Nano dimensional Colossal Magnetoresistive (CMR) in Manganites

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OUTLINE

- CMR phenomenon
- CMR manganites
- Synthesis
- XRD, Resistivity results
Magnetoresistance

- Discovered in 1856, the MR is change in the electrical resistance in the presence of a magnetic field.

- The value of MR is extremely small for most substances, even at high fields, but is relatively large (a few percent) for strongly magnetic substances.

\[
\% \text{MR} = \frac{\Delta \rho}{\rho_0} \times 100
\]

\[
= \left[ \frac{\rho_H - \rho_0}{\rho_0} \right] \times 100
\]
COLOSSAL MAGNETORESISTANCE

- CMR is the substantial fall in resistance observed in the vicinity of the Curie temperature of materials such as transition metal oxides when they are subjected to a large applied magnetic field.

- The field aligns the partly disordered magnetic spins, which promotes electron hopping, and in turn enhances the exchange.

Magnetoresistance of La$_{0.7}$Ca$_{0.3}$MnO$_3$ in a field of 10 T.
RARE EARTH MANGANITES

- Manganites- an example of CMR materials:
  - Strongly correlated electrons
  - Ferro and Paramagnetic transitions
  - Metal-insulator transitions
  - Strong electron phonon coupling
  - Half metallicity
CHEMICAL FORMULA & CRYSTAL STRUCTURE

- The manganites crystallize in a "perovskite" structure $\text{ABO}_3$ which is cubic.
PHASES IN CMR MATERIALS

- Ferromagnetic and metallic (FM) phase at $T<T_C$
- Paramagnetic insulating (PI) phase at $T>T_C$
- The CMR is a magnetic-field-induced transition from a (PI) state to a (FM) one caused to the alignment of the magnetic moments resulting in drastic decrease in resistivity.
Lattice polarons in undoped manganite

- The Mn$^{3+}$ ions in the parent manganite.
- Mn ions in their trivalent valence state $3d^4$ ($t_{2g}^3$, $e_g^1$)
- Jahn-Teller distortion results in a lattice polaron.
- If the $t_{2g}$ spins are randomly aligned in the high-temperature regime we have the paramagnetic state and conductivity drops resulting in an insulating behaviour.

[Diagram of Mn$^{3+}$ ions showing mobile and localized electrons and Jahn-Teller distortion]
DOPED MANGANITES AND FM PHASE

- FM can be introduced through charge carriers doping
  - \( \text{R.E}_{1-x}^{3+} \text{ A.E}_x^{2+} \text{Mn}_{1-x}^{3+} \text{Mn}_x^{4+} \text{O}_3^{2-} \)
- Parent manganite contains \( \text{Mn}^{3+} \) ions while hole doping leads to the creation of \( \text{Mn}^{4+} \) ions which dilutes the cooperative distortion in pure \( \text{LaMnO}_3 \).
- The holes become mobile transforming the system into a ferromagnetic metal.
- Holes move only if adjacent spins are parallel, to give a “colossal” decrease in the resistivity.
- Achieved either by lowering the temperature or applying a magnetic field.
**FM phase: Double exchange model**

- The electron hopping maintains the projection of the spin.

- The electrons need a polarized background to improve their kinetic energy. If adjacent $t_{2g}$ spins are parallel - the ferromagnetic state and conduction is favoured giving a metallic behaviour.
Effect of A-site Cationic Radius

- The average A-site cationic radius is given as
  \[ <r_A> = (1-x)r_{R.E}^{3+} + (x)r_{A.E}^{2+} \]
- Perovskite structure contains R.E (or A.E)-O and Mn-O planes. For small A-site cations tilting of the cubic structure.
  - distortion of the octahedral cage of MnO$_6$
  - Decrease in the Mn-Mn distances
  - Reduction in Mn-O-Mn bond angle
Structures of distorted perovskite manganites
Orthorhombic or Rhombohedral tilting to the connective pattern of the MnO$_6$ octahedra
EXPERIMENTAL TECHNIQUES AND DATA

Nano particle synthesis
X-ray diffraction data
Resistivity measurements
## Compositions Prepared

<table>
<thead>
<tr>
<th>Serial No.</th>
<th>Manganese name</th>
<th>Symbol adopted</th>
<th>$&lt;r_A&gt;$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Lanthanum Calcium Manganese Oxide</td>
<td>LCMO</td>
<td>1.21</td>
</tr>
<tr>
<td>2</td>
<td>Lanthanum Strontium Manganese Oxide</td>
<td>LSMO</td>
<td>1.26</td>
</tr>
<tr>
<td>3</td>
<td>Lanthanum Barium Manganese Oxide</td>
<td>LBMO</td>
<td>1.31</td>
</tr>
</tbody>
</table>
REACTION SCHEME

Metal salts

Dissolving in water

Chemical reaction in citric acid

Precipitation

Calcination

Nano particles
X-ray diffraction data

- Identifying of phases
- Calculating the lattice parameters
- Predicting the particle size
PARTICLE SIZE CALCULATION

- The solid’s small size interrupts the periodicity of the lattice and produces broader peaks.
- The width of the diffraction curve increases as the thickness of the crystal decreases.
- Scherrer’s formula
  - $D = \frac{k\lambda}{\beta \cos \theta}$

Effect of the size of finite crystal on diffraction curves
RESISTIVITY MEASUREMENTS

- Electrical resistivity ($\rho$) measurements of LCMO, LSMO and LBMO made through Four Probe method.

- Temperature variation (in the range 77-300K) of resistivity using liquid nitrogen.

- All these resistivity measurements were taken during cooling the sample.
Block diagram of resistivity measurement setup
RESISTIVITY VERSUS TEMPERATURE BEHAVIOR
Polaron activation energy

In the PI phase, the electrical resistivity generally exhibits a strong temperature dependence.

The conduction process in manganites for the insulating phase ($T > T_{IM}$) is attributed mainly to the presence of thermally activated polarons. The polaronic model for the temperature dependence of resistivity is given as

$$\rho(T) = \rho_0 \exp \left( \frac{E_A}{k_B T} \right) T$$

$E_A$: A polaron can be imagined to be trapped inside a local energy well having height $E_A$. The polaron gains thermal energy at high temperatures to come out of this well and thus cause conduction in the insulating state.

Equation can also be stated as

$$\ln \left( \frac{\rho}{T} \right) = \ln \rho_0 + \frac{E_A}{k_B T}$$
$E_A$ values for these nano-manganites are found to decrease with increase in $<r_A>$, since charge localization decreases with increasing $<r_A>$.
## Conclusions

<table>
<thead>
<tr>
<th>Sample code</th>
<th>LCMO</th>
<th>LSMO</th>
<th>LBMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estimated Grain Size (nm)</td>
<td>14nm</td>
<td>18nm</td>
<td>17nm</td>
</tr>
<tr>
<td>Average Cationic radius $\langle r_A \rangle$ (Å)</td>
<td>1.21</td>
<td>1.26</td>
<td>1.31</td>
</tr>
<tr>
<td>Metal-Insulator transition temperature $T_{IM}$ (K)</td>
<td>$&lt; 77$</td>
<td>90</td>
<td>139</td>
</tr>
<tr>
<td>Activation energy (meV)</td>
<td>214</td>
<td>152</td>
<td>147</td>
</tr>
</tbody>
</table>

![Graph showing $T_{IM}$ vs. $\langle r_A \rangle$]
REFERENCES

- E. Dagotto, Nanoscale Phase Separation and Colossal Magnetoresistance, Springerlink.