Half Metallic Oxide Thin Films

國立高雄大學
www.nuk.edu.tw

Chin-Chung Yu

Spin polarized current

- In metallic ferro- and ferrimagnetic materials, the energy bands are
- split into spin-up and spin-down states.
- Two independent parallel channels for electrical current are formed, one for spin-up and one for spin-down electrons.
- When current passes through a ferromagnetic metal it becomes spin polarized, with the majority of electrons being either spin up or spin down.

$$P = \frac{N_\uparrow - N_\downarrow}{N_\uparrow + N_\downarrow}$$

where N↑↓ are the spin-up and spin-down density of states at the Fermi level.

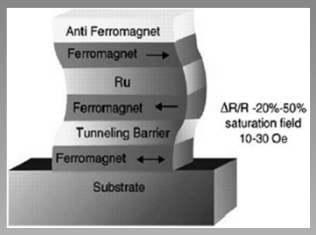
國立高雄大學
www.nuk.edu.tw

Chin-Chung Yu

higher values of spin polarization ~100%

- Heussler alloys, namely NiMnSb and PtMnSb, first theoretically proposed by de Groot et al.
- Half metals are characterized by a unique band structure in which one electron spin has a band gap at the Fermi level, while the other intersects it.
- This type of band structure creates a phenomenon in which only one spin carrier contributes to the conduction.
- magnetic metallic oxides such as Fe3O4, CrO2 and the manganites.

Tunneling Magneto-Resistance (TMR)



Two current model
Magnetic tunnel junction (MTJ)

Jullierre model,

$$\mathrm{TMR} = \frac{2P_1P_2}{1 - P_1P_2}$$

whereP_1 and P_2 stand for the normalized difference between the density of states at the Fermi level for the majority and minority spin.

In the case of an ideal half metal, TMR approaches infinity.

Spin transfer torque (STT)

- STT effect was predicted theoretically in 1996 and experimentally observed in 2000.
- the angular momentum carried by a spin-polarized current can exert a torque on the magnetization of a magnetic film that is magnetized in any nonparallel direction.
- The STT-RAM has the promise of becoming a universal memory
- However, the current required in switching the free layer is still at least one order of magnitude too high!
- the very high spin polarization will also reduce the critical switching current density in STT-RAM as suggested by the theory developed by Slonczewski.

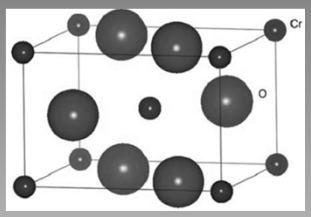
Measurement techniques

- spin-polarized photoemission spectroscopy -- The major drawback to this method is that it lacks the necessary energy resolution. (1meV required to precisely probe the electron spectrum
- near the Fermi level.

- Tedrow and Meservey developed another effective technique, making use of spin-polarized tunneling through a planar junction geometry in a ferromagnetic-superconductor tunnel junction. Applying a magnetic field and utilizing the Zeeman splitting o f the superconductors' strongly peaked single particle excitation spectrum results in two fully spin-polarized peaks from which the spin
- polarization of the ferromagnet can be extracted. This approach allows the prob-ing of the electron spectrum at the

Chromium Dioxide

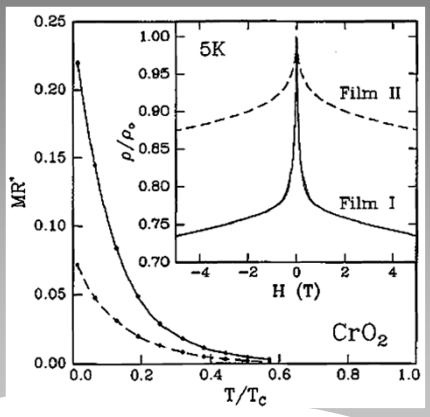
- It was theoretically predicted to be a half metal in 1986 by Schwarz using band structure calculations.
- spin-polarized photoemission➔ a spin polarization of nearly 100%
- PCAR➔ 98%



Crystal structure of CrO_2 (rutile)
lattice parameters a= 4.422A, c= 2.920A

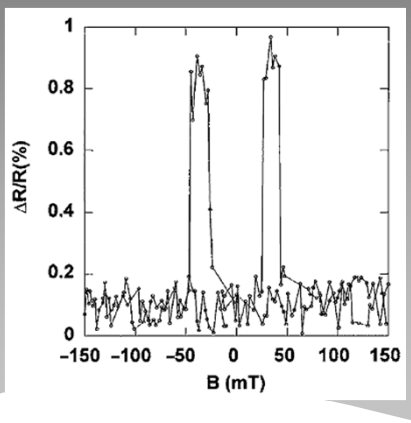
- CrO_2 is metastable at atmospheric pressures and is known to readily irreversibly
- decompose to Cr_2O_3 at temperatures between 250 and 460°C.
- There exists a narrow process window at very high oxygen pressure and constricted temperature regime that CrO_2 is thermodynamically stable in the bulk.

MR



The temperature dependence of the low-field MR extrapolated to zero field for two CrO_2 polycrystalline films. Film I was a CrO_2 and Cr_2O_3 mix phase and Film II was a phase pure CrO_2. The inset shows the field-dependence of the normalized resistance at 5 K normalized to the maximum value for the two films.

$CrO_2/Cr_2O_3/Co$ TMR junction



The magnetoresistance curve at 77 K of the 25um² $CrO_2/Cr_2O_3/Co$ tunnel junction.

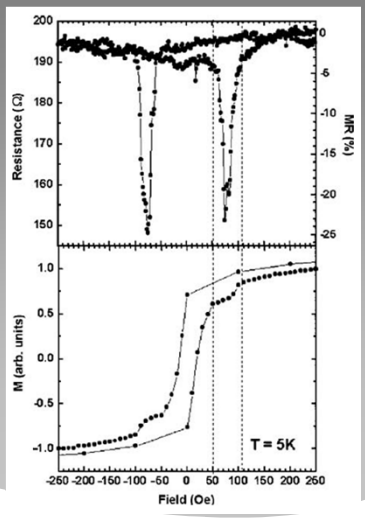
Poor TMR value! Positive TMR

- The main cause is believed to be Cr_2O_3 which is usually formed on the surface of CrO_2.
- Cr_2O_3 is an antiferromagnetic insulator with a Neel temperature near 300 K and therefore it significantly reduces the spin polarization and hence the TMR.

Chin-Chung Yu

CrO_2/CrO_x-AlO_x/Co

- Wet chemical etching has been used to remove Cr_2O_3 but a nonstoichiometric CrO_x surface layer still persisted.
- a much im-proved TMR of 25% at 5K.
- Negative TMR
- TMR became negative probably due to the fact that both majority and minority spins participated in the transport across the tunnel barrier. The minority spins were from the Co electrode that has minority spin-polarized d states.



Chin-Chung Yu

Stabilization of Cr_2O_3

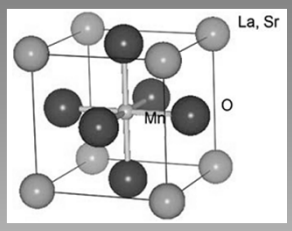
- Ruthenium dioxide (RuO_2) -- tetragonal rutile structure with lattice constants a= 4.497A and c= 3.105A.
- In bulk experiments, Ru^{4+} impurities of a few atomic percent (2–4%) are reported to have increased the Tc of CrO_2 to 415K.
- In a novel bias target ion beam deposition, we did not see Cr_2O_3 surface layers with 10–20 at. % Ru. The spin polarization of $Cr_{0.8}Ru_{0.2}O_2$ was 70% by PCAR measurement.

$La_{1-x}Sr_xMnO_3$ (LSMO)

- The general chemical formula for mangantites is $A_{1-x}R_xMnO_3$. The A-cations usually are La, Pr, and Nd and R-cation Sr, Ca, and Ba.
- $La_{1-x}Sr_xMnO_3$
  - ✓ $LaMnO_3$
  - ✓ mixed-valence manganites
  - ✓ doping of Sr^{2+} leads to the charge change in Mn ions (some Mn^{3+} transfer to Mn^{4+}, in order to maintain charge neutrality, regarded as the creation of a hole)
    $x < 0.17$ ➔ insulating state, holes remain localized
    $x \sim 0.17$ ➔ conducting and ferromagnetic state, holes delocalize

Structure

- La1-xSrxMnO3
  - ✓ maximum Curie temperature is 360K when x is 0.3–0.4
  - ✓ Jahn–Teller distortion ➔ change the magnetic ordering as well as the transport properties
  - ✓ double-exchange mechanism ➔ a half metal
  - ✓ the high spin polarization
  - ✓ mixed-valence manganites



La1-xSrxMnO3
cubic perovskite structure

Jahn–Teller effect

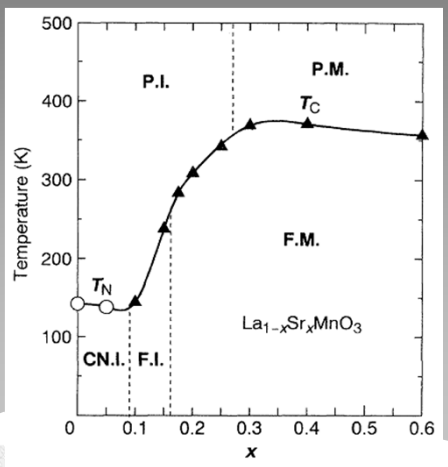
- **Jahn–Teller distortion**, or the **Jahn–Teller theorem**
- This electronic effect is named after Hermann Arthur Jahn and Edward Teller
- Using group theory, that orbital nonlinear spatially degenerate molecules *cannot* be stable.
- Any nonlinear molecule with a spatially degenerate electronic ground state will undergo a geometrical distortion that removes that degeneracy, because the distortion lowers the overall energy of the species.
- most often encountered in octahedral complexes of the transition metals

Double-exchange mechanism

A hole is created when Mn3+ becomes Mn4+ to balance the charges after the doping of Sr2+. Abovethe critical doping concentration, the electrons start to hop into holes among adjacent Mn ions. In addition, these electrons are spin polarized because of the Hund's interaction with Mn ions. The adjacent Mn ions are ferromagnetically coupled which is energetically favorable for electron hopping.

Chin-Chung Yu

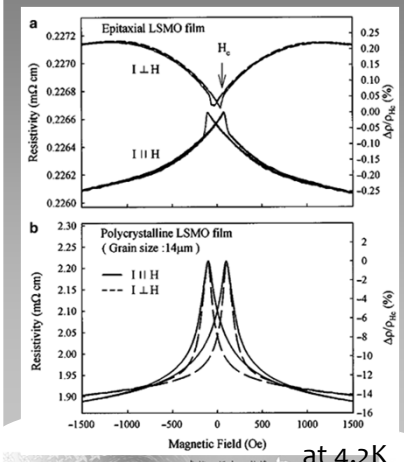
Electronic phase diagram



TN: Neel temperature,
TC: Curie temperature,
P. I.: paramagnetic insulator,
CN.I.: spin canted insulator,
F. I.: ferromagnetic insulator,
F. M.: ferromagnetic metal,
P. M.: paramagnetic metal

Chin-Chung Yu

grain boundaries dominate magnetotransport



at 4.2K

- Single crystal ➔ low MR
- Polycrystal ➔ high MR
- magnetic domains that are weakly coupled in the polycrystal sample
- grain/domain boundaries become strong scattering centers
- grain boundaries dominate the magneto-transport

Chin-Chung Yu

Anisotropic MR

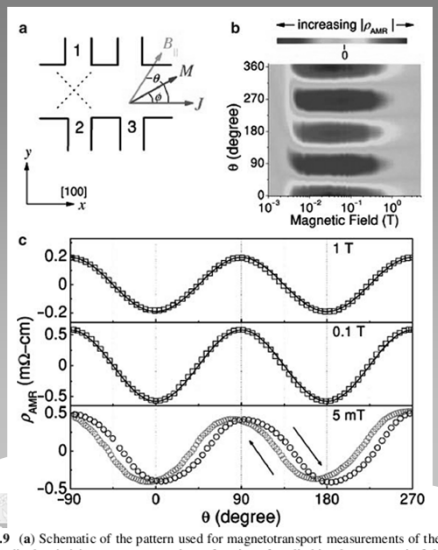


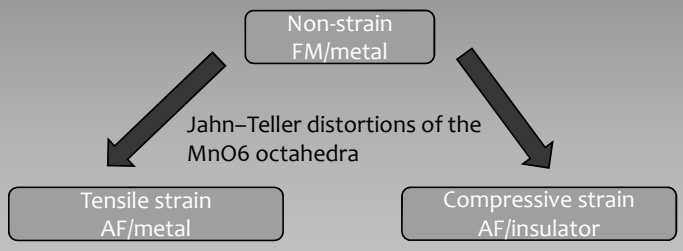
Fig. 3.9 (**a**) Schematic of the pattern used for magnetotransport measurements of the AMR. (**b**) Longitudinal resistivity ρ_{AMR} measured as a function of applied in-plane magnetic field and angle θ at $T = 200$ K in $La_{0.84}Sr_{0.16}MnO_3$. (**c**) ρ_{AMR} vs. θ at $T = 200$ K in $La_{0.84}Sr_{0.16}MnO_3$ with different in-plane magnetic fields (Reproduced from [46])

- AMR reaches a maximum at 210 K then decreases as the temperature decreases.
- an intrinsic inhomogeneous nature of the manganites that comes from the doping.
- inhomogeneity is responsible for the increase in the AMR by enhancing the spin-dependent scattering.

Chin-Chung Yu

Strain effect

ferromagnetic ← Tetragonal distortion → antiferromagnetic



國立高雄大學 www.nuk.edu.tw

Chin-Chung Yu

Control of strain

Single crystal substrate

STO(001)/LSMO → small tensile strain → metal-insulator transition
LSAT(001)/LSMO → compressive strain → metal-insulator transition

large tensile strain → lowers Tc to below room temperature
→ increased the resistivity of the LSMO films by several orders of magnitude
→ altered the shape of the resistivity curves
→ metal-insulator transition was shifted well below room temperature (~200K)

國立高雄大學 www.nuk.edu.tw

Chin-Chung Yu

Control of strain

Piezoelectric effect

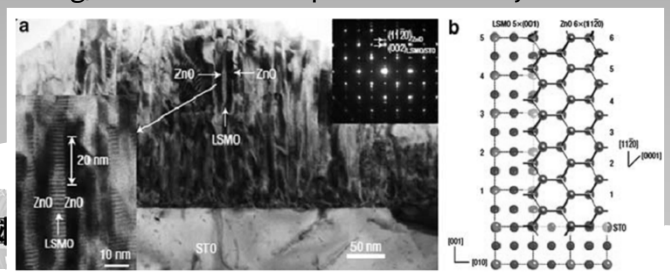
$La_{0.7}Sr_{0.3}MnO_3$ film on $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMN-PT) single-crystal substrates

➔Produce an in-plane compressive strain in LSMO

➔Applying an electric field of 1 kV/mm to the PMN-PT yielded a 5.5% change in the resistivity of LSMO film

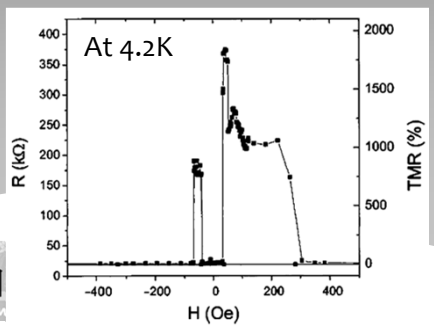
STO sub./LSMO/ZnO

- lattice mismatch ➔ out-of-plane strain
  ➔ nano column structure ~10nm
- one of the keys to formthe nano-composite structure is to select materials with different elastic constants
- LSMO embedded in a ferroelectric or piezoelectric phase
- it is conceivable to realize a very effective electric-field tuning/control over the spin and resistivity of LSMO



MTJs with LSMO

- STO as the barrier layer because of the same crystal structure and a close lattice mismatch.
- LSMO/STO/LSMO grown on (100) STO single crystal substrate
- 1800% and 10000% TMR were reported by Bowen and Feng, respectively.



For 1800% TMR, spin polarization of LSMO ~ 95%

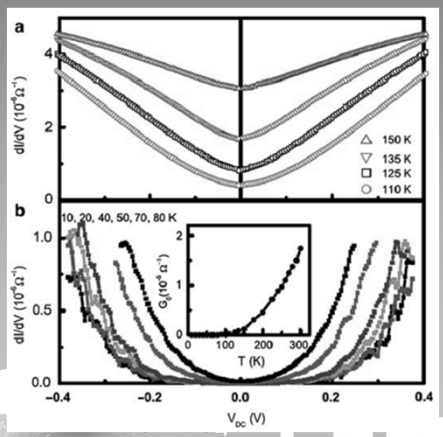
Chin-Chung Yu

- TMR ratios for LSMO/STO/LSMO diminished quickly as the temperature increased and entirely disappeared at200 K.
- The disappearance of TMR could not be explained by the reduction in the spin polarization. (because Tc of LSMO> room temp.)
- below 100 K, the transport mechanism through the STO barrier was simple direct tunneling (猜測)
- above 100 K, the tunneling transport was dominated by the variable range hopping across the barrier through defect states inside the barriers (猜測)
- The magnetic impurities and short spin diffusion length in the STO barrier caused the high spin scattering rate which greatly reduced the TMR ratio. (猜測)

國立高雄大學
www.nuk.edu.tw

Chin-Chung Yu

Conductance blockade

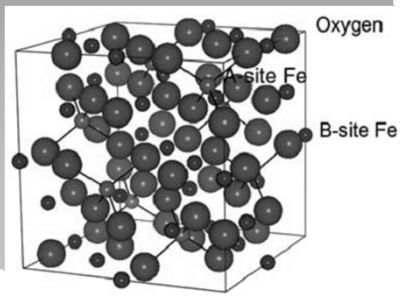


- TMR ~ 10000% at 10K
- the very high TMR also
- diminished quickly above 100 K
- Conductance blockade blow 100K

Chin-Chung Yu

Magnetite Fe3O4

- Lodestone
- ferrimagnet and Tc~ 860 K
- inverse Spinel structure
- Fe3+ions are positioned at tetrahedrally coordinated A-sites and mixed Fe3+ and Fe2+ at octrahedrally coordinated B-sites.
- Fe3+(Fe2+Fe3+)O4
- strong antiferromagnetic coupling between the A-site and B-site Fe ions ➔ ferrimagnetic
- B-site Fe2+ contribute the net magnetic moment and Ms ~ 480 emu/cc
- poor conductor. 200 S/cm at 25°C

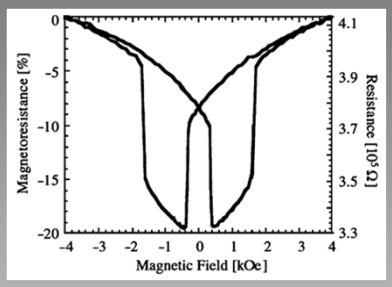


Chin-Chung Yu

- band structure calculations indeed showed a gap in the majority spin at the Fermi level, where there is no gap in the minority spin
- Half metallicity in Fe_3O_4 comes from the double-exchange interaction be-tween Fe 2+ and Fe3+ in the B-lattice.
- Spin polarization 40~80% by spin-polarized photoemission spectroscopy
- Verwey transition at ~120 K
  ➔first-order phase change and Fe_3O_4 becomes much more insulating below the transition
- electrically driven phase transition below Verwey transition temp.
- magnetic ordering in the presence of such current driven phase transitions

TMR

- $Fe_3O_4/CoCr_2O_4$(6nm)/$La_{0.7}Sr_{0.3}MnO_3$ trilayer on STO(110)
- $CoCr_2O_4$ has the spinel structure with a very small lattice mismatch to FeO_4 ➔ epitaxy,
- ferrimagnetic below 95K ➔ additional spin scattering
- $CoCr_2O_4$ (6nm) ➔ Instead of the direct tunneling, the inelastic hopping facilitated by localized states such as oxygen vacancies



Hu G, Suzuki Y (2002)