow kinetic access to the metastable nanoscaled magnetic phases and structures that remain inaccessible with conventional metallurgical processing methods, and hence allows attainment of the ε -phase, from which the L1₀ phase is derived *via* heat treatment. It is anticipated that melt spinning of MnAl will produce a nanocrystalline material of high homogeneity and a large degree of metastability that is amenable to the creation of small crystallites *via* a small input of mechanical and/or thermal energy. Recent results indicate that melt-spun MnAl exhibits a very large exchange bias, or unidirectional shift in the magnetic hysteresis loop, at low temperature (Figure 10(b)) attributed to a metastable nanoscale phase separation with ε -structure with potentially useful properties for magnetic nanocomposite formation.^[172]

Typical coercivity values reported in the literature for MnAl and MnAl(C) alloys after melt spinning and appropriate heat treatment are on the order of 1500 to 2000 Oe^[173,174] with an observed experimental energy product varying around $(BH)_{\max} \approx 4$ to 7 MGOe (37 to 56 kJ/m³).^[160,175] Another nonequilibrium synthesis process, mechanical alloying, fosters reduction of the MnAl(C) grain size to enhance coercivity. It has been observed that mechanical milling of single-phase L1₀-type MnAl(C) has effectively reduced the grain size, resulting in a dramatic increase in coercivity from ~ 1700 Oe to 4000 Oe

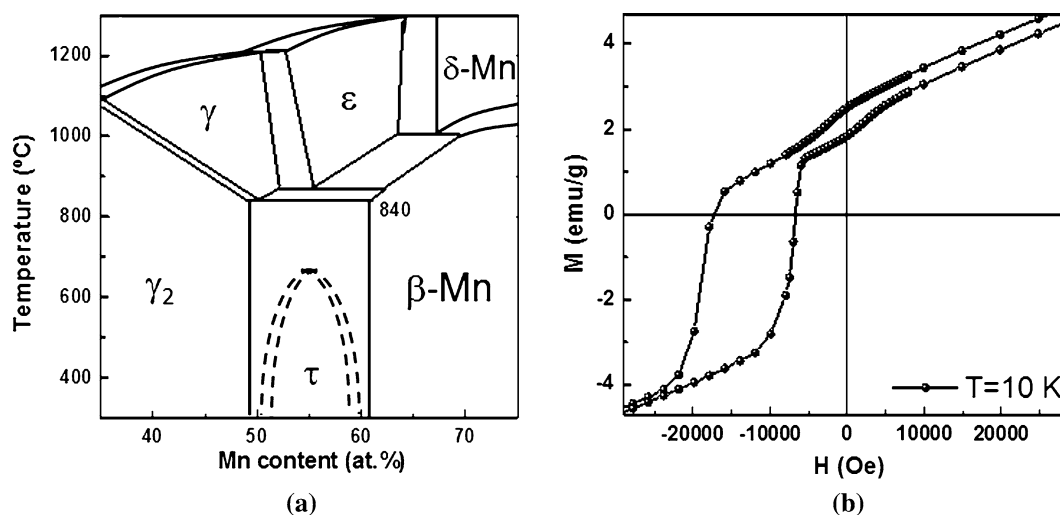


Fig. 10—(a) MnAl phase diagram, based on Ref. 147 and^[159]. (b) Magnetization loop, at 10 K (-263°C), of $\text{Mn}_{55}\text{Al}_{45}$ ribbons prepared by rapid solidification, showing an exchange bias of $H_E \approx 13$ kOe.

(135 to 318 kA/m), comparable with the highest reported coercivity for MnAl(C).^[176]

MnAl magnets have a good performance apart from their low cost; however, to be able to compete with hard ferrite magnets and spread their field of application, improved permanent magnet attributes are still required. A promising hybrid material could result from the creation of a high energy-product, rare-earth-free magnet *via* nanometer-level structural development of a material consisting of interstitially-modified L1₀-type MnAl(C) combined with high-moment bcc α -Fe or FeCo to create a nanocomposite magnetic system—a magnetic “exchange spring”, as discussed earlier—that ideally exhibits the best technical attributes of both constituent phases. Employing nonequilibrium processing techniques, a major goal is to combine these two hard/soft magnetic phases at the nanoscale with good interphase exchange coupling and without interdiffusion that would likely degrade the technical magnetic properties. In this manner, it may be possible to create a new and successful magnetic nanocomposite to replace the lower end (isotropic) rare-earth-containing magnets that possess energy products $(BH)_{\max}$ in the range of 10 to 15 MGOe (80 to 120 kJ/m³) at room temperature. It is anticipated that in its optimized state, this proposed rare-earth-free exchange spring magnetic system will exhibit a Curie temperature in the vicinity of 573 K (300 °C), sufficiently high to maintain good magnetic performance to 400 K (673 °C), with an intrinsic coercivity of $iH_c \sim 4$ kOe (318 kA/m) and a relatively high saturation magnetization >7 kG (0.7 T) to exhibit a theoretical energy products in excess of 12 MGOe. These attributes are expected to increase at temperatures below room temperature.

The combination of materials, L1₀-type MnAl(C) and Fe or FeCo, described here to make a magnetic monolithic compact, has not been previously attempted nor has this sequential and specific processing route previously been applied. Conventional approaches to the creation of magnetic nanocomposites for bulk hard magnet applications include melt spinning or mechanical milling/alloying. Combining these processes and adding an additional step of surfactant-assisted milling to produce tailored structures at multiple length scales, from the nanometer to micrometer scale, are anticipated to provide a robust magnetic nanocomposite with good thermal properties.

3. Cobalt carbide nanoblades

Recently, it has been reported that cobalt carbide phases, synthesized by the polyol reduction chemistry method, exhibit room-temperature coercivities greater than 3.4 kOe and maximum energy products greater than 20 kJ/m³ (2.5 MGOe).^[75] These particles are composed of Co₃C and Co₂C nanophases with an acicular morphology and apparent Curie temperatures near 510 K (237 °C). The unexpectedly large room-temperature coercivities originate from dipolar and magneto-crystalline anisotropies of carbide phases but may be additionally affected by interparticle exchange. While the development of these materials is in the early stages,

the technical magnetic properties attained thus far show promise as a new rare-earth-free permanent magnetic material and warrant more extensive investigation of this carbide system in which particle size, chemistry, and morphology are optimized.

VII. OUTLOOK: NEXT-GENERATION PERMANENT MAGNETIC MATERIALS

It is apparent that ultrastrong magnets with superior thermal and chemical stability are essential to address ongoing and future technological needs in society. In particular, escalating demand for cheaper, smaller, and more powerful motors and generators for consumer, military, and energy applications such as wind turbines and hybrid or electric vehicles will require a steady and secure supply of high-energy-product permanent magnets. In this context, the rare-earth elements, in their role as enabling chemical components of high-energy product magnets, will remain extremely important.

Going forward, it is anticipated that the so-called “rare-earth crisis” will subside—somewhat—over the next decade as new rare-earth element supplies are secured, new permanent magnetic materials are developed, and new device and motor designs that utilize lower amounts of rare-earth permanent magnets are implemented. While there currently exists a shortage of rare earth production capacity, with over 95 pct of production capability located in China, it is predicted that this situation will be partially relieved in the relatively near future as additional rare-earth mines come on line in the United States (Molycorp, Mountain Pass, CA)^[177] and in other locations in the world (Lynas, Malaysia; TRE Project, Madagascar; Quest Rare Minerals, Canada, *etc.*)^[65] Furthermore, new motor designs will be employed in the future that do not require substantial quantities of rare-earth magnets for efficient operation.^[178]

Nonetheless, even with a sustainable supply of the light rare earths (Pr, Nd, Sm, ...), the “rare-earth crises” will not disappear entirely. The intrinsically scarce supply of selected rare-earth elements such as terbium (Tb) and dysprosium (Dy) will remain strategically important for high-temperature performance of NdFeB magnets.^[138] Economically-speaking, permanent magnet manufacturers and end-users, such as the automotive and computer industries, require a stable, and ideally diversified, supply chain of raw materials to maintain competitive prices and operations. The successful development of new rare-earth-free “supermagnets,” perhaps as described in this review, will contribute strongly to this goal and is closely aligned with domestic security as well as job creation and growth. Additionally, environmental concerns remain, including appropriate handling of radioactive uranium- and thorium-bearing waste produced as a byproduct of mining rare-earth materials. All of these factors combined indicate that creative new concepts for the creation of low- or rare-earth-free permanent magnet materials will remain an important pursuit in magnetic materials science.

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REFERENCES

1. S. Chikazumi and C.D. Graham: *Physics of Ferromagnetism*, Oxford University Press, Oxford, U.K., 1997.
2. R.C. O'Handley: *Modern Magnetic Materials: Principles and Applications*, Wiley, New York, NY, 2000.
3. J.M.D. Coey: *Magnetism and Magnetic Materials*, Cambridge University Press, New York, NY, 2010.
4. AIC, Flexible magnetic sheeting, http://www.flexible-magnet.com/page/en/Flexible_Magnetic_Sheeting.htm.
5. J.D. Livingston: *Driving Force, the Natural Magic of Magnets*, Harvard University Press, Cambridge, MA, 1996.
6. J.M.D. Coey: *Endeavor*, 1995, vol. 19, pp. 146–51.
7. K. Hozelitz: *Ferromagnetic Properties of Metals and Alloys*, Clarendon Press, Oxford, U.K., 1952.
8. T. Mishima: *Ohm*, 1932, vol. 19, p. 353.
9. B.D. Cullity and C.D. Graham: *Introduction to Magnetic Materials*, Wiley, Hoboken, NJ, 2008.
10. C. Kittel, E.A. Nesbitt, and W. Shockley: *Phys. Rev.*, 1950, vol. 77, pp. 839–40.
11. K.H.J. Buschow and F. R. de Boer: *Physics of Magnetism and Magnetic Materials*, Springer, New York, NY, 2003.
12. J.W. Cahn: *J. Appl. Phys.*, 1963, vol. 34, pp. 3581–86.
13. P. Marin and A. Hernando: *Appl. Phys. Lett.*, 2009, vol. 94, pp. 122507-1–122507-3.
14. L.I. Mendelsohn, F.E. Luborsky, and T.O. Paine: *J. Appl. Phys.*, 1955, vol. 26, pp. 1274–80.
15. F.E. Luborsky, L.I. Mendelsohn, and T.O. Paine: *J. Appl. Phys.*, 1957, vol. 28, pp. 344–50.
16. A.H. Geisler: *Rev. Mod. Phys.*, 1953, vol. 25, pp. 316–22.
17. F.E. Luborsky: *J. Appl. Phys.*, 1966, vol. 37, pp. 1091–94.
18. J. Went, G.W. Rathenau, E.W. Gorter, and G.W. van Oosterhout: *Philips Tech. Rev.*, 1952, vol. 13, pp. 194–208.
19. J.B. Goodenough: *Magnetism and the Chemical Bond*, Interscience Publishers, New York, NY, 1963.
20. A. Mann: *Nature*, 2011, vol. 475, pp. 280–82.
21. J. Heber: *Nature*, 2009, vol. 459, pp. 28–30.
22. S.A. Wolf, D.D. Awschalom, R.A. Buhrman, J.M. Daughton, S. von Molnár, M.L. Roukes, A.Y. Chtchelkanova, and D.M. Treger: *Science*, 2001, vol. 294 (5546), pp. 1488–95.
23. V.G. Harris, A. Geilera, Y. Chen, S.D. Yoon, M. Wu, A. Yang, Z. Chen, P. He, P.V. Parimi, X. Zuo, C.E. Patton, M. Abe, O. Acher, and C. Vittoria: *J. Magn. Magn. Mater.*, 2009, vol. 321 (14), pp. 2035–47.
24. K. Strnat, G. Hoffer, J. Olson, W. Ostertag, and J.J. Becker: *J. Appl. Phys.*, 1967, vol. 38, pp. 1001–02.
25. G. Hoffer and K. Strnat: *IEEE Trans. Magn.*, 1966, vol. 2, pp. 487–89.
26. K.J. Strnat: *IEEE Trans. Magn.*, 1972, vol. 8, pp. 511–16.
27. K.H.J. Buschow: *Magnetism and Processing of Permanent Magnet Materials, Handbook of Magnetic Materials*, vol. 10, K.H.J. Buschow, ed., Elsevier Science B.V., Atlanta, GA, 1997, pp. 463–593.
28. J. Zhou, R. Skomski, C. Chen, G.C. Hadjipanayis, and D.J. Sellmyer: *Appl. Phys. Lett.*, 2000, vol. 77, pp. 1514–16.
29. Z.D. Zhang, W. Liu, J.P. Liu, and D.J. Sellmyer: *J. Phys. D: Appl. Phys.*, 2000, vol. 33, pp. R217–R246.
30. J.M.D. Coey: *Rare-Earth-Iron Permanent Magnets, Proc. International School of Physics "Enrico Fermi" Course CVI*, G.F. Chiarotti, F. Fumi, and M.P. Tosi, eds., Villa Marigola Italy, 1988 Current Trends in the Physics of Materials, North-Holland, Amsterdam, the Netherlands, 1990, pp. 265–313.
31. F.J. Cadieu: *Int. Mater. Rev.*, 1995, vol. 40 (4), pp. 137–48.
32. L.H. Lewis, V. Panchanathan, and J.Y. Wang: *J. Magn. Magn. Mater.*, 1997, vol. 176, pp. 288–96.
33. J.M.D. Coey and H. Sun: *J. Magn. Magn. Mater.*, 1990, vol. 87, pp. L251–54.
34. Y. Otani, D.P. Hurley, H. Sun, and J.M.D. Coey: *J. Appl. Phys.*, 1991, vol. 69, pp. 5584–89.
35. S. Sugimoto: *J. Phys. D: Appl. Phys.*, 2011, vol. 44, p. 064001.
36. J. Ding, P.G. McCormick, and R. Street: *Appl. Phys. Lett.*, 1992, vol. 61, pp. 2721–22.
37. T. Saito, H. Sato, and H. Takeishi: *Appl. Phys. Lett.*, 2006, vol. 89, pp. 162511–12.
38. H.H. Stadelmaier, F.J. Cadieu, and N.C. Liu: *Mater. Lett.*, 1987, vol. 6, pp. 80–81.
39. H.S. Li, J.M. Cadogan, R.L. Davis, A. Margarian, and J.B. Dunlop: *Solid State Commun.*, 1994, vol. 90, pp. 487–92.
40. K.H. Buschow: *J. Appl. Phys.*, 1988, vol. 63, pp. 3130–35.
41. O. Kalogirou, V. Psycharis, L. Saettas, and D. Niarchos: *J. Magn. Magn. Mater.*, 1995, vol. 146, pp. 335–45.
42. K.V.S. Rama Rao, G. Markandeyulu, K.G. Suresh, V.R. Shah, U.V. Varadaraju, M. Venkatesan, M.Q. Huang, K. Sirisha, M.E. McHenry, and V.G. Harris: *Bull. Mater. Sci.*, 1999, vol. 22, pp. 509–17.
43. J.M. Cadogan, H.S. Li, A. Margarian, J.B. Dunlop, D.H. Ryan, S.J. Collocott, and R.L. Davis: *J. Appl. Phys.*, 1994, vol. 76, pp. 6138–43.
44. A. Yan, O. Gutfleisch, A. Handstein, T. Gemming, and K.-H. Muller: *J. Appl. Phys.*, 2003, vol. 93, pp. 7975–77.
45. USGS Mineral resources program, <http://minerals.usgs.gov/>.
46. United States Congressional Budget Office Special Study: Cobalt: Policy Options for a Strategic Mineral, 1982, O-98_700.
47. J.J. Croat: U.S. Patent 4,496,395, 1985.
48. Y. Matsuura, M. Sagawa, and S. Fujimura: U.S. Patent 4,597,938, 1986.
49. N.C. Koon: U.S. Patent 4,402,770, 1983.
50. J.F. Herbst: *Rev. Mod. Phys.*, 1991, vol. 63, pp. 819–98.
51. R. Pond and R. Maddin: *Trans. TMS-AIME*, 1969, vol. 245, pp. 2475–76.
52. M.C. Narasimham: U.S. Patent 4212343, 1980.
53. V. Panchanathan: *J. Mater. Eng. Perf.*, 1995, vol. 4 (4), pp. 423–29.
54. R.K. Mishra: *J. Appl. Phys.*, 1987, vol. 62, pp. 967–71.
55. D.B.-M. Ma and Z. Chen: *J. Magn. Magn. Mater.*, 2002, vol. 248, pp. 432–40.
56. Neo Material Technologies, <http://www.magnequench.com/>.
57. Arnold Magnetic Technologies, <http://www.arnoldmagnetics.com/>.
58. T. Folger: *National Geographic Magazine*, June, 2011, <http://ngm.nationalgeographic.com/2011/06/rare-earth-elements/folger-text>.
59. K. Bourzac: *MIT Technology Review*, May/June 2011, <http://www.technologyreview.com/energy/37344/>.
60. W.T. Benecki: *A Producer's and Buyer's Perspective: The Permanent Magnet Outlook*, Magnetics 2008 Conference, Denver, CO, 2008.
61. K. Bradsher: *New York Times* August 31, 2009, <http://www.nytimes.com/2009/09/01/business/global/01minerals.html>.
62. H. Yuan: "China May Double Rare Earth Exports as Demand Rebounds," *Bloomberg News*, Feb 27, 2012, <http://www.bloomberg.com/news/2012-02-26/china-may-double-rare-earth-exports-as-overseas-demand-rebounds-on-price.html>.
63. USGS, Rare Earths Statistics and Information, http://minerals.usgs.gov/minerals/pubs/commodity/rare_earth/.
64. Z. Chen: *J. Rare Earths*, 2011, vol. 29 (1), pp. 1–6.
65. M. Humphries: *Rare Earth Elements: The Global Supply Chain Congressional Research Service 7-5700*, www.crs.gov R41347, 2011.

66. G. Herzberg: *Atomic Spectra and Atomic Structure*, Dover Books on Physics, New York, NY, 2010.
67. R. Skomski: *J. Phys.: Condens. Matter*, 2003, vol. 15, pp. R841–R896.
68. L. Steinbeck, M. Richter, U. Nitzsche, and H. Eschrig: *Phys. Rev. B*, 1996, vol. 53, pp. 7111–27.
69. “Rare Earth Materials in the Defense Supply Chain,” U.S. United States Government Accountability Office Report GAO-10-617R, 2010.
70. B. Jaffe and J. Price: Co-Chairs: Critical Elements for New Energy Technologies, An MIT Energy Initiative Workshop Report, 2010, co-sponsored by Massachusetts Institute of Technology’s Energy Initiative (MITEI), the American Physical Society’s (APS) Panel on Public Affairs (POPA) and the Materials Research Society (MRS).
71. U.S. Department of Energy: “2011 Critical Materials Strategy,” December, 2011.
72. K.A. Gschneidner, Jr.: Rare Earth Minerals and 21st Century Industry—Detailed Written Responses to Subcommittee’s Questions, March 16, 2011, Testimony to a subcommittee of the U.S. House Committee on Science and Technology, <http://gop.science.house.gov/Media/hearings/oversight10/mar16/Gschneidner.pdf>.
73. J.M.D. Coey: *Rare-Earth Iron Permanent Magnets*, J.M.D. Coey, ed., Clarendon Press, Oxford, U.K., 1996.
74. T.J. Nummy, S.P. Bennett, T. Cardinal, and D. Heiman: *Appl. Phys. Lett.*, 2011, vol. 99, p. 252506.
75. V.G. Harris, Y. Chen, A. Yang, S. Yoon, Z. Chen, A.L. Geiler, J. Gao, C.N. Chinnasamy, L.H. Lewis, C. Vittoria, E.E. Carpenter, K.J. Carroll, R. Goswami, M.A. Willard, L. Kurihara, M. Gjoka, and O. Kalogirou: *J. Phys. D: Appl. Phys.*, 2010, vol. 43, p. 165003.
76. P. Gaunt: *Phil. Mag. B*, 1983, vol. 48 (3), pp. 261–76.
77. J. Dubowik: *Phys. Rev. B*, 1996, vol. 54, pp. 1088–91.
78. A.E. Berkowitz and K. Takano: *J. Magn. Magn. Mater.*, 1999, vol. 200, pp. 552–70.
79. C.-W. Chen: *Magnetism and Metallurgy of Soft Magnetic Materials*, Dover Publications, New York, NY, 1986.
80. C. Kittel: *Rev. Mod. Phys.*, 1949, vol. 21 (4), p. 541.
81. C.T. Yang: *National Geographic Magazine*, March 2012, <http://news.nationalgeographic.com/news/energy/2012/03/120330-china-rare-earth-minerals-energy/>.
82. E.F. Kneller and R. Hawig: *IEEE Trans. Magn.*, 1991, vol. 27, pp. 3588–60.
83. G. Herzer: *Mater. Sci. Eng. A*, 1991, vol. A133, pp. 1–5.
84. R. Skomski and J.M.D. Coey: *Phys. Rev. B*, 1993, vol. 48, pp. 15812–16.
85. R. Coehoorn, D.B. Mooji, and C. DeWaard: *J. Magn. Magn. Mater.*, 1989, vol. 80, pp. 101–04.
86. G.C. Hadjipanayis: *J. Magn. Magn. Mater.*, 1999, vol. 200, pp. 373–91.
87. H. Zeng, J. Li, J.P. Liu, Z.L. Wang, and S. Sun: *Nature*, 2002, vol. 420, pp. 395–98.
88. X. Rui, Z. Sun, L. Yue, Y. Xu, D.J. Sellmyer, Z. Liu, D.J. Miller, and J.E. Shield: *J. Magn. Magn. Mater.*, 2006, vol. 305, pp. 76–82.
89. J.E. Shield, J. Zhou, S. Aich, V.K. Ravindran, R. Skomski, and D.J. Sellmyer: *J. Appl. Phys.*, 2006, vol. 99, p. 08B508.
90. L.H. Lewis, A.R. Moodenbaugh, D.O. Welch, and V. Panchanathan: *J. Phys. D: Appl. Phys.*, 2001, vol. 34, pp. 744–51.
91. K. Raviprasad, M. Funakoshi, and M. Umemoto: *J. Appl. Phys.*, 1998, vol. 83, pp. 921–29.
92. S.K. Chen, J.L. Tsai, and T.S. Chin: *J. Appl. Phys.*, 1996, vol. 79, pp. 5964–66.
93. G. Sreenivasulu, R. Gopalan, V. Chandrasekaran, G. Markandeyulu, K.G. Suresh, and B.S. Murty: *Nanotechnology*, 2008, vol. 19, p. 335701.
94. C.L. Harland, L.H. Lewis, Z. Chen, and B.-M. Ma: *J. Magn. Magn. Mater.*, 2004, vol. 271, pp. 53–62.
95. J.P. Liu, E. Fullerton, O. Gutfleisch, and D.J. Sellmyer: *Nano-scale Magnetic Materials and Applications*, Springer, New York, NY, 2009.
96. C. Suryanarayana: *Progr. Mater. Sci.*, 2001, vol. 46 (1–2), pp. 1–184.
97. W.H. Meiklejohn and C.P. Bean: *Phys. Rev.*, 1956, vol. 102, pp. 1413–14.
98. K.-W. Lin, R.J. Gambino, and L.H. Lewis: *J. Appl. Phys.*, 2003, vol. 93, pp. 6590–92.
99. F. Jiménez-Villacorta and C. Prieto: *J. Phys.: Condens. Matter*, 2008, vol. 20, p. 085216.
100. V. Skumryev, S. Stoyanov, Y. Zhang, G. Hadjipanayis, D. Givord, and J. Nogues: *Nature*, 2003, vol. 423, pp. 850–53.
101. J. Nogués, J. Sort, V. Langlais, V. Skumryev, S. Suriñach, J.S. Muñoz, and M.D. Baro: *Phys. Rep.*, 2005, vol. 422, pp. 65–117.
102. J. Nogués and I. K. Schuller: *J. Magn. Magn. Mater.*, 1999, vol. 192, pp. 203–32.
103. H.C. Tong, C. Qian, L. Miloslavsky, S. Funada, X. Shi, F. Liu, and S. Dey: *J. Magn. Magn. Mater.*, 2000, vol. 209, pp. 56–60.
104. S.R. Mishra, I. Dubenko, J. Losby, S. Roy, N. Ali, and K. Marasinghe: *IEEE Trans. Magn.*, 2004, vol. 40, pp. 2716–20.
105. B.H. Miller and E.D. Dahlberg: *J. Appl. Phys.*, 1997, vol. 81, p. 5002.
106. S.A. Wolf, D.D. Awschalom, R.A. Buhrman, J.M. Daughton, S. von Molnár, M.L. Roukes, A.Y. Chtchelkanova, and D.M. Treger: *Science*, 2001, vol. 294, pp. 1488–95.
107. A. Inoue, T. Zhang, W. Zhang, and A. Takeuchi: *Mater. Trans. JIM*, 1996, vol. 37, pp. 99–108.
108. M.J. Kramer, A.S. O’Connor, K.W. Dennis, R.W. McCallum, L.H. Lewis, L.D. Tung, and N.P. Duong: *IEEE Trans. Magn.*, 2001, vol. 37 (4), pp. 2497–99.
109. R.W. McCallum, L.H. Lewis, M.J. Kramer, and K.W. Dennis: *J. Magn. Magn. Mater.*, 2006, vol. 299, pp. 265–80.
110. J. Sort, J. Nogués, X. Amils, S. Suriñach, J.S. Muñoz, and M.D. Baró: *Appl. Phys. Lett.*, 1999, vol. 75, pp. 3177–79.
111. J. Sort, S. Suriñach, J.S. Muñoz, M.D. Baró, J. Nogués, G. Chouteau, V. Skumryev, and G.C. Hadjipanayis: *Phys. Rev. B*, 2002, vol. 65, p. 174420.
112. T.A. Anhoj, C.S. Jacobsen, and S. Mørup: *J. Appl. Phys.*, 2004, vol. 95, pp. 3649–54.
113. S.R. Mishra, I. Dubenko, J. Losby, S. Roy, N. Ali, and K. Marasinghe: *IEEE Trans. Magn.*, 2004, vol. 40, pp. 2716–20.
114. L.H. Lewis, C.L. Harland, R.W. McCallum, M.J. Kramer, and K.W. Dennis: *J. Appl. Phys.*, 2006, vol. 99, p. 08E908.
115. L.H. Lewis, C.L. Harland, R.W. McCallum, M.J. Kramer, and K.W. Dennis: unpublished research, 2005.
116. F. Jiménez-Villacorta, J.L. Marion, and L.H. Lewis: unpublished research, 2012.
117. P. Gibbs, T.M. Harden, and J.H. Smith: *J. Phys. F: Met. Phys.*, 1985, vol. 15, pp. 213–23.
118. G.E. Bacon, I.W. Dunmur, J.H. Smith, and R. Street: *Proc. Roy. Soc. Lond.*, 1957, vol. A241, pp. 223–38.
119. A. Banerjee and A.K. Majumdar: *Phys. Rev. B*, 1992, vol. 46, pp. 8958–73.
120. M. Acet, C. John, and E.F. Wassermann: *J. Appl. Phys.*, 1991, vol. 70, pp. 6556–58.
121. R. Bali, B.B. Nelson-Cheeseman, A. Scholl, E. Arenholtz, Y. Suzuki, and M.G. Blamire: *J. Appl. Phys.*, 2009, vol. 106, p. 113925.
122. K. Komagaki, K. Yamada, K. Noma, H. Kanai, K. Kobayashi, Y. Uehara, M. Tsunoda, and M. Takahashi: *IEEE Trans. Magn.*, 2007, vol. 43, pp. 3535–37.
123. L.E. Fernandez-Outon, K. O’Grady, S. Oh, M. Zhou, and M. Pakala: *IEEE Trans. Magn.*, 2008, vol. 44, pp. 2824–27.
124. F. Jiménez-Villacorta, J.L. Marion, T. Sepehrifar, and L.H. Lewis: *J. Appl. Phys.*, 2012, vol. 111, p. 07E141.
125. J.S. Kouvel: *J. Phys. Chem. Solids*, 1961, vol. 21, pp. 57–70.
126. J.S. Kouvel: *J. Appl. Phys.*, 1960, vol. 31, pp. 142S–147S.
127. J. Ederth, A. Hoel, C.I. Johansson, L.B. Kiss, E. Olsson, C.G. Granqvist, and P. Nordblad: *J. Appl. Phys.*, 1999, vol. 86, pp. 6571–75.
128. T. Sato and K. Komatsu: *J. Phys. D: Appl. Phys.*, 2010, vol. 43, p. 474003.
129. J.M.D. Coey: *J. Appl. Phys.*, 1994, vol. 76, pp. 6632–36.
130. M.Q. Huang, W.E. Wallace, S. Simizu, A.T. Pedziwiatr, R.T. Obermyer, and S.G. Sankar: *J. Appl. Phys.*, 1994, vol. 75, pp. 6574–76.
131. M.Q. Huang, W.E. Wallace, S. Simizu, and S.G. Sankar: *J. Magn. Magn. Mater.*, 1994, vol. 135, pp. 226–30.

132. T.K. Kim and M. Takahashi: *Appl. Phys. Lett.*, 1972, vol. 20, pp. 492–94.
133. H. Takahashi, K. Mitsuoka, M. Komuro, and Y. Sugita: *J. Appl. Phys.*, 1993, vol. 73, pp. 6060–62.
134. K.H. Jack: *Proc. Roy. Soc. Lond. A*, 1951, vol. 208, pp. 200–15.
135. K.H. Jack: *Proc. R. Soc. Lond. A*, 1951, vol. 208, pp. 216–24.
136. Y. Sugita, H. Takahashi, M. Komuro, K. Mitsuoka, and A. Sakuma: *6th Joint MMM-Intermag Conf.*, Paper #EB-4, Albuquerque, NM, June 20–23, 1994.
137. M. Takahashi and H. Shoji: *J. Magn. Magn. Mater.*, 2000, vol. 208, pp. 145–57.
138. Conference on Critical Materials for a Clean Energy Future, October 4–5, 2011, Workshops hosted by the U.S. Department of Energy, Washington, DC, http://energy.gov/sites/prod/files/DOE_CMS2011_FINAL_Full.pdf.
139. Y.A. Izyumov and V.N. Syromyatnikov: *Phase Transitions and Crystal Symmetry*, Kluwer Academic Publishers, Dordrecht, the Netherlands, 1990, pp. 29–31.
140. P. Ehrenfest: *Verhandlingen der Koninklijke Akademi van Wetenschappen*, 36, Supplement no. 75b. (Communications from the Physical Laboratory of the University of Leiden, Amsterdam, the Netherlands, 1933), pp. 153–57.
141. J.B. Newkirk, R. Smoluchowski, A.H. Geisler, and D.L. Martin: *Trans. AIME*, 1950, vol. 188, pp. 1249–60.
142. F.N. Rhines and J.B. Newkirk: *Trans. AIME*, 1950, vol. 45, pp. 1029–55.
143. T. Klemmer, D. Hoydick, H. Okumura, B. Zhang, and W.A. Soffa: *Scripta Metall.*, 1995, vol. 33, p. 1793.
144. S. Sun, C.B. Murray, D. Weller, L. Folks, and A. Moser: *Science*, 2000, vol. 287, pp. 1989–92.
145. S. Sun, E.E. Fullerton, D. Weller, and C.B. Murray: *IEEE Trans. Magn.*, 2001, vol. 37, pp. 1239–43.
146. D.J. Sellmyer, M. Yan, Y. Xu, and R. Skomski: *IEEE Trans. Magn.*, 2005, vol. 41, pp. 560–65.
147. J. Zhou, R. Skomski, X. Li, W. Tang, G.C. Hadjipanayis, and D.J. Sellmyer: *IEEE Trans. Magn.*, 2001, vol. 38, pp. 2802–04.
148. J.P. Liu, Y. Liu, R. Skomski, and D.J. Sellmyer: *IEEE Trans. Magn.*, 1999, vol. 35, pp. 3241–46.
149. C.-Y. Yang, D.B. Williams, and J.I. Goldstein: *J. Phase Equil.*, 1996, vol. 17 (6), pp. 522–31.
150. T. Shima, M. Okamura, S. Mitani, and K. Takanashi: *J. Magn. Magn. Mater.*, 2007, vol. 310, pp. 2213–14.
151. J. Danon, R. Scorzelli, I. Souza Azevedo, W. Curvello, J.F. Albersen, and J.M. Knudsen: *Nature*, 1979, vol. 277, pp. 283–84.
152. J.I. Goldstein, J.R. Michael, and P. Kotula: *Microsc. Microanal.*, 2008, vol. 14, pp. 520–21.
153. J. Paulevé and D. Dautreppe: *Compte Rendus Acad. Sci.*, 1960, vol. 250, pp. 3804–06.
154. J. Paulevé, D. Dautreppe, J. Laugier, and L. Néel: *Compte Rendus Acad. Sci.*, 1962, vol. 254, pp. 965–68.
155. L. Néel, J. Paulevé, R. Pauthenet, J. Laugier, and D. Dautreppe: *J. Appl. Phys.*, 1964, vol. 35, pp. 873–76.
156. N. Kurti: *Selected Works of Louis Néel*, Gordon and Breach Science Publishers, New York, NY, 1988.
157. T. Kojima, M. Mizuguchi, and K. Takanashi: *J. Phys.: Conf. Ser.*, 2011, vol. 266, p. 012119.
158. L. Ma, D.B. Williams, and J.I. Goldstein: *J. Phase Equil.*, 1998, vol. 19, pp. 299–309.
159. J. Zhang, D.B. Williams, and J.I. Goldstein: *Metall. Mater. Trans. A*, 1994, vol. 25A, pp. 1627–37.
160. J.H. Park, Y.K. Hong, S. Bae, J.J. Lee, J. Jalli, G.S. Abo, N. Neveu, S.G. Kim, C.J. Choi, and J.G. Lee: *J. Appl. Phys.*, 2010, vol. 107, p. 09A731.
161. D.P. Hoydick, E.J. Palmiere, and W.A. Soffa: *J. Appl. Phys.*, 1997, vol. 81, pp. 5624–26.
162. K. Kamino, T. Kawaguchi, and M. Nagakura: *IEEE Trans. Magn.*, 1966, vol. 2, pp. 506–10.
163. Z.C. Yan, Y. Huang, Y. Zhang, G.C. Hadjipanayis, W. Soffa, and D. Weller: *Scripta Mater.*, 2005, vol. 53, pp. 463–68.
164. H. Kono: *J. Phys. Soc. Jpn.*, 1958, vol. 13, pp. 1444–51.
165. A.J.J. Koch, P. Hokkelling, M.G. Steeg, and K.J. de Vos: *J. Appl. Phys.*, 1960, vol. 31, pp. 75S–77S.
166. T. Ohtani, N. Kato, S. Kojima, K. Kojima, Y. Sakamoto, I. Konno, M. Tsukahara, and T. Kubo: *IEEE Trans. Magn.*, 1977, vol. 13, pp. 1328–30.
167. Y.C. Yang, W.W. Ho, C. Lin, J.L. Yang, H.M. Zhou, J.X. Zhu, X.X. Zeng, B.S. Zhang, and L. Jin: *J. Appl. Phys.*, 1984, vol. 55, pp. 2053–54.
168. C. Yanar, J.M.K. Wiezorek, V. Radmilovic, and W.A. Soffa: *Metall. Mater. Trans. A*, 2002, vol. 33A, pp. 2413–23.
169. J.M.K. Wiezorek, A.K. Kulivitis, C. Yanar, and W.A. Soffa: *Metall. Mater. Trans. A*, 2011, vol. 42A, pp. 594–604.
170. X.J. Liu, R. Kainuma, H. Ohtani, and K. Ishida: *J. Alloy. Compd.*, 1986, vol. 235, pp. 256–61.
171. J.J. Van Den Broek, H. Donkersloot, G. Van Tendeloo, and J. Van Landuyt: *Acta Metall.*, 1979, vol. 27, pp. 1497–1504.
172. F. Jiménez-Villacorta, J.L. Marion, T. Sepehrifar, M. Daniil, M.A. Willard, and L.H. Lewis: *Appl. Phys. Lett.*, 2012, vol. 100, p. 112408.
173. R.A. McCurrie, J. Rickman, P. Dunk, and D.G. Hawkrige: *IEEE Trans. Magn.*, 1978, vol. 14, pp. 682–84.
174. E. Fazakas, L.K. Varga, and F. Mazaleyrat: *J. Alloy. Compd.*, 2007, vols. 434–435, pp. 611–13.
175. Q. Zeng, I. Baker, J.B. Cui, and Z.C. Yan: *J. Magn. Magn. Mater.*, 2007, vol. 308, pp. 214–26.
176. Q. Zeng, I. Baker, and Z. Yan: *J. Appl. Phys.*, 2006, vol. 99, p. 08E902.
177. MolyCorp, <http://www.molycorp.com>.
178. Y. Kido, N. Hoshi, A. Chiba, S. Ogasawara, and M. Takemoto: *Proc. of the 2011–14th European Conference on Power Electronics and Applications (EPE 2011)*, Birmingham, U.K., 2011, pp. 1–10.