Multiferroicity

Materials that exhibit more than one primary ferroic properties, are called multiferroics. In our case, magnetic and electric properties are coupled to each other.

**Type I**
- Ferroelectricity and magnetism have different origin.
- **Origin of ferroelectricity:**
  * Lone-pair effect,
  * Geometrical frustration
  * Charge ordering

**Type II**
- Ferroelectricity originates from magnetism.
- **Mechanism of ferroelectricity:**
  * Exchange striction
  * Inverse DM interaction
  * Spin dependent \( p-d \) hybridization.

Spin-glass

Spin-glass can be defined as a state having a large number of degenerate ground states which has spins frozen in random directions below a critical temperature.

### Ingredients of Spin-glass

1. **Disorder**
   - Can be due to site randomness or bond randomness. E.g.: \( \text{Cu}_{1-x}\text{Mn}_x \), \( \text{Fe}_{1-x}\text{Mn}_x\text{O}_3 \)

2. **Frustration**
   - Lattice geometry inhibits ordered configurations.
   - Simplest example: Triangular lattice with antiferromagnetic ordering. E.g.: \( \text{Li}_2\text{Mn}_3\text{O}_7 \)
Mn + 2Sb + 4Se $\rightarrow$ MnSb$_2$Se$_4$

**XRD Pattern**

Crystal Structure

- $a = 13.3299(15)$ Å,
- $b = 3.9658(4)$ Å,
- $c = 15.4834(15)$ Å,
- $\beta = 116.1278(2)^\circ$

- $a = 13.2656(11)$ Å,
- $b = 3.9965(6)$ Å,
- $c = 14.7893(12)$ Å,
- $\beta = 115.0176(3)^\circ$

Antisite Disorder = 26% for Sample 1

Antisite Disorder = 40% for Sample 2

Sample 1: Slow cooled (0.2° C/min)
Sample 2: Quenched

**DC Magnetization**

$T_N = 22.5$ K

$\mu_{eff} = 6.02 \mu_B$

$\theta_{CW} = -75$ K

No long-range ordering for the quenched sample
Sample 1 shows AFM ordering below 22.5 K.

Dielectric measurements also show anomaly at the magnetic transition temperature.

Pyroelectric measurements confirm the ferroelectric nature of the dielectric anomaly.
Magnetic Properties of Sample 2

- **Relaxation Measurement**
- **M vs. H**: Magnetic moment vs. magnetic field (kOe)
- **Heat Capacity**: Graph showing $C_v/T$ vs. temperature (K)
- **Magnetic Memory**
- **AC Susceptibility**: Graph showing magnetic moment (emu) vs. temperature (K)

- Sample 2 did not show any magnetic ordering.
- AC susceptibility shows shifting of peak position towards high temperature.
- Presence of magnetic relaxation and magnetic memory effect confirm the glassy state.
Comparison of Resistive Properties

A New Compound Having Negative Colossal Magnetoresistance!

- Resistivity data show gradual change from insulator to semiconductor to metallic state within a narrow temperature range.
- Increase in antisite disorder resulted into magnetic glassy state.
- With increase in magnetic field, spin-disorder decreased and hence resulted into lower resistivity. (Mechanism?)
- Absence of mixed valency, rules out the double exchange mechanism.
- Increase in magnetic field resulted in increased volume of ferromagnetic domains which reduced the electron scattering.
Conclusion

- Antisite-disorder plays an decisive role in determining magnetic ground state.
- Presence of ferroelectricity in sample 1 has magnetic origin as paramagnetic phase is centrosymmetric.
- Glassy behaviour of sample 2 is due to site randomness of the magnetic ion.
- A new non-manganite compound with negative colossal magnetoresistance.
- Origin of colossal magnetoresistance is not double exchange mechanism.

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