

Faster than fairies

[*Faster than fairies*, faster than witches, Bridges and houses, hedges and ditches-R L Stevenson]

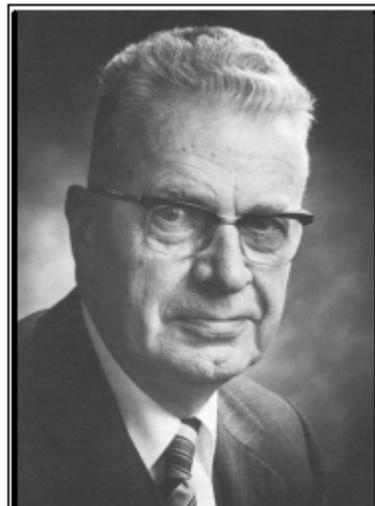
Ultra-fast changes in the nature of materials could speed up electronics, says S. Ananthanraayanan.

Magnetite, or Ferric Oxide, the magnetic ore of iron, is known to change suddenly from being a conductor of electricity to an insulator at the low temperature of about 153°C below freezing. It is known that the change is one of crystal structure, but the steps by which the change takes place are still not clear. Understanding the nature of the transformation could help develop new kinds of electronic devices.

S. de Jong, R. Kukreja, C. Trabant, N. Pontius, C. F. Chang, T. Kachel, M. Beye, F. Sorgenfrei, C. H. Back, B. Bräuer, W. F. Schlotter, J. J. Turner, O. Krupin, M. Doehler, D. Zhu, M. A. Hossain, A. O. Scherz, D. Fausti, F. Novelli, M. Esposito, W. S. Lee, Y. D. Chuang, D. H. Lu, R. G. Moore, M. Yi, M. Trigo, P. Kirchmann, L. Pathey, M. S. Golden, M. Buchholz, P. Metcalf, F. Parmigiani, W. Wurth, A. Föhlisch, C. Schüßler-Langeheine and H. A. Dürr. from California, Indiana, Germany, Italy, the Netherlands and Switzerland report in the journal, *Nature*, their work which shows that the change in magnetite occurs in two steps – one that is under a third of a million millionth of a second long and the next that lasts less than 2 million millionths of a second.

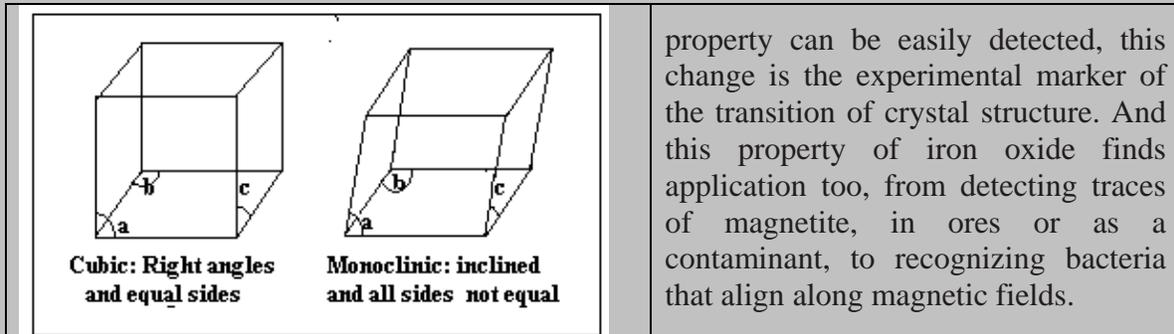
Verweij transition.

The transition in magnetite is called the *Verweij transition*, after *Evert Johannes Willem Verweij* (also spelt Verwey), who did important work in the field of crystals of metal compounds, among others things. The transition has been known to arise through a change in the crystal structure of the iron oxide. As the temperature falls, the structure changes from an upright, *cubic* form to an inclined form with unequal sides, called the *monoclinic* form. The crystal structure is made up of a framework of the positive core of atoms, with outer electrons participating in forming links with neighbouring atoms or groups of atoms. Rearrangement of the framework leads to changes in mobility of electrons, which can result in dramatic changes in conductivity, both electric and thermal.



Evert Johannes Willem Verweij

When magnetite cools to nearly the transition temperature (-153°C), the direction of easy magnetization of the crystals changes from along the cubic diagonal to the edge directions, and at the transition from the cubic form changes to the monoclinic form and one of the edges becomes the axis of magnetisation. As the change in the magnetization



But, how this remarkable property comes about in Ferric Oxide is still not understood. The change in crystal structure is a change like a change from solid to liquid (melting) or from liquid to gas (evaporation). In such a change, the energy balance established among the molecules in the collection becomes unstable with increasing energy. The assembly then remains without increase of temperature till the additional energy needed in the next equilibrium state has been acquired and then abruptly transforms to that state, which is called another *'phase'*.

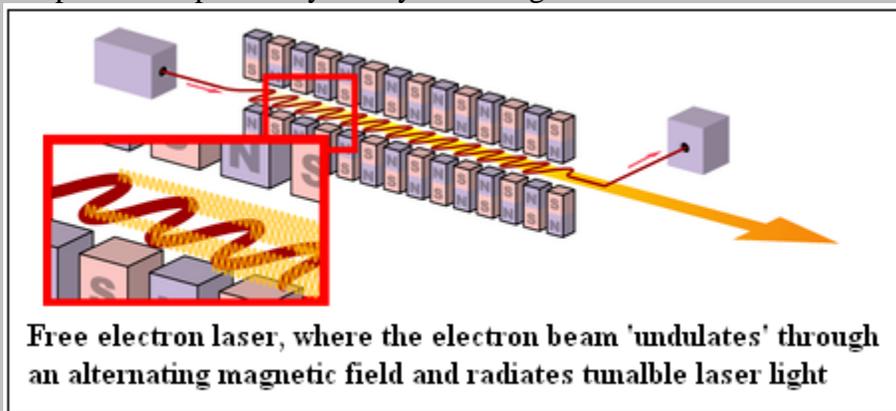
The authors of the paper in Nature explain that when Ferric Oxide is cooled to cross the Verweij transition, the higher temperature state of electrons that are not always bound to atoms, which allows conduction, 'freezes' into an ordered structure where iron atoms, which are charged because they have lost either 2 or 3 electrons, hold together in an eight-sided, stable formation. This tying down, as it were, of electrons, results in a jump in resistivity, along with the change from the cubic arrangement to the lower temperature, monoclinic phase. While the details of the change in structure have been elusive, there has been recent progress, in understanding the group of atoms that makes up the network of basic units in magnetite. This unit consists of three iron atoms, two that have lost 3 electrons around on atom that has lost 2 electrons – a unit called a *trimeron*. These are the groups that present the extent of bound or unbound electrons that account for the electrical properties of magnetite.

In many metal oxide materials, like magnetite, it is the behaviour of such units that is examined to explain the freeing or freezing of charge carriers, sometimes found to arise at the same time as changes in the crystal structure. But as there are usually a great number of factors present and the different phases are close together, in terms of energy, it has not been possible to prise apart the changes that go into phase transitions. The case of magnetite, among these, has features that make it simpler than others and magnetite offers the possibility of allowing the basic mechanism in the group of materials to be viewed.

The researchers used what amounts to high speed motion picture recording of the phase transition, as the energy of the crystal material was pumped, in doses that were a fraction

of million millionths of a second apart. The pumping was with a laser that fired in pulses, at this rate, and the response of the crystal formation was monitored by watching the way X rays were scattered by the plane faces of the crystals. Scattering of X Rays is a well worn way of finding out the how atoms are placed in crystals. X Rays have wavelength that are of the order of the distance between scattering layers and X Rays scattered in any direction by different layers would be 'in or out of step', depending on the distance between the layers and the angle of scattering. Examining the scattering pattern can then reveal the structure of the crystal, particularly, in the case of magnetite, whether it is cubic or monoclinic, and also any conditions in between.

The researchers used a pumping laser with pulses that were 70 thousand- million millionths of a second apart, synchronized with X Rays in pulses 10 thousand- million millionths of a second apart, generated by the *Free Electron Laser* at the *Linac Coheretn Light Source* in Stanford. In this facility, coherent, laser-like light is emitted not from transitions in atoms, but by the motion of the wriggling of a beam of electrons that is passed through an alternating magnetic field. Starting from a low temperature, well below the transition temperature, energy was pumped in, while the crystal structure and electronic response was probed by X Ray scattering.



It was found that the transition from the low temperature insulator to the high temperature conductor took place in two steps – first the very fast, 300 thousand-million millionths of a second breaking down of the existing network of trimerons and then a rearrangement, which takes a longer, 1.5 million millionths of a second.

Electronic devices work by switching electric currents on of off, depending on other electric signals, using silicon based devices, like transistors. The speed of the arrangement depends on and is limited by how fast the switching can happen. While silicon based devices are at their limir of speed. development of graphene transistors has pushed the speed of switching up to 100 billion times a second. But the switching from insulator to conductor and back in the case of ultracold Ferric Oxide is many times faster. "The understanding we have gained as to how the transformation between the two states straddling the Verwey transition takes place could aid in the choice and design of oxide materials aiming at harnessing the enormous differences in electrical conductivity available in these systems," say the authors in their paper.
