Review of the theoretical understanding of CMR

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Abstract

The study on colossal magnetoresistance (CMR) materials has gained great attention in recent years as they are testing ground of existing theory and its possible application in Spintronics. The perovskite complex maganites to which the colossal at magnetoresistive manganites belong are represented by general chemical formula. R_1-x D_xMno_3. Here R is rare earth element (La, Pr, nd. etc) and D is adivalent Metal (Ca, Sr, Ba, etc. Magnetoresistance, quantum phase transition and crystal change are the fundamental scientific issues exhibited in these novel CMR. materials. The existing theoretical understanding has been reviewed in this study.

Key words: colossal magnetoresistance, spintronics, magnites and perovskite.

1. Introduction:

Intensive studies of perovskite manganites has been going on, not only because these materials have great potential in applications related to the colossal magnetoresistance (CMR) effect [1- 3], but also because they offer a testing ground for theories related to strongly correlated systems. Following the discovery of the remarkable CMR effect in manganites, interest have grown to understand this family of material, which exhibits very diverse and unusual properties. Depending on temperature, composition, and magnetic field, manganites can have various ground states. They show insulating states, which can be paramagnetic, ferromagnetic, or anti-ferromagnetic. What is strange and most exotic about these solid-state oxides is that, even in a single crystal sample of high chemical purity, different phases having different electronic and magnetic properties can coexist at different locations in the sample [4, 5]. Thus, manganites have an intrinsic electronic in homogeneity, which can evolve on application of external stimuli like temperature and magnetic field.

The complex manganites to which the colossal magneto-resistive manganites belong are derived from a structure that consists on a lattice of oxygen octahedra with Mn in their center. They have the general chemical formula: $R_{1-x}D_xMnO_3$, where R is a rare earth element (La, Pr, Nd, etc.) and D is a divalent metal (Ca, Sr, Ba, etc.) [4].

Barium, calcium, strontium, and most lanthanoids have been found to form hexa-boride structures [5]. Depending on the metal used, these crystals have many interesting properties that make them relevant to research today. Divalent metal cations, for instance, typically give rise to narrow gap semiconductors, such as YbB_6 [6, 7].

Trivalent and tetravalent ions produce a hexaboride with metallic nature ideally having 1 or 2 electrons for transport, respectively, existing in a charge conducting state [7]. Pauli-paramagnetic, ferromagnetic, diamagnetic, conductive, superconductive, semiconductive, and more complex spin-ordered hexaborides have also been discovered and characterized [5].

Due to their unique electronic properties, metal hexaborides (MB_6) have found use in a variety of applications such as field-electron-emitters, electrical coatings for resistors, transmission metal catalysts, high energy optical systems, and sensors for high-resolution detectors [6, 8]. High melting points, chemical stability, magnetic properties, narrow band semiconductivity, superconductivity, hardness, thermionic emission, and electron emission efficiency are among the list of reasons these are attractive materials for such utilization. The most common use for lanthanum hexaboride has been for TEM (Transmission Electron Microscope) and SEM (Scanning Electron Microscope) electron sources. Cold field emitters (such as LaB_6) generate a more temporally coherent and brighter electron source.

2. Methods employed in theoretical studies:

Much of the challenge and interesting phenomenon, including the CMR effect starts to show up as soon as the parent compound is doped. However, many of the basic ingredients, such as orbital ordering and Jahn-Teller distortion, are already present in pure $LaMnO_3$ [9]. Thus, a complete understanding of the parent compound is a prerequisite to understanding fully the doped manganites. Owing to this reason a large number of theoretical investigations has already been undertaken on stoichiometric $LaMnO_3$.: using the LDA + U method [10], and within the LSDA [11, 12]. It was shown that many properties such as the correct magnetic ground state are well described by these methods, provided that the correct experimental crystal structure is used in the calculations.

Earlier theoretical works focused on the undistorted cubic structure and it was found that the usual LSDA couldn't reproduce the observed insulating ground state for $LaMnO_3$ [13]. This is partly due to the absence of structural distortions in the cubic phase, which play a significant role in reproducing the insulating character of the material. Other theoretical calculations on the orthorhombic structure have used the experimental geometry so as to account for the role of structural distortion on the electronic and magnetic properties of the material. Nevertheless, the value of the insulating gap obtained from those calculations is rather very small when compared against the experimental value [14].

Hill and Rabe [15] performed LSDA pseudopotential calculations to study the electronic and magnetic properties of $LaMnO_3$ in its high-temperature cubic perovskite structure. They used the experimental lattice parameter for the ideal cubic structure to calculate the electron band structures and densities of states with and without spin polarization. They calculated densities of states and bands structures for the paramagnetic and ferromagnetic phases, respectively, of the cubic structure. From these results the authors were able to confirm that the paramagnetic phase is highly unstable and that a lower energy structure could be achieved by allowing spin polarization and/or structural distortion.

Mastrikov [14] used the experimental geometry for the orthorhombic structure with A-AF ordering to calculate the electronic band structures. The insulating gap obtained in this calculation is about 0.6eV, which is considerably smaller than the experimental value of 1.7eV. This is a typical underestimate of DFT calculations. Therefore, a systematic study of the parent compound, especially, as to which the mechanisms are responsible in the stabilization of the insulating ground state, is still lacking.

The DFT is the result of two theorems proved by Hohenberg and Kohn. The first theorem states that "the external potential $V_{ext}(\vec{r})$ is a unique functional of $\rho(\vec{r})$; since, in turn $V_{ext}(\vec{r})$ fixes $\hat{H}$(Hamiltonian) we see that the full many particle ground state is an unique functional of $\rho(\vec{r})$" [17]. Here $\rho(\vec{r})$ is the electron density, $V_{ext}(\vec{r})$ is the electron-ion interaction potential. The second theorem states that "the functional that delivers the ground state energy of the system, delivers the lowest energy if and only if the input density is the true ground state density $\rho_o(\vec{r})$", [17]

i.e.

$$E_o[\rho_o] = \int \rho_o(\vec{r}) V_{ext}(\vec{r}) d\vec{r} + F_{HK}[\rho_o] \qquad (1)$$

where,

$$F_{HK}[\rho] = T[\rho] + E_{ee}[\rho] \qquad (2)$$

is the Hohenberg-Kohn Energy functional, $T[\rho]$ is the kinetic energy of the electrons, and $E_{ee}[\rho]$ is the classical Coulomb interaction energy.

Another important contribution to the development of DFT was given by Kohn and Sham. They suggested that the system of N interacting electrons in an external potential $V_{ext}(\vec{r})$ can be related to a system of N non-interacting Kohn-Sham electrons in an effective Kohn-Sham potential $V_{eff}(\vec{r})$ such that both the real and the non-interacting system have the same electron density[17]. While the non-interacting kinetic energy $T_s[\rho]$ is not equal to kinetic energy of the real interacting system, Kohn and Sham adjusted for that by introducing the energy functional as [17]:

$$F[\rho(\vec{r})] = T_s[\rho(\vec{r})] + J[\rho(\vec{r})] + E_{xc}[\rho(\vec{r})] \qquad (3)$$

where, $J[\rho(\vec{r})]$ is the classical Coulomb interaction, $E_{xc}[\rho(\vec{r})]$ is the exchange-correlation energy and contains the non-classical effects of self-interaction correction, exchange and correlation and also a portion belonging to kinetic energy.

The total energy of the real interacting system thus becomes [17]:

$$E[\rho(\vec{r})] = T_s[\rho(\vec{r})] + J[\rho(\vec{r})] + E_{xc}[\rho(\vec{r})] + E_{Ne}[\rho(\vec{r})] \qquad (4)$$

where, $E_{Ne}[\rho(\vec{r})]$ is electron-core interaction energy.

Now variational principle can be applied to search for the conditions that φ_i's (Kohn-Sham orbitals) must satisfy in order to get the minimum energy given by equation (4) under the condition $<\varphi_i|\varphi_j>=\delta_{ij}$. This results in the following equation [17]:

$$\left(-\frac{1}{2}\nabla^2 + \left[\int \frac{\rho(\vec{r}_2)}{r_{12}} d\vec{r}_2 + V_{xc}(\vec{r}_1) - \sum_A^M \frac{Z_A}{r_{1A}}\right]\right)\varphi_i = \varepsilon_i \varphi_i \qquad (5)$$

Or, $\left(-\frac{1}{2}\nabla^2 + V_{eff}(\vec{r}_1)\right)\varphi_i = \varepsilon_i \varphi_i$ (6)

Equation (6) is the one-electron Schrödinger's-like Kohn-Sham equation. By solving this we can determine the single-particle electron density of the interacting system [17]:

$$\rho(\vec{r}) = \sum_{i}^{N}\sum_{s} |\varphi_i(\vec{r},s)|^2 \quad (7)$$

Equations (5-7) are the basic equations used for electronic-structure simulations in DFT using plane waves and pseudopotentials to represent electron-ion interaction.

The above equations are solved by applying plane wave self-consistent field method which implements an iterative approach to reach self-consistency, using at each step iterative diagonalization techniques, in the frame work of the plane-wave pseudopotential method [16].

3. Existing theoretical models:

For understanding of the magnetic and transport properties of CMR generally two theoretical models are employed namely double exchange (DE) and Electron-lattice interaction.

3.1. **Double exchange:**

The perovskite structure is shown in Fig. 1. Small metal ions, manganese ions in this case, form a simple cubic lattice. Oxygen ions are at the centers of the cube edges. Large metal ions, such as La, Sr, Ca, Ba are at the center of each unit cube. As an example we may consider $La_{1-x}AxMnO_3$, (where A= Ca, Sr, or Ba). Compounds having extreme values of x are neither ferromagnetic nor good conductors. Zener [18] double exchange (DE) was proposed by Zener [18] in order to explain the simultaneous occurrence of ferromagnetism and metallicity, as functions of x and Temperature (T).

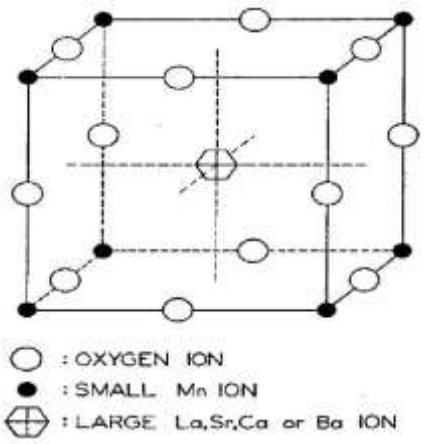

Fig. 1. Structure of manganese compounds with the perovskite lattice [19].

The problem of charge exchange between two Mn ions separated by an O^{2-} ion within the theory of double exchange [18, 19] may be considered. The model system is shown in Fig. 1.

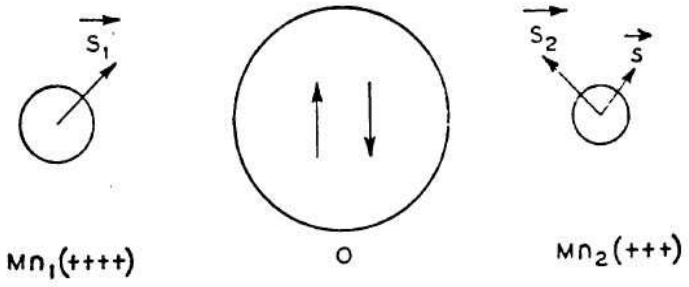

Fig. 2. Model for double exchange [19].

It has been considered that the O^{2-} ion has a closed shell and that the Mn ions have the number of d-electrons appropriate to give them each a spin S as well as one extra charge which can be equally on one or other. It may be assumed that the extra electro may go to unique orbital d_1 or d_2. There is need of solving problem of configuration overlapping between the two degenerate configurations with the electron on one atom or other needs to be solved.

In order for there to be any coupling between the two Mn atoms, the electron must be able to move from one to the other. The transfer process must occur through the O atom, the intermediary in this picture. There are several ways that this transfer process can take place. The first is suggested by Zener [18], via an exchange type integral,

$$J^* = \int d\tau\, \psi_{d1}(1)\, \psi_p(1)\, H\, \psi_p(2)\, \psi_{d2}(2) \qquad (8)$$

Here H is the Hamiltonian of the system. This exchange integral is negligibly small since the two Mn atoms do not overlap unless the p and d wavefunctions used are not orthogonal in which case it is equal to

$$J^* = S_{p\text{-}d} \int d\tau\, \psi_p\, V\, \psi_d = S_{p\text{-}d}\, H_{p\text{-}d} \qquad (9)$$

Where S is the overlap integral and V is the averaged potential. The simple effect of J* is to move an electron from M_{n1} to M_{n2}, and vice versa, without changing the spin. In case of orthogonal wavefunctions, higher order configuration interaction is to be considered. The configuration which must be introduced is that in which a single *p* electron has been transferred from O to Mn. This is connected to the initial configuration by the transfer integral Hp-d. Then this same transfer integral connects it with second configuration as both are symmetrical

relative to the third configuration. Both processes give transfer integrals of order of magnitude 0.1 eV, while the intra-atomic exchange integral J is of the order of 1 eV. The two primary transfer mechanisms in double exchange are both of the a type which tends to simply transfer a single electron with a change of spin from the first atom to the second atom.

As pointed by, Millis et al. [20] that a Hamiltonian incorporating only the double exchange interaction cannot explain the most obvious feature of the manganites, i.e. namely the magnitude of the change in resistivity and the ferromagnetic transition. Millis et al. as well as Roder et al. [21, 22], proposed, that in addition to double exchange, an electron-phonon coupling term is to be included. Such an interaction is expected for systems where transport takes place by hopping between Mn^{3+} and Mn^{4+} ions. Here the hole, corresponding to an Mn^{4+} (d_3) ion must displace a Mn^{3+} (d^4) ion which, in the dilute limit, can be associated with a large Jahn-Teller coupling. An analysis of acoustic resonance experiments for dilute Cr^{2+} in MgO shows that O^{2-} ions are displaced by roughly 1.5 Å from their undistorted positions [23]. Here Cr^{2+} is like Mn^{3+} in LaMnO, a d^4 ion in an octahedral oxygen environment. This distortion is of similar magnitude to that in LaMnO3 and, most likely, arises from the manifestation of strong electron phonon coupling implied by the Jahn-Teller theorem in the dilute case [23].

3.2. Electron-lattice interaction:

Assuming that the ground state is degenerate when the ions near the center are fixed to their regular lattice sites. If these ions are allowed to rearrange their distribution, the region becomes more stable as the electrons makes transition to states in which the symmetry is lower than that of the original distribution, and the degeneracy of the ground state may be lifted by the new lower symmetry. This is known as the Jahn-Teller effect. Due to Jahn-Teller effect crystals having simple structures makes transition to complicated structures with low symmetries. The dynamic problem represents a degenerate electronic state whose degeneracy is removed in first order by a doubly degenerate vibration [24-26]. The ground state degeneracy is removed by coupling between the nuclear vibration and the electron configuration, but also for strong coupling the electrons are in a "Born-Oppenheimer" potential so that the electron configuration follows the nuclear vibration. Thus for sufficiently large coupling the electron configuration corresponds to the symmetry of the nuclei.

4. Conclusion and summary:

In this paper a brief review of double exchange and electron-lattice interaction model used in the theoretical study of CMR and brief description of density functional theory (DFT) has been presented. The CMR materials offer a testing ground for existing theories.

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