Powerful New Magnet Material Found

Several groups in Japan and the United States independently hit upon the same iron-based compound, which is already going to market

If a person thinks of a material for a permanent magnet at all, it is likely to be of something with lots of iron in it. In fact, however, for many years the best permanent magnets have contained little or no iron. Now iron is back.

During the past few months, several research groups in Japan and in the United States have announced the discovery of a new compound—probably of composition $R_2Fe_{14}B$, where R is a light rare earth (usually neodymium)—that has some of the best magnetic properties ever. In Japan, the Sumitomo Special Metals Company has begun taking orders for magnets made of the new compound. In the United States, Crucible, Inc., intends to begin production later this year, and General Motors is gearing up to make the material for its own use. "Almost every magnet manufacturer in the world is working on it," bubbled a spokesman for a fourth firm.

The impact of the breakthrough will depend on both technological and economic factors. Magnets made of the compound tend to lose their desirable properties at elevated temperatures. If this fault can be cured—there is evidence that it can—and if the cost drops, as it should when volume production begins, the new material could push aside all but the most inexpensive alternatives and dominate the magnet market, the most optimistic observers say.

Applications for permanent magnets span a wide range from the butterflies that hold children's drawings on refrigerator doors to microwave devices in the military and in telecommunications. Speakers in audio systems are probably the most widespread, though seldom noticed, home for magnets. The largest potential market for the new magnet material is electric motors, which could have half the size and weight they do now. At least one company is considering permanent magents made of the rare earth–iron-boron compound for the next generation of nuclear magnetic resonance medical imaging systems. "I look at neodymium-iron as the ultimate answer to our materials problem," says Ronald Holsinger of Field Effects, Inc., of Carlisle, Massachusetts, who is looking at the imaging application.

Permanent magnets have a number of parameters that measure their performance. The two most important are the coercivity and the energy product. The coercivity is the strength of the external field needed to demagnetize the material. A high coercivity is needed to prevent the demagnetization of permanent magnets when they encounter fields produced by other sources. The energy product is a composite parameter determined both by the strength of the magnet and the coercivity and is the most frequently cited figure of merit.

Until the new iron-based compound popped up, the materials that most closely satisfied requirements for high values of these parameters were compounds principally comprising samarium and cobalt. The original compound, $SmCo_5$, was discovered in the mid-1960's by Karl Strnat (now at the University of Dayton) and his co-workers at the Air Force Materials Laboratory, Wright-Patterson Air Force Base, and the General Electric R & D Center, Schenectady. This compound has an energy product of 143 kilojoules per cubic meter (kJ/m^3), more than six times that of the widely used ceramic or ferrite materials.

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Subsequent development led to more complex materials containing limited amounts of copper, zirconium, and iron that have energy products up to 239 kJ/m^3. Samarium-cobalt is manufactured worldwide nowadays. The lightweight earphones of Sony Walkman–type portable radios and cassette players, for example, are made possible by samarium-cobalt magnets. Most of the wiggler magnets that serve as the most intense sources of synchrotron radiation from electron storage rings are likewise made of these materials.

The high price of samarium-cobalt magnets has limited their use in large volume, however. For example, starter motors in automobiles now rely on battery-driven electromagnets. Samarium-cobalt permanent magnets could make smaller, more reliable starters, and General Motors once considered them for that purpose. But the company decided against them partly because of their cost.

Fluctuations in the price and availability of cobalt made General Motors even more nervous. Cobalt is a by-product of copper and nickel mining, and the main source for the United States is southern Africa, Zaire in particular. When fighting broke out there in 1978 and the copper mines were at risk, the price of cobalt on the spot market rocketed up by a factor of 8 and was still up by a factor of 5 a year later. It is back down to its old price now.

Cobalt is also an essential ingredient of high-temperature superalloys for aircraft and is therefore classified as a strategic material. Both for economic reasons and to relieve any possible drain on cobalt resources required for strategic applications, the 1978 cobalt crunch precipitated a search for cobalt-free permanent magnet materials.

Metallurgists searching for new magnetic materials face a formidable task. The strength of the ideal magnet depends on the elements making up the material. Each atom has a magnetic moment due to the orbital and spin angular momenta of its electrons. The macroscopic magnetization of a material is the resultant sum of the moments of each atom, which would all be aligned in the fully magnetized state. Transition elements such as iron and cobalt have large moments, so one likes to put large amounts of these elements into the mix. However, the coercivity depends first on the crystal structure of the compound and then on the metallurgical microstructure of the final material.

Magnetic materials resist demagnetization when it takes a large energy to rearrange the aligned magnetic moments of the atoms in the material. Crystal structures come into play because, with respect to ease of magnetization, some crystallographic directions are easy (do not take much energy) and some are hard. A high coercivity requires a crystal structure with very hard directions separating the easy ones so that it takes a great deal of energy to reorient the magnetic moments from one easy direction to another.

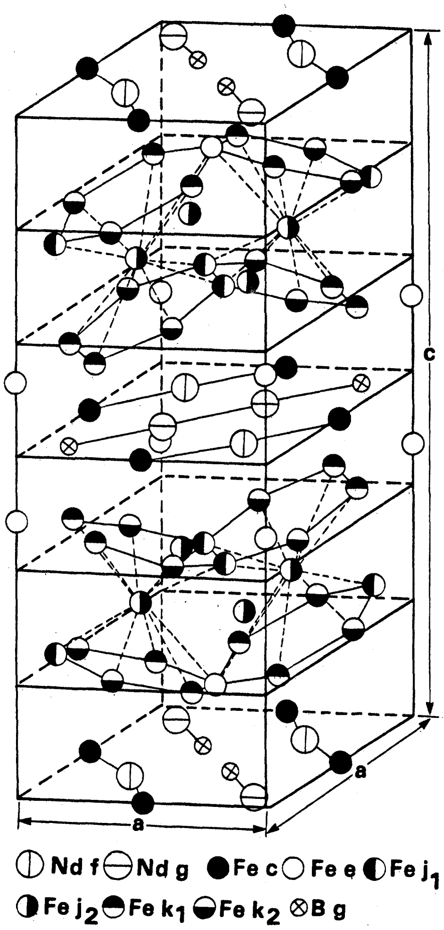
Transition metals such as iron and cobalt do not have what researchers call high magnetocrystalline anisotropy energies. Metallurgists therefore add rare earths to transition metals because the compounds they form sometimes have structures with the required high anisotropy energies. The trick is to achieve this without losing the high magnetization through dilution of the magnetic moments.

The actual mechanism by which the direction of the magnetization changes is not one in which the atomic moments flip simultaneously throughout the material. Instead, entities called domain walls that separate regions of different directions of magnetization move through the material, reorienting moments only where they pass. The highest coercivity, therefore, requires the inhibition of domain wall motion. In general, this is done by adjusting the composition of the material so that two phases form with different magnetic properties, one the magnetic compound and the other something else. The second phase must be very finely distributed (for example, scattered throughout the magnetic phase). It then pins or traps the domain walls and thereby raises the strength of the magnetic field needed to demagnetize the material.

Research in the United States sprang from two primary sources. The Office of Naval Research sponsored work at several industrial and academic laboratories, while the General Motors Research Laboratories in Warren, Michigan, mounted an independent effort. All the groups apparently used for their starting point the 1973 work of Arthur Clark of the Naval Surface Weapons Center in White Oak, Maryland. The 1960's studies of Strnat's group, as well as the studies of a number of others, had shown that binary rare earth–iron compounds were few in number and had unimpressive magnetic properties. Clark found, however, that compounds of the form RFe_2, where R is terbium, dysprosium, or samarium, had much improved coercivities, provided they were first prepared in a noncrystalline or amorphous state.

With no long-range crystal structure and hence no anisotropy, amorphous materials would not seem to be candidates for permanent magnets. However, amorphous materials provide a nice starting point from which to prepare crystalline materials with unusual metallurgical microstructures or to make crystalline nonequilibrium (metastable) phases with novel properties. Clark's results had suggested the possibility that annealing amorphous material could give rise to magnetically active material composed of very fine crystallites or grains.

The investigators who followed Clark's lead in looking at rare earth–iron compounds used a technique called melt spinning in which a stream of molten material is blown out through the orifice of a crucible onto a spinning copper wheel. For example, at the Naval Research Laboratory in Washington, D.C., Norman Koon and Badri Das started from the well-known observation that the presence of boron enhances the likelihood of rapidly cooled materials being amorphous. They studied terbium-lanthanum-iron-boron mixtures in the hope that magnetically active compounds with optimized microstructures would form upon annealing the amorphous material. Upon annealing at successively higher temperatures, they found the coercivity rose sharply, then decreased. Moreover, x-ray data showed the formation of a complex multiphase structure comprising well-known rare earth–iron, boron-iron, and iron phases with grains near 300 angstroms in diameter.



Crystal structure

Jan Herbst, John Croat, and Frederick Pinkerton of General Motors, in collaboration with William Yelon of the University of Missouri, obtained a detailed crystal structure of the magnetic compound by means of neutron diffraction. The proposed structure has a tetragonal unit cell that is almost 50 percent taller than it is wide and comprises four $Nd_2Fe_{14}B$ units. [Courtesy Physical Review **B1** *(April 1984), in press]*

During the same 1980 to 1982 period, reports from John Croat's group at General Motors described experiments on melt-spun praseodymium-cobalt, praseodymium-iron, and neodymium-iron materials. Neodymium-iron was the most interesting. A series of specimens was prepared by spinning the wheel at different speeds. In general, one would expect faster cooling at higher speeds and hence an increased tendency toward the formation of amorphous material. However, the coercivity of unannealed specimens increased dramatically with spinning speed at first, then dropped off more gently. Croat's interpretation was that at the lowest speed a magnetically active phase did not form. At higher speeds one did, and the coercivity rose. At still higher speeds, the grains became so small that their properties deteriorated. X-ray analysis of the material yielded no structural information because of the small particle size. Thus, it was not possible to say whether the active phase was an equilibrium or a metastable one.

It is clear that these investigations formed the background for the development of the new rare earth–iron-boron permanent magnets. But the line of thinking that led the various participants to their goal is not so clear. Nearly everyone missed a 1979 report in a Soviet journal by crystallographers at the Lvov Ivan Franko State University in the Ukraine. During their study of the neodymium-iron-boron phase diagram, they found an equilibrium ternary compound, which turned out to be the one that makes the new magnets possible. They did not report its structure or magnetic properties. Because of the paucity of binary iron–rare earth compounds, any active magnet researcher would have looked into it as soon as possible, but they were not magnet makers.

One American scientist who did notice the report was Hans Stadelmaier of North Carolina State University in Raleigh, who was investigating rare earth–transition metal–boron systems. Stadelmaier was only beginning work on permanent magnets, however, and did not immediately follow up on the discovery. He and his colleagues later found an identical samarium-cobalt-boron compound and gathered some structural information.

Things began moving faster in April of last year. Spurred by new results from a group comprising George Hadjipanayis and Robert Hazelton of the Kollmorgen Corporation in Radford, Virginia, and K. R. Lawless of the University of Virginia in Charlottesville, ONR program director Donald Polk suggested his contractors compare notes prior to an international magnetic materials meeting in Philadelphia. Hadjipanayis discussed some of the results obtained by the group and later sent some data and samples to Stadelmaier. Stadelmaier immediately identified the Kollmorgen material (which consisted of a praseodymium-iron-boron-silicon mixture that was annealed following rapid solidification by the melt-spinning technique) as containing a compound with the same composition as that reported by the Ukrainians. The new material had an energy product of 96 kJ/m^3, which is at the lower end of the range of values in commercial samarium-cobalt.

Apparently work was progressing independently at General Motors, NRL, and elsewhere. But in June an unexpected announcement from Japan set magnetics people buzzing. The Sumitomo Special Metals Company of Osaka revealed that it had made magnets from a new compound based on neodymium and iron that had an energy product of 290 kJ/m^3, higher than the best samarium-cobalt material. Moreover, the company was making the material by conventional powder metallurgical techniques of the type used to manufacture samarium-cobalt magnets. Finally, Sumitomo said it would begin making samples of the material available to prospective customers in the fall.

The Japanese company did not stop there. At the 29th Annual Conference on Magnetism and Magnetic Materials held last November in Pittsburgh, all the players were called to lay their cards on the table. At a symposium devoted to the subject, researchers from General Motors, NRL, General Electric, Kansas State University, to which Hadjipanayis had migrated, and North Carolina State summarized their findings. Koon from NRL, for example, reported that he and Das had made, by annealing melt-spun praseodymium- and neodymium-iron-boron material, magnets with energy products up to 103 kJ/m^3.

Similarly, GM's Croat discussed praseodymium-iron-boron and neodymium-iron-boron compounds that had energy products of up to 120 kJ/m^3 that were produced by the same method that his group had been using before. Croat also revealed that the laboratory had found a way to double this value, but he would not say how it had been done. General Motors still has not disclosed its manufacturing method, for that matter.

Rather surprising, given Japan's reputation as eager to soak up information from abroad but quite reluctant to give much out, Sumitomo's Masato Sagawa was forthcoming in his presentation in a separate session of the conference. Says Lyman Johnson of General Electric, "It was so explicit and well done that anyone who knows how to make samarium-cobalt could make rare earth–iron-boron in a week."

Since then a number of firms have said privately that they are making good magnets from the new compound in the laboratory. Late in January, Crucible's Research Center in Pittsburgh announced publicly that it had made by a powder-metallurgical method the highest energy product material yet, 341 kJ/m^3. Moreover, Crucible's magnetics division intends to begin commercial production this fall of Crumax, the trade name for its magnet material. Crucible's Kalatur Narasimhan says that the company's search for a cobalt-free magnet began about 2 years ago. An interesting patent situation may be brewing as more companies begin manufacturing the new compound by the powder-metallurgical method. Sumitomo is said to have a large number of patents already on file for its Neomax material.

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An important difference between the General Motors magnet material and that of Sumitomo and Crucible may affect the patent situation and also the range of applications. The published accounts of General Motors' material, called Magnequench, describe isotropic magnets. Isotropy is a result of the melt-spinning production method. This means that the crystallites within the material are oriented randomly, so that overall the material has no preferred direction of magnetization. It is the isotropy that is responsible for the lower energy product of the melt-spun material.

The powder method begins with an ingot solidified from the melt in the ordinary way so that mainly the magnetic compound of composition $Nd_2Fe_{14}B$ forms. The ingot is ground in several stages to small particles a few micrometers in diameter. The particles are aligned and pressed together in a magnetic field so that they are all magnetized in the same direction; that is, the compacted body has some of the anisotropy of the crystal structure. Then the particles are sintered to form a dense solid. During the sintering at high temperature, the particles lose their magnetization, so the sintered material must be remagnetized.

One interesting question is, with all the early emphasis on rapid solidification, why is it possible to make the earth-iron-boron compound by ordinary methods? Part of the answer is that the boron stabilizes the new compound. The resulting crystal structure is tetragonal, an anisotropic structure that contributes to the high coercivity (see the figure on p. 921). The relatively small concentrations of light rare earths and boron allow the magnetization to remain high.

Somewhat conjectural still is the nature of the metallurgical microstructure that enhances the coercivity. Those making the new compound by the power metallurgy method find that the overall composition must differ slightly from that of the compound to allow the formation of one or more additional phases that are richer in rare earth or boron than the magnetic compound and that are seen near the grain boundaries. The General Motors group is sticking to its original explanation that the grains are so small that they contain no domain boundaries and that it takes a lot of energy to nucleate any.

The main limitation of the new magnetic compound is that it has a low Curie temperature, 585 K as compared to over 1000 K in samarium-cobalt compounds. Since magnets lose their magnetization above the Curie temperature, the magnet strength and the coercivity of the new material drop off severely when it is heated to only 100 degrees above room temperature, as they might be in an automobile starter motor. Sumitomo's Sagawa reported, and several laboratories have since confirmed, that the addition of cobalt raises the Curie temperature. Sumitomo researchers added 10 to 20 percent cobalt. Hadjipanayis says that 6 percent cobalt is enough to raise the Curie temperature 100 K. Addition of heavy rare earths also enhances the coercivity, rendering it less sensitive to temperature effects.

If cobalt is needed to make the rare earth–iron-boron compound useful, can one still speak of cobalt-free magnets? The literal answer is no, but the concentration of that element is nonetheless greatly reduced. Strnat says the likeliest outcome is the development of a large family of magnets of varying composition. Rare earth–iron-boron and rare earth–cobalt will be the extremes at each end of the family.

—Arthur L. Robinson