First principal calculation and Monte Carlo simulations of the Magnetocaloric effect, Electronic and Magnetic properties in perovskite oxide Pr$_{0.65}$Sr$_{0.35}$MnO$_3$

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Abstract. We have used the first principal calculation and Monte Carlo simulations (MCS) to investigate the magnetocaloric effect, electronic and magnetic properties of Pr$_{0.65}$Sr$_{0.35}$MnO$_3$ (PSMO) perovskite. The exchange-correlation potential was treated with the generalized gradient approximation (GGA) for the electronic and magnetic properties. The ferromagnetic phase of PSMO is half metallic with 100% spin polarization, which is important in the relation to the colossal magnetoresistance properties of this compound. The magnetic moment is obtained. The thermal variation of magnetization of PSMO has been obtained. The temperature dependence of the magnetic entropy change and the adiabatic temperature are obtained by MCS. The Curie temperature of PSMO has been deduced. The field dependence of relative cooling power PSMO has been obtained.

1. Introduction
The search for energy-efficient technologies for developing new refrigerator appliances has made the magnetocaloric effect a field of current scientific interest [1]. At present, there are several interesting groups of magnetocaloric materials, which are good candidates for active regenerator material used in the room temperature cooling devices. The first group of materials is hydrogenated as well as cobalt doped lanthanum based La(Fe, Si)$_{13}$ intermetallic compounds. The second one is related to the manganese-based compounds, mainly Fe$_2$P type compounds such as (Mn, Fe)$_2$(P, X) [X = Ge, Si, As] [2-5]. Magnetic as well as calorimetric measurements have been performed on single crystal samples of Pr$_{0.6}$Sr$_{0.4}$MnO$_3$ and Nd$_{0.6}$Sr$_{0.4}$MnO$_3$ to develop a complete critical behavior study of the paramagnetic to ferromagnetic transition in both manganites [6]. Previously, the development of a new magnetic refrigeration (MR) technology, based upon the magnetocaloric effect (MCE) [7], has brought an alternative to the conventional gas compression (CGC) technique [8,9]. A thorough understanding of the magnetocaloric properties of existing magnetic refrigerant materials has been an important issue in magnetic refrigeration technology. This paper reviews a new class of magnetocaloric material that is, the ferromagnetic perovskite manganites (R$_{1-x}$M$_x$MnO$_3$, where R =La, Nd, Pr and M= Ca, Sr, Ba, etc.) [10-12].

The different research activities can be gathered in the major following axes:
- Study of MCE and research of new materials with high magnetocaloric effect [13-14];
- Study and modeling of thermodynamic cycles [15];
- Design and realization of magnetic refrigeration device with its magnetic source [16–18].
In this spirit, an oxide expected to show promising magnetocaloric properties around room temperature Pr$_{0.65}$Sr$_{0.35}$MnO$_3$ was produced in large scale and shaped in order to build a regenerator [19]. on other hand, the perovskite type manganite systems, LnSrMnO$_3$ (Ln=La, Pr, Nd, Sm, and Gd; 0≤x≤0.5) were studied as the electrode materials for solid oxide fuel cells from the viewpoint of applications to the co-firing process of the electrolyte and electrode at a higher temperature [20]. In previous works [21-22], the magnetocaloric effect on SmFe$_{1-x}$Mn$_x$O$_3$ and La$_{0.67}$Ba$_{0.33}$Sr$_{0.11}$MnO$_3$ perovskites has been investigated using the Monte Carlo simulations. In this work, both approaches First principal calculations and Monte Carlo simulations are used to study the Pr$_{0.65}$Sr$_{0.35}$MnO$_3$ perovskite. The electronic structure are studied. The thermal of the magnetic entropy change and the adiabatic temperature are determined. The Curie temperature of Pr$_{0.65}$Sr$_{0.35}$MnO$_3$ and the field dependence of relative cooling power Pr$_{0.65}$Sr$_{0.35}$MnO$_3$ has been obtained.

2. Ab initio calculations
The electronic and magnetic properties of Pr$_{0.65}$Sr$_{0.35}$MnO$_3$ were calculated using the density functional theory (DFT) [23-25]. This method is based on the full-potential linearized augmented plane wave method (FPLAPW) [26]. Exchange and correlation effect are treated by the gradient generalized approximation GGA [27]. The structure file of PrMnO$_3$ contains 20 atoms (4 Pr, 4 Mn and 12 O) with lattice parameters a = 5.90(Å), b = 7.72(Å), c = 5.52 (Å) and α = β = γ = 90° with the space group Pnma [28]. To mimic the realistic concentration of Sr (x = 0.35) in the PrMnO$_3$ Pnma lattice, (1 *1)*5 supercell is formed containing 100 atoms (20 Pr, 20Mn and 60 O atoms in Figure 1).

![Figure 1. The structure of PrMnO3](image)

A Sr / Pr substitution in the supercell of the total atom of 13 Pr leads to a composition Pr$_{0.65}$Sr$_{0.35}$MnO$_3$ (Figure 1), which is even of the composition Pr$_{0.65}$Sr$_{0.35}$MnO$_3$ prepared experimentally [19]. The energy of separation between the valence and core states is -9.0 Ry. The valence wave functions inside the muffin-tin spheres are expanded in terms of spherical harmonics up to $l_{max}$ = 10. The muffin-tin (MT) radii of Pr, Sr, Mn and O were chosen to be 2.45, 2.23, 1.95 and 1.68 respectively. Both the muffin-tin radius and the number of k-points were varied to ensure total energy convergence. To reduce the calculation time for structural alignment, we based on a distance cutoff 16.281 Bohr.

3. Model and Monte Carlo simulation
The Ising model of Pr$_{10.65}$Sr$_{0.35}$MnO$_3$ perovskite is given by:

$$H = - \sum_{<i,j>} J_{ij}S_iS_j - h\sum_i S_i$$

(1)

with $J_{ij}$ is the first, second and third exchange interactions and $h$ is the external magnetic field. The values of $J_1$=+42.0, $J_2$=+39.0 and $J_3$=+36.0 are found from the mean field theory [29]. The spin moment of Mn$^{3+}$ is S=2. The Pr$_{0.65}$Sr$_{0.35}$MnO$_3$ perovskite such as given in Figure 1 is assumed to reside in the unit cells and the system consists of the total number of spins N=896. Cyclic boundary conditions on the lattice were applied and the configurations were generated by sequentially traversing the lattice and making single-spin flip attempts. Our data were generated with 10$^5$ Monte Carlo steps.
per spin, discarding the first $10^4$ Monte Carlo simulations. Starting from different initial conditions, we performed the average of each parameter and estimate the MCSs, averaging over many initial conditions. The different parameters who calculate are given by the following equations:

The internal energy per site is:

$$E = \frac{1}{N} \langle H \rangle$$

(2)

Magnetizations of material are:

$$M = \frac{1}{N} \left\langle \sum_i \sigma_i \right\rangle$$

(3)

Magnetic entropy is:

$$S(T, h) = \int_0^T \frac{C_m}{T} dT$$

(4)

With $$C_m = \frac{\beta^2}{N} \left( \langle E^2 \rangle - \langle E \rangle^2 \right)$$

(5)

$\Delta S_m$ can be calculated indirectly from the experimental magnetization curves by using Maxwell relation [30]:

$$\Delta S(T, h) = h \left( \frac{\partial M}{\partial T} \right)_h$$

(6)

The adiabatic temperature change is given by:

$$\Delta T_{ad} = -T \frac{\Delta S_m}{C_m}$$

(7)

The relative cooling power (RCP) described as an area under the dependence of $\Delta S_m(T)$ on temperature, is a compromise between the magnitude of the magnetic entropy change and the width of the peak is given by:

$$RCP = \int_{T_c}^{T_h} \frac{T_h}{T_c} \Delta S_m(T) dT$$

(8)

where $T_c$ and $T_h$ are the cold and the hot temperatures corresponding to both ends of the half-maximum value of $\Delta S_m^{max}$, respectively.

3. Results and discussion

In Figure 2a, we present the total DOS of $\text{Pr}_{0.65}\text{Sr}_{0.35}\text{MnO}_3$ between -7 eV and 5eV as a function of energy. The presence of gap energy close to the Fermi level for spin down shows that this compound has a half metallic character. The summation of the total density of spin up and spin down greater than zero emphasizes that this compound has ferromagnetic behavior. To understand the bonding mechanisms between the atoms, the analysis of partial density of states (PDOS) has been performed Figure 2b. The atoms Mn and O have a significant contribution of the total density in the vicinity of the Fermi level. While Pr has a strong contribution from energy range -0.53eV to 0.85 eV. The contribution from Sr to the total DOS near Fermi level is negligible. Moreover, the Mn atom is dominant by the 3d orbital, and the O atom is dominant by the 2p orbital. Therefore, the strong contribution of Mn-d is due to the hybridization occurring with O(p) states [31]. This suggests that the half-metallicity and the magnetic spin moment are mainly due to the 2p (O) -3d (Mn) coupling. From the Mn-d orbital projected density of states (PDOS) (Figure 2c), one can clearly see that the $d_{x^2-y^2}$ and $d_{xy}$ orbitals are predominants at $E_F$, while the $d_{xy}$, $d_{yz}$ and $d_{xz}$ orbitals are predominants at [-2.36 eV, -1.13 eV]. From O-p we have strong contribution of $p_x$, $p_y$ and $p_z$ spin up in energy range -6.8 eV to -1.11 eV Figure 2d.
Figure 2. The TDOS (a), PDOS(b), Mn-d orbital projected partial (c) and O-p orbital projected partial (d) of Pr$_{0.65}$Sr$_{0.35}$MnO$_3$

We neglected the spin-orbit coupling and using the simple equation: $p(N) = \frac{N\uparrow \uparrow - N\downarrow \downarrow}{N\uparrow \uparrow + N\downarrow \downarrow}$ where $N$ is the density of states at $E_F$ for spin up $\uparrow$ or spin down $\downarrow$ [32, 33]. It is found that this system present 100% spin polarization. The calculated Mn spin magnetic moment is 3.37$\mu_B$ calculated by GGA-PBE (Table 1).

Table 1. The values of magnetic moment of Mn, and spin polarization (SP)

| Compound       | Magnetic moment ($\mu_B$) | SP (%) |
|----------------|---------------------------|--------|
| Pr$_{0.65}$Sr$_{0.35}$MnO$_3$ | 3.37617                  | 100%   |

We have presented in Figure 3 the thermal magnetization obtained by Monte Carlo simulations. From this curve, we deduce that the Curie temperature is equal to $T_C=294$ K. This value is in good agreement with the experimental one in ref [19] (see Table 2). The magnetization curve shows a classical phase transition of the 2$^{nd}$ order at $T_C$ (ferromagnetic / paramagnetic).

Figure 3. The thermal magnetization for h=0 T

Table 2. The values of $T_C$, $\Delta S_{\text{max}}$, $\Delta T_{\text{ad}}$ and $C_p$ obtained by Ref.[19] and Monte Carlo simulations.

| Perovskite          | $T_C$(K) | $\Delta S_{\text{max}}$(J/kg.K) at h=1 T | $\Delta T_{\text{ad}}$(K) at h=1 T | $C_p$(J/kg.K) at $T_C$ |
|---------------------|----------|----------------------------------------|----------------------------------|------------------------|
| Pr$_{0.65}$Sr$_{0.35}$MnO$_3$ | 295 [19] | 2.3 [19]                              | 1.1 [19]                          | 580 [19]               |
|                     | 294      | 2                                      | 1.13                             | 581                    |
| Monte Carlo         | MCS      | MCS                                    | MCS                              |                        |
| simulations(MCS)    |          |                                        |                                   |                        |

Figure 4. shows the variation of thermal magnetic entropy change of Pr$_{0.65}$Sr$_{0.35}$MnO$_3$ obtained by Monte Carlo simulations. The value of $\Delta S_{\text{max}}$ increases with increasing the values of external magnetic
field increases while the Curie temperature remains stable. The maximum of magnetic entropy is \( \Delta S_{\text{max}} = 1.98 \text{ J.K}^{-1}.\text{kg}^{-1} \). This value is in good agreement with the experimental one in ref [19] (see Table 2). The large magnetic entropy change peak, which would be different if the sample is either measured with increasing or decreasing magnetic field. This change in peak is not associated with the intrinsic properties of the sample but to a wrong application of Maxwell relation.

**Figure 4.** The magnetic entropy change \( \Delta S_{\text{m}} \) for a several magnetic fields.

The thermal adiabatic temperature change \( \Delta T_{\text{ad}} \) and heat specific \( C_P \) obtained by Monte Carlo simulations are given in Figure 5 for \( h=1 \text{ T} \). The maximum of adiabatic temperature change (Figure 5a) and heat specific (Figure 5b) are situated at the transition temperature \( T_c = 294 \text{ K} \). This value of \( T_c \) is confirmed by the magnetization curve (Figure 3) and magnetic entropy change curve (Figure 4) which exhibits a clear transition around 294 K. The values obtained of \( \Delta T_{\text{ad}} \) and \( C_P \) by Monte Carlo are comparable with that given by experimental results of Ref. [19] (see Table 2).

**Figure 5.** The adiabatic temperature change \( \Delta T_{\text{ad}} \) (a) and heat specific \( C_P \) (b) for \( h=1 \text{ T} \).

We give in Figure 6, the variation of relative cooling power with the magnetic field for \( \text{Pr}_{0.65}\text{Sr}_{0.35}\text{MnO}_3 \) using Monte Carlo simulations. RCP varies linearly with magnetic field \( h \). The maximum value of RCP is 17557 J/kg is given for \( h=5\text{ T} \).

**Figure 6.** The field dependence of relative cooling power for \( \text{Pr}_{0.65}\text{Sr}_{0.35}\text{MnO}_3 \).

It is very interesting to note here that usually, this type of giant magnetocaloric effect and large RCP is observed for samples possessing heavier rare-earth elements whose magnetic moments are large [34]. Finally, we have given in Figure 7, the thermal dependence of relative cooling power for \( \text{Pr}_{0.65}\text{Sr}_{0.35}\text{MnO}_3 \) for a several magnetic fields. The values of RCP increase with increasing the values.
of magnetic field for a fixed value of temperature. The RCP value increases with increasing the values of temperatures until reached their saturation for each value of magnetic field.

**Figure 7.** The thermal dependence of relative cooling power for a several magnetic fields.

### 4. Conclusion

We investigated the magnetocaloric effect, electronic and magnetic properties of Pr$_{0.65}$Sr$_{0.35}$MnO$_3$ by using first principle studies and Monte Carlo simulation. The spin polarization for Pr$_{0.65}$Sr$_{0.35}$MnO$_3$ show half metallic ground state with the ferromagnetic coupling of Mn spin. The transition temperature has been obtained from the variation of magnetization versus the temperatures for a fixed value of magnetic field. The obtained values of $T_c=294$ K using Monte Carlo simulations are comparable with that obtained by Ref. [19]. The obtained results of magnetic entropy change and heat specific for Monte Carlo simulations are comparable with that obtained by Ref. [19]. The maximum of magnetic entropy change is situate at the transition temperature and heat specific are obtained. The maximum of curves are situated at the transition temperature. The variation of RCP values versus the magnetic fields and temperatures values are found. The RCP values increase with increasing the magnetic field.

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