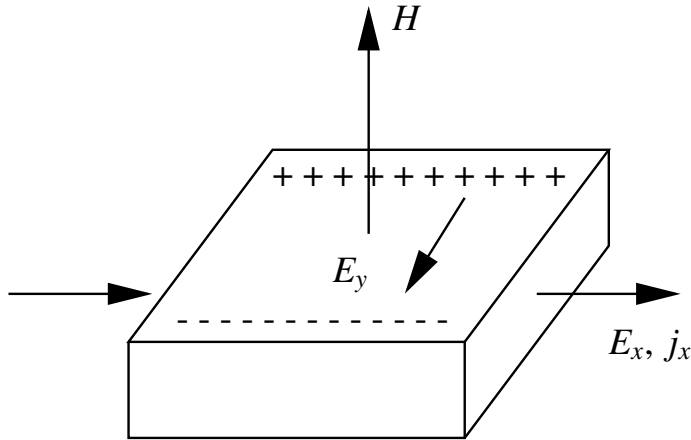


MATRL 218/CHEM 227: Class XIII — Colossal Magnetoresistance

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- The simplest example of magnetoresistance is *transverse* magnetoresistance associated with the Hall effect:



When an electrical conductor is subject to an electric field E_x along x and simultaneously, a magnetic field H along z , a new transverse field arises due to the Lorentz force of H on the electrons moving along x . This field E_y acts along y (because the Lorentz force is a cross product) giving rise to the Hall voltage. There is a magnetoresistance associated with the transverse field.

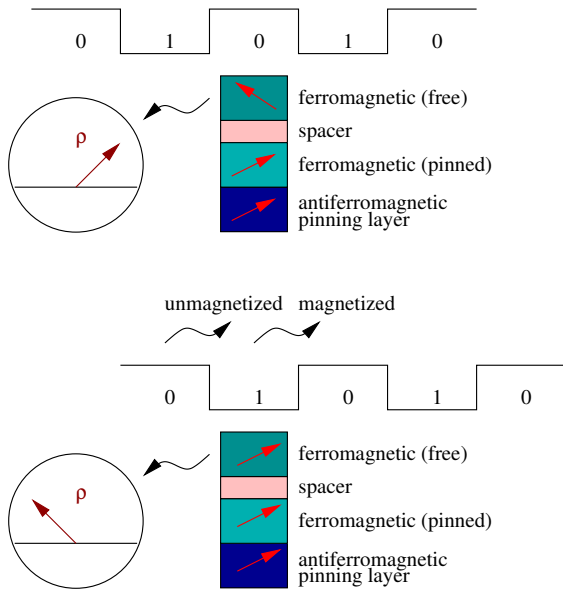
Such magnetoresistance measurements allow the number of free carriers to be obtained experimentally, as well as allow mapping of the Fermi surface *etc.*

- Negative magnetoresistance is the term given to the large *decrease* in the electrical resistance when certain systems are exposed to a magnetic field. The (negative) magnetoresistance is usually defined as a percentage ratio:

$$MR = -\frac{\rho(0) - \rho(H)}{\rho(0)} \times 100\%$$

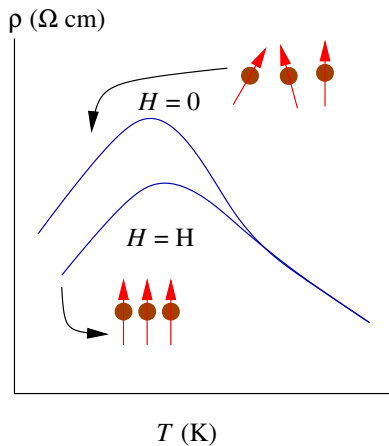
where $\rho(H)$ is the resistivity in the presence of a magnetic field of strength H and $\rho(0)$ is the resistivity in the absence of a magnetic field.

- The term Giant Magnetoresistance (GMR) has come to be associated with certain thin metallic multilayer devices that are commonly used in the read-heads of magnetic hard disks.

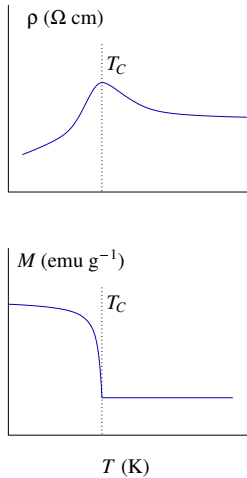


When the head (the free ferromagnetic layer) runs over a magnetized region on the hard disk, the magnetization of the magnetic layer is aligned with the magnetization of the pinned magnetic layer. This reduces the electrical resistivity of the assembly.

- Many ferromagnetic elements display an intrinsic negative magnetoresistance in the vicinity of their ferromagnetic transitions. This is because in the vicinity of the ferromagnetic transition, conduction electrons are scattered by magnetic fluctuations. Switching on a magnetic field suppresses such fluctuations and this results in a reduction of such scattering and consequently, a reduction in the electrical resistivity.



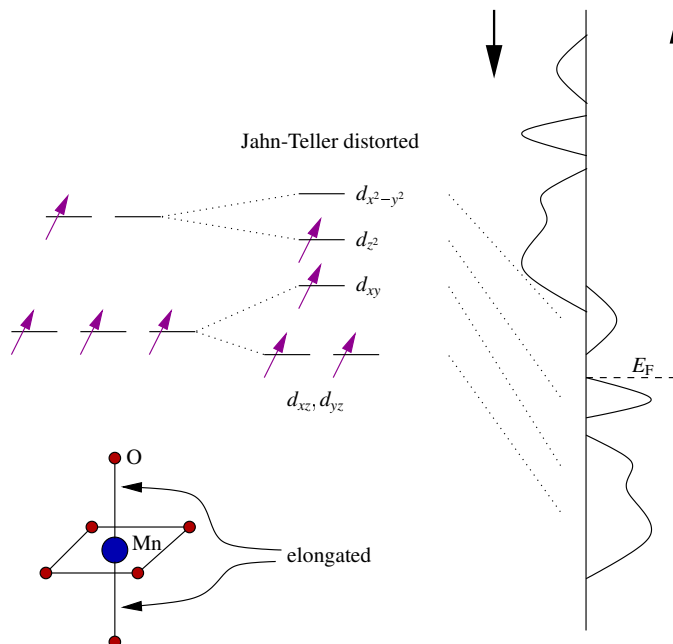
- In 1950, Jonker and van Santen in the Netherlands found that the perovskite LaMnO_3 which is an antiferromagnetic insulator, becomes metallic when La is substituted by Sr; in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, when x is around 0.3, the system becomes displays an insulator-metal transition on cooling. Concurrently, at the same temperature as the metal-insulator transition, the system becomes ferromagnetic:



At T_C , the system becomes metallic [indicated by the change of temperature coefficient of resistance (TCR) from negative to positive] and ferromagnetic (indicated by a sharp rise in the magnetization).

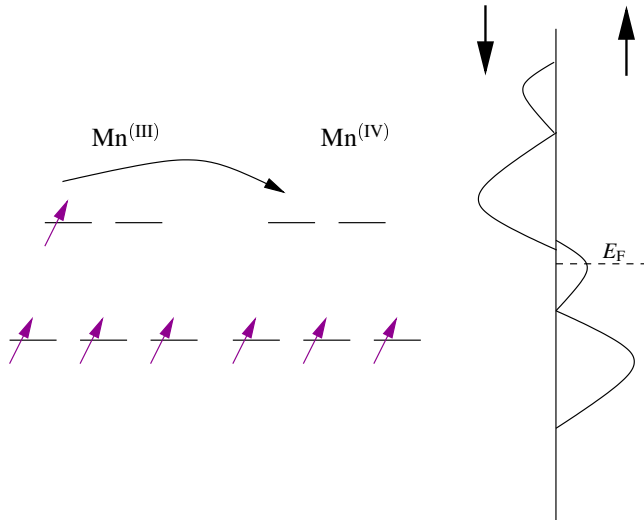
The reason why this happens is called Zener Double Exchange (DEX).

- The electronic configuration of d^4 Mn in LaMnO_3 is octahedral and high spin with a Jahn-Teller distortion.



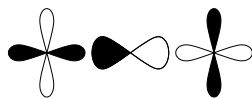
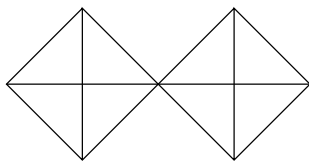
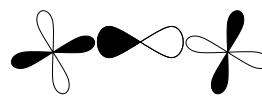
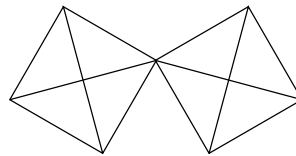
- The substitution of 30% Sr in the La site results in a change in the oxidation state according to

$\text{La}_{1-x}^{3+}\text{Sr}_x^{2+}\text{Mn}_{1-x}^{(III)}\text{Mn}_x^{(IV)}\text{O}_3$ with $x = 0.3$. The removal of electrons from trivalent d^4 Mn results in a loss of most of the Jahn-Teller nature (the elongation of 2 Mn-O bonds in the MnO_6 octahedra) and the possibility that the e_g electron on one $\text{Mn}^{(III)}$ can hop to its neighboring $\text{Mn}^{(IV)}$.

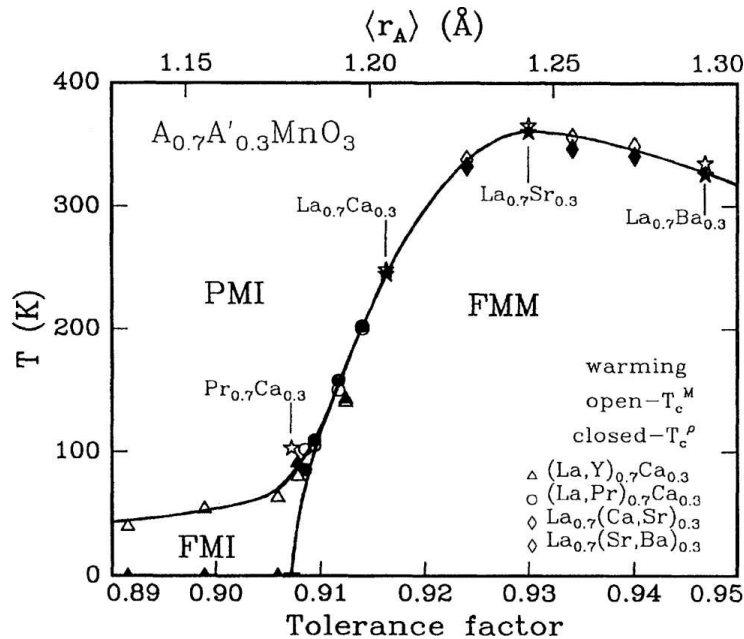


The important ingredient in the Zener DEX mechanism is that the electron retains a “memory” of its spin when it hops from one site to the next. Such hopping is therefore favored in the ferromagnetic state. This is why $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ displays metallic behavior and ferromagnetism at the same time.

- What is the mechanism for the colossal magnetoresistance. Near the magnetic transition, when the spins are tending to line up, switching on a magnetic field helps align neighboring spins. Hopping from $\text{Mn}^{(III)}$ to neighboring $\text{Mn}^{(IV)}$ is therefore facilitated. In certain materials, the application of a 7 T magnetic field can result in a 13 order of magnitude decrease in the electrical resistivity (“turning wood into silver”)
- Issues in colossal magnetoresistance (CMR) manganese oxides:
 - The effect of oxidation state in $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$ where Ln is a trivalent rare-earth (Ln = La, Pr, Nd ...) and A is an alkaline earth metal (A = Ca, Sr, Ba). The most studied compositions are $x \sim 0.3$, when about one-third of the Mn are in the 4+ oxidation state.
 - The effect of the perovskite tolerance factor. When the average size on the A site (the weighted average of $\text{Ln}_{1-x}\text{A}_x$) is small, t is small and the Mn-O-Mn bond angle deviates greatly from 180° . This results in the electrical resistivity being greater and the transition from insulator to metal taking place at lower temperatures.

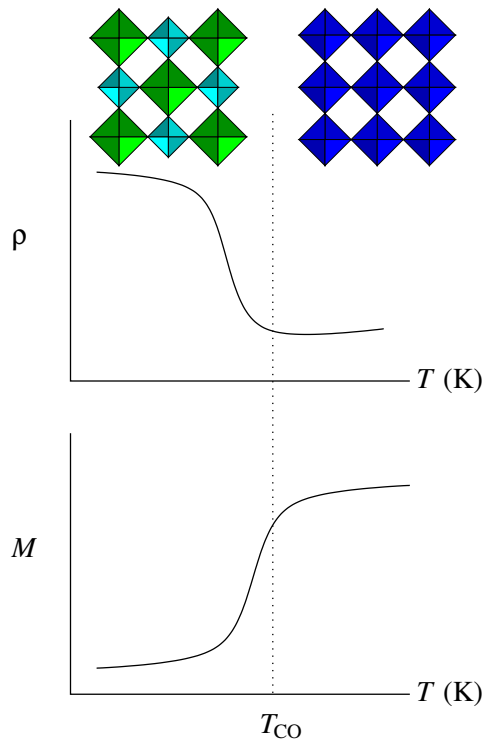
Mn-O-Mn near 180° Mn-O-Mn less than 180°

The reduction of the Mn-O-Mn bond angle because of tilting of octahedra (a consequence of small t) results in poorer overlap between orbitals (the figure shows $d_{x^2-y^2}$ on Mn and p_x on O). This makes the system a poorer metal.



From H. Y. Huang *et al. Phys. Rev. Lett* 75 (1995) 914. This plot shows the temperature at which the different compounds become ferromagnetic as a function of the average size of the A cation. The tolerance factor t , and the average 9-coordinate Shannon-Prewitt radii form the different ordinate (x) axes. Note how the highest transition temperature is found for a specific tolerance factor. PMI = paramagnetic insulator, FMM = ferromagnetic metal, FMI = ferromagnetic insulator.

- Charge ordering when $x = 0.5$: In compositions such as $La_{0.5}Ca_{0.5}MnO_3$, when the amounts of Mn^{III} and Mn^{IV} are equal, there is the possibility of forming a crystalline ordering of two different kinds of octahedra. The material becomes an antiferromagnetic insulator at a certain temperature, called the *charge-ordering* temperature. Such a phase transition is also called Wigner crystallization or the Verweij transition.



Schematic diagram displaying the charge-ordering transition in a ferromagnetic metals such as $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. Above the charge-ordering transition T_{CO} , the MnO_6 octahedra are all equivalent, with an average Mn oxidation state of $\text{Mn}^{3.5+}$. Below T_{CO} , the extra electron corresponding to Mn^{III} orders on alternate Mn (forming a rock-salt like arrangement) resulting in insulating behavior (upper plot) and antiferromagnetism (lower plot). The structure now has two kinds of ordered octahedra: large ones corresponding to Mn^{III} and small ones corresponding to Mn^{IV} .