UNDERSTANDING THE MAGNETIC, ELECTRONIC AND STRUCTURAL BEHAVIOR OF TECHNOLOGICALLY IMPORTANT MAGNETIC MATERIALS OF CURRENT INTEREST

S. M. Yusuf
Solid State Physics Division

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Abstract

We have investigated magnetic, electronic and structural properties of several classes of technologically important magnetic materials, such as molecular magnetic materials, magnetic nano-materials, CMR manganites, low dimensional magnetic materials, and high magnetocaloric effect materials. A brief overview of our research and developmental activities on these magnetic materials, highlighting basic as well as applied aspects, is given.

From simple door magnets to computer hard disks, magnetism has become an essential part of our daily life. Magnetism is one of the main constituents of the modern condensed matter physics. It is also an important part of several modern topics of research, like giant magnetoresistive (GMR) multilayer materials, colossal magnetoresistive (CMR) perovskites, nano-sized materials, magnetism in materials that show high temperature superconductivity, etc. We have been studying the magnetic, electronic and structural properties of a variety of materials of current interest such as molecular magnetic materials, magnetic nano-materials, CMR manganites, low dimensional magnetic materials, and high magnetocaloric effect materials. Our studies aim to have fundamental understanding of magnetism and to tune/tailor the structural and magnetic properties of the magnetic materials for any possible practical application. The current article gives a glimpse of our research and developmental activities in some of the above mentioned class of magnetic materials.

Molecular Magnetic Materials

Traditionally, magnets are made of 3d, 4f, and 5f metals and their alloys prepared by using high temperature based metallurgical methods. With the advancement of modern science and technology, now it is possible to prepare magnets made of purely organic molecules or a combination of organic radicals and conventional metal ions. These magnetic materials, so called molecular magnets, can be prepared at ambient temperatures and have several advantages over conventional magnets. These molecules can be easily manipulated at ambient temperatures to incorporate various functionalities e.g. photo-activity, conductivity, transparency, pressure sensitivity, etc. The imagination of these kinds of functionalities in conventional magnets is rather difficult. However, it is very much essential to devise efficient methods for the synthesis of molecular magnets and understand the factors that can fine tune their structural and magnetic properties for their optimal functionality. We have been studying the role of crystal structure, structural defects, crystallite size, and type of magnetic ion in determining various magnetic properties such as transition temperature, temperature and magnetic field dependence of magnetization, saturation magnetization, coercive field, remanence, magnetic ground state, and magnetic exchange interactions in these multifunctional magnetic compounds. These materials have low density...
(− 1gm/cc) and excellent structural integrity and flexibility for incorporation of different magnetic ions. Our structural and magnetic investigations have revealed a crucial role of structural defects and quenched disorder in controlling the magnetism of \((\text{Ni}_{1-x}\text{Co})_{x}[\text{Fe(CN)}_6]_2\cdot\text{H}_2\text{O} \quad (0 \leq x \leq 1)\) and \(\text{Ni}_{3(1-x/2)}\text{Ru}_{x}[\text{Cr(CN)}_6]_2\cdot\text{H}_2\text{O} \quad (0 \leq x \leq 0.5)\) molecular compounds\(^4,5\). The study of electronic properties of above materials reveals that these materials are insulators. We have obtained a first microscopic understanding of the novel phenomenon of magnetic pole reversal in Prussian blue-type molecular magnets \(\text{Cu}_{x}\text{Mn}_{1-(x/2)}\text{Cr}(\text{CN})_6\cdot\text{H}_2\text{O}\) by employing the reverse Monte Carlo (RMC) simulation and Rietveld refinement techniques on the neutron scattering data [Figs. 1 (a) & (b)].\(^2\) The molecular field theory (MFT) has been used to calculate the Cu, Mn, and Fe sublattice magnetizations as a function of temperature and magnetic field [Figs. 2 (a) & (b)].

The MFT calculations reproduce the observed temperature dependant magnetization reversal very well and provide an insight of Mn ion spin-flipping under higher magnetic fields. A highly reversible (bipolar) switching of magnetization using low magnetic fields is demonstrated. The studied molecular compounds also show both normal and inverse magnetocaloric effects (MCEs) below their magnetic ordering temperatures for low applied magnetic fields (− 2 kOe). We have revealed the possible applications of the observed magnetic pole reversal phenomenon in novel magnetoelectronic and magnetocaloric devices such as magnetic memory, thermomagnetic switches, and magnetic cooling/heating based constant temperature bath.\(^1\)

**Materials Showing High Magnetocaloric Effect (MCE)**

The materials showing large magnetocaloric effect (MCE), i.e., a large change of temperature of a material upon a moderate change of an external magnetic field under adiabatic condition, have attracted a lot of attention in recent years due to their practical application in magnetic...
refigeration. The magnetic refrigeration technology can be considered as an alternative to the conventional gas compression technology with higher efficiency and environment friendly attributes. We have been investigating MCE in a variety of magnetic systems, such as, Heusler alloys, half Heusler alloys, rare-earth intermetallics, uranium intermetallic compounds, perovskites, and molecular magnets.11-13 Our aim is to first understand the physics principles that are responsible for their large magnetocaloric behavior and then to tune their physical properties for achieving better MCE for use in an efficient magnetic refrigerator.

Fig. 3 shows the temperature dependence of the change in magnetic entropy ($-\Delta S_m$) for La$_{0.67}$Ca$_{0.33}$Mn$_{0.9}$Fe$_{0.1}$O$_3$ perovskite.11 The maximum value of $\Delta S_m$ (for $\Delta H = 3$ Tesla) has been found to be 1.18 J kg$^{-1}$ K$^{-1}$ at 113 K with a relative cooling power of ~87 J kg$^{-1}$. Besides, a quite broad operative temperature range of 65 –160 K has been observed. From our study on the TbCo$_{2-x}$Fe$_x$ alloys,$^{13}$ the value of maximum $-\Delta S_m$ is found to be 3.7 J kg$^{-1}$ K$^{-1}$ ($x=0.1$) for a 5 Tesla field change with a quite broad operative temperature range of 245 –340 K. The operating temperature range for the $x=0.1$ sample is much broader than that for other reported giant MCE materials, such as Gd in the same temperature range. Such a broad operating temperature range is important for practical applications. The temperature-dependent neutron-diffraction [Fig. 4] study on the magnetostructural transitions in the TbCo$_2$Fe$_x$ compounds has given an understanding of their intertwined magnetic and structural properties in these important alloys.$^{13}$ We have also studied the magnetocaloric properties of Heusler alloys Ni$_{2-x}$Mn$_x$Sn and Ni$_{2-x}$Mn$_x$Sb. The parent compounds Ni$_2$MnSn and Ni$_2$MnSb show a paramagnetic to ferromagnetic transition below ~340 and 350 K, respectively. It is found that by substituting Ni at the Mn site, the magnetic phase transition temperature can be tuned towards room temperature, hence giving a possibility of using these
Heusler alloys as room temperature magnetic refrigeration materials.

**Colossal Magnetoresistance (CMR) Manganites**

The phenomenon of a huge change (~100%) in the electrical resistance of a material under the application of magnetic field is called colossal magnetoresistance (CMR) effect. The basic understanding of the CMR effect offers tremendous opportunities for the development of new technologies such as data-storage devices with increased data density and reduced power requirements. The oxide compounds of $ABO_3$ [Fig. 5] type ($A$-rare earth/Ca, Sr, Ba, etc. and $B$-transition metal ions) exhibit a variety of structural, electronic and magnetic properties. The rare earth ion site plays an important role in stabilizing the crystal structure, while the valence state of the transition metal ions decides the magnetic and the transport properties in these systems. Amongst these compounds, the manganites ($AMnO_3$) have been of great interest due to the CMR effect, charge ordering and metal insulator transition properties exhibited by them. We have studied the structural and magnetic properties of a large number of such mixed perovskite manganites.\(^{14-21}\)

By tuning the size mismatch of $R$- (rare earths) and $Z$-site (Ca, Sr, Ba, etc.) ions in the $R_{1-x}Z_xMnO_3$-type perovskites, we have controlled the double-exchange interaction as well as the underlying superexchange, and Coulomb interaction among Mn ions in several manganites such as $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_0.9\text{Fe}_0.1\text{O}_3$, $\text{La}_{0.67}\text{Ca}_{0.33}\text{Mn}_0.9\text{Ga}_0.1\text{O}_3$, $(\text{La}_{0.59}\text{Dy})_{0.5}\text{Ca}_{0.3}\text{MnO}_3$, $(\text{Nd}_{0.55}\text{Tb})_{0.45}\text{Sr}_{0.45}\text{MnO}_3$, and $\text{Sm}_{0.52}\text{Sr}_{0.48}\text{MnO}_3$.\(^{14-21}\) Our study essentially brings out the tunability as well as tailoring aspects of the CMR effect in these manganites. Our neutron diffraction and depolarization studies in $(\text{La}_{1-x}\text{Dy})_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ CMR perovskites\(^{17}\) infer that increasing Dy concentration drives the system first into a local canted ferromagnetic state with a reduced metal-insulator transition temperature (for $x = 0.114$ and 0.243) and then (for $x = 0.347$) to an “insulating” cluster-spin glass state. Further, neutron diffraction and small angle neutron scattering studies under magnetic field down to 5 K, have given a demonstration of the possible quantum critical point (QCP) [Fig. 6] behavior.\(^{18}\) We have also studied the evolution of ferromagnetic correlation length in $(\text{Nd}_{1-x}\text{Tb})_{0.55}\text{Sr}_{0.45}\text{MnO}_3$ manganites\(^{19}\) using neutron depolarization study under an international collaborative project, using the facilities at the Dhruva reactor, BARC.

**Low Dimensional Magnetic Materials**

Low dimensional magnetic materials\(^{22-27}\) are in the limelight due to their unique electronic and magnetic properties.
Many opportunities exist to modify their intertwined physical properties. We have studied naturally occurring quasi 1-D spin-chain compounds $\text{Ca}_3\text{Co}_{2-x}\text{Fe}_x\text{O}_6$ as well as 2-D $(\text{Ca/La/Sr})_3\text{GaMn}_2\text{O}_8$ layered compounds from their importance as magnetoelectronic materials.

For $\text{Ca}_3\text{Co}_{2-x}\text{Mn}_x\text{O}_6$, the spins within a chain are aligned along the crystallographic c-axis with up-up-down-down spin configuration. This kind of spin-configuration breaks the inversion symmetry and induces an electric polarization via symmetric magnetostriction. Our neutron diffraction study on these $\text{Ca}_3\text{Co}_{2-x}\text{Mn}_x\text{O}_6$ compounds confirms a rhombohedral structure with space group $R3\bar{c}$. With increasing Fe concentration, a deviation from quasi-1D character of spins has been established.

Neutron diffraction study as a function of temperature on the bilayered manganite $\text{Ca}_{2.5}\text{Sr}_{0.5}\text{GaMn}_2\text{O}_8$ has revealed antiferromagnetic correlations between the (010) oriented Mn spins in the a-c plane. The electrical resistivity is found to decrease with the increasing value of La substitution in $\text{Ca}_{2.5}\text{La}_{0.5}\text{Sr}_{0.5}\text{GaMn}_2\text{O}_8$. We have given a novel concept of introduction of ferromagnetic (FM) interaction in $\text{Ca}_{2.5}\text{La}_{0.5}\text{Sr}_{0.5}\text{GaMn}_2\text{O}_8$ Brownmillerite-like layered systems [Fig. 7] to attain the alternating “FM-metallic” and nonmagnetic-insulating layers, which would be helpful to model/prepare new functional materials based on naturally occurring layered materials for spintronics applications.

### Magnetic Nano-materials

One of the exciting areas of modern research in magnetism is the study of magnetic nanoparticles due to their unique magnetic properties which make them very appealing both fundamentally and technologically. The magnetic behavior of the nano-materials depends on their intrinsic properties, such as size and shape, size distribution, magnetic anisotropy, etc. However, a rational design of various magnetic properties of the nanomaterials requires systematic studies of the dependencies of the above mentioned properties. We have been studying structural and magnetic properties of a variety of nanomaterials such as $\gamma\text{-Fe}_2\text{O}_3$, amorphous $\text{Fe}_2\text{O}_3$, $\text{Fe}_3\text{O}_4$, Fe-Al, CoO, and Ni-Pt, core-shell structure of $\text{Fe}_2\text{O}_3$ and MnO, clusters of Co and Ni in NaY zeolites, $\text{Zn}_{0.95}\text{Zn}_{0.05}\text{O}$ (TM: Fe, Mn and Co), and Fe filled carbon nanotubes. These nanostructure-materials have immense scope of applications in high-density magnetic storage media, spintronics devices, catalysis, radionuclide separation from nuclear waste, and drug delivery. The results of some of studies are discussed below.
The nanoparticles of $\gamma$-Fe$_2$O$_3$ [Fig. 8] (prepared using a reverse micelle technique) show log-normal distribution of particle size. Superparamagnetic behavior of noninteracting nanoparticles with a log-normal distribution of blocking temperature (with a particle moment of $-28000 \mu_B$ for the sample annealed at 200 °C) is found in our dc magnetization study at room temperature. Such type of superparamagnetic nanoparticles with high magnetization at room temperature can have applications in magnetic drug delivery.

It is noteworthy to mention here that recently we have built a prototype Fe-oxide nanoparticle-loaded membrane device for use in artificial heart pump support.

We have observed an extraordinary coexistence of sign reversal of both magnetization and exchange bias field [Fig. 9 (a)] in the La$_{0.2}$Ce$_{0.8}$CrO$_3$ nanoparticles for the first time. These nanoparticles are found to be of core-shell nature. The core-shell configuration with an antiferromagnetic core of the Cr$^{3+}$ and Ce$^{3+}$ spins and a disordered shell with uncompensated spins, explains the sign reversal of both magnetization and exchange bias field. The phenomenon of switching of exchange bias in these nanoparticles offers new possibilities to fabricate magneto-electronic nano-devices [Fig. 9 (b)].

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