Imitating Iron's Magnetism

Researchers report the first steps on the road to plastic magnets

By IVARS PETERSON

Everyday experience teaches us what to expect when we use or handle common materials. Thus, for anyone who has played with a bar magnet, finding a chunk of iron that attracts a fringe of iron filings or picks up a string of paper clips is hardly surprising. Iron is known to be one of a few metals, termed ferromagnetic materials, that can be magnetized. On the other hand, it would be astonishing to see a lump of plastic acting like a permanent magnet. Nevertheless, researchers are now on the track of polymers and molecular solids that could readily pass for metallic ferromagnets.

Recently, three different research groups announced varying degrees of success in synthesizing organic ferromagnetic materials, consisting of compounds largely made up of carbon, hydrogen and nitrogen atoms. Two of the products are polymers; the third is a type of crystalline solid known as a charge-transfer salt.

This achievement parallels the unexpected discovery during the last decade of organic materials with a range of electrical properties. Whereas scientists once considered organic materials, such as polymers, to be insulators, now they can turn these materials into electrical conductors. Previously, only metals and some inorganic substances were known to conduct electricity.

Like the discovery of conducting polymers, the demonstration of the existence of organic or molecular ferromagnets opens up a new field of study. Although the road to plastic magnets, novel coatings for magnetic recording tape and other potential applications is likely to be a long one, the first steps have been taken.

Magnetic materials owe their magnetism mainly to the spin of their electrons. Each electron can be thought of as a tiny magnet pointing up or pointing down. Often, these electrons occur as pairs, each pair consisting of electrons with opposite spin. An atom or molecule with paired electrons has no net spin and exhibits only mild, subtle magnetic effects.

Iron atoms happen to have unpaired electrons. As a result, these atoms have a net magnetic moment. When iron atoms cluster, as they do when iron crystallizes, the unpaired electrons tend to align their individual spins so that electrons in large regions of the material have the same spin. These regions of common spin are called domains. A weak, externally applied magnetic field aligns all the domains so that the whole material behaves in a coordinated fashion to create a permanent magnet. This type of magnetic effect is called ferromagnetism. Because ferromagnetism is apparent only if a sufficiently large number of atoms cooperate, it's considered to be a "bulk" property of a material rather than a property of the atoms themselves.

In general, individual molecules have an even number of electrons. These are paired so that the material shows no net magnetism. The trick to creating a molecular rather than an atomic ferromagnet is to build molecules with an odd number of electrons so that at least one electron on each molecule is unpaired. A ferromagnet will result if the spins of neighboring molecules are somehow lined up so that all the spins are in the same direction.

That's much easier said than done. For one thing, molecules with unpaired electrons, also known as radicals, are often highly reactive. Moreover, just as opposite magnetic poles attract, spins on adjacent molecules are more likely to be in opposite directions rather than in the same direction.

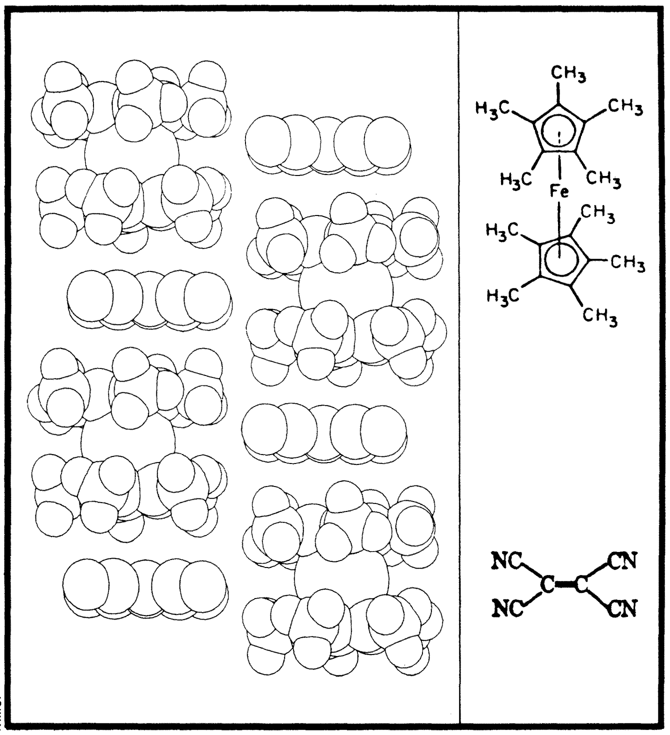
"There are a large number of people who will tell you [that synthesizing an organic ferromagnet] is impossible," says Jerry B. Torrance of the IBM Almaden Research Center in San Jose, Calif., "yet a lot of us feel it is possible, and we think we can see how to do it." Nevertheless, he adds, "most people are in this for the challenge. The difficulty is beyond belief."

One group of researchers has constructed a crystalline ferromagnetic material using two different types of molecules. One ingredient is an organometallic compound called decamethylferrocene; the other is tetracyanoethylene. The ferrocene molecule (the donor) readily transfers an electron to a tetracyanoethylene molecule (the acceptor), leaving each component with an unpaired electron. The resulting ions sit stacked in an orderly three-dimensional lattice in which the two types of molecules alternate in position. The distance between donors and acceptors in adjacent stacks is about the same as the distance between donors and acceptors within a stack. In bulk, the compound appears as pale green crystals, up to a few millimeters in length.

At room temperature, the ions jiggle so much that the spins of the unpaired electrons don't notice each other. However, as the temperature is lowered, the electron spins begin to cooperate and align spontaneously. At temperatures below 5 kelvins, all the spins are in line, and the compound behaves like a ferromagnet. Although an iron atom sits at the center of each sandwichlike ferrocene molecule, it doesn't play its usual ferromagnetic role.

"There's no question that we're seeing a bulk ferromagnet created by lining up the spins on the individual molecules," says Arthur J. Epstein of Ohio State University in Columbus. "The ferromagnetic moment that we get is exactly the moment that one would calculate if one adds up the little magnets on each of the decamethylferrocenium and tetracyanoethanide ions." When fully magnetized, the material's magnetic strength compares favorably with that of pure iron. Epstein, Joel S. Miller of E.I. du Pont de Nemours & Co. in Wilmington, Del., and William M. Reiff of Northeastern University in Boston report their findings in the Feb. 4 JOURNAL OF THE AMERICAN CHEMICAL SOCIETY.

Epstein and Miller have also worked out a theory that accounts for why the spins on the molecules spontaneously align at sufficiently low temperatures. On the basis of their model, they have been able to predict the behavior of the compound when the ferrocene component is modified. Substituting a chromium or a



Miller

Combining sandwich-like decamethylferrocene molecules (top right) with pancake-like tetracyanoethylene molecules (bottom right) produces a crystalline material that is ferromagnetic at liquid-helium temperatures. The two types of molecules sit in alternating positions within stacks, and adjacent stacks in the crystal's three-dimensional lattice are staggered so that tetracyanoethylene molecules always have ferrocene molecules as nearest neighbors (left).

nickel atom for the central iron atom in decamethylferrocene, for instance, changes the material's magnetic character, and the ferromagnetism disappears.

"Once you begin to have some model of what's going on," says Epstein, "you can generalize it and test it. This is the phase we're in now."

Because the new material becomes a ferromagnet only at liquid-helium temperatures, its practical value is limited. However, it provides an excellent platform for exploring the magnetic behavior of some unusual materials. "There are very few examples of organic-like materials that exhibit cooperative behavior," says Miller. "The more we know about it, the better a chance that we can develop [related materials] for technological applications."

Chemist Ronald Breslow of Columbia University in New York City is also interested in building a ferromagnet out of a crystalline material. However, instead of using stacks of separate donor and acceptor molecules, he's trying to synthesize a single molecule that when stacked properly would have a good chance of becoming a ferromagnet. Although Breslow and his colleagues have created some chemically interesting compounds, they haven't yet reported any success in putting together a molecular ferromagnet.

Several research groups in the United States, the Soviet Union and Japan are taking a close look at polymers. The idea is to create long molecular chains that have lots of unpaired electrons, whose spins can then be lined up. It's here that the results appear most tantalizing yet frustratingly ambiguous.

Two years ago, Torrance and his colleagues discovered, "somewhat by accident," a polymer that sometimes shows ferromagnetism. The researchers create the polymer by reacting triaminobenzene with iodine to produce a black, insoluble material. "The reaction is complex," they report in a recent issue of SYNTHETIC METALS (Vol.19, p.709), "and the resulting polymer is not very reproducible. Nevertheless, on a number of occasions a ferromagnet material has been obtained." This material remains ferromagnetic until it decomposes near 400°C.

"It's a very messy chemical system," says Torrance. "It's hard to tell what's going on." The presence of unpaired electrons created by the iodine reaction makes the compound extremely reactive. Thousands of different things can happen, he says, and every once in a while, subtle shifts in the reaction conditions swing the balance toward creating a material in which the molecular spins are appropriately lined up. At best, the yield of ferromagnetic material is 2 percent, and often, it's close to zero.

The Soviet effort has a similar problem. Soviet researchers, led by A.A. Ovchinnikov of Moscow's Institute of Chemical Physics, prepare their ferromagnetic material by polymerizing a molecule consisting of nitroxyl groups attached to both ends of a diacetylene fragment. Only about 0.1 percent of the polymer product typically ends up being ferromagnetic. It remains ferromagnetic up to about 150°C. The Soviet report appears in the March 26 NATURE.

Because the yields are so low, other scientists have wondered whether the ferromagnetic effects seen in polymers may be due to iron impurities trapped in the material. "It's almost impossible to eliminate iron from organic chemistry," admits Torrance. "It's everywhere." However, one test, in which the triaminobenzene polymer was heated up until it burned, showed that the ash contained far too little iron to account for the material's ferromagnetism.

Japanese efforts to duplicate the Soviet results confirm that the acetylene polymerization is explosive and that only a small amount of the product is ferromagnetic. Apparently, they were also able to show that inorganic impurities do not play a significant role. On the other hand, says Miller, "we tried to make that compound because we think it's interesting. We couldn't do it."

Meanwhile, Japanese researchers Hiizu Iwamura of the Institute of Molecular Science in Okazaki and Koichi Itoh of Osaka City University have had some notable success in hooking together up to five small molecules to create a longer molecule with two electrons of the same spin at each link. Although such high-spin molecules are extremely reactive, the researchers are trying to develop an effective method for safely bringing them together so that their spins interact but the molecules themselves don't react. Their most recent findings were reported last year in the JOURNAL OF THE AMERICAN CHEMICAL SOCIETY (Vol.108, p.368 and p.4272).

Who gets credit for discovering the first organic ferromagnet? That question is currently the center of a minor dispute. The IBM and Soviet results are ambiguous and hard to reproduce. Their polymeric compounds are difficult to characterize. On the other hand, the charge-transfer salt produced by Miller and his co-workers, though well characterized and reproducible, contains iron. To some scientists, that means it isn't truly organic, although the salt is certainly a molecular ferromagnet at very low temperatures. All agree, however, that several crucial steps have been taken in an exciting new area of research.

Commenting in the March 26 NATURE, Richard Friend of the University of Cambridge in England says, "The discovery of ferromagnetism now completes the list for organic materials of those electronic properties (metallic conduction, superconductivity and ferromagnetism) formerly associated only with inorganic materials." He adds, "It will be some time to come, however, before organic ferromagnets find applications in place of traditional magnetic materials."

"It's an opening," says Epstein. "As in any new area, you're never quite sure where it's going to lead in the long term." □