The orbital and charge ordering in Pr$_{1-x}$Ca$_x$MnO$_3$ ($x=0$ and 0.5) from the *ab initio* calculations

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Abstract

The electronic structure of the doped manganites Pr$_{1-x}$Ca$_x$MnO$_3$ was calculated by the LSDA+U method which takes into account the local Coulomb interaction between d-electrons of transition metal ions. In contrast to the standard local spin density approximation (LSDA) no Jahn-Teller lattice distortions are needed to reproduce the experimentally observed orbital ordering in the undoped PrMnO$_3$. The correct ground state: a charge and orbital ordered antiferromagnetic insulator, was obtained for Pr$_{1/2}$Ca$_{1/2}$MnO$_3$. The results are in good agreement with the neutron diffraction data.

I. INTRODUCTION

The doped rare earth manganites $Re_{1-x}A_x$MnO$_3$ ($Re$ is a rare earth such as La and $A$ is a divalent element such as Sr or Ca) due to their peculiar correlation between magnetism and conductivity have been extensively studied during 1950s and 60s [1]. The most thoroughly investigated was the La$_{1-x}$Sr$_x$MnO$_3$ system. Undoped ($x=0$), LaMnO$_3$ is an antiferromagnetic insulator. Upon doping with Sr, this perovskite oxide becomes a ferromagnetic metal;
the connection between metallicity and ferromagnetism was well explained by the double exchange hopping mechanism \[2\]. The discovery of colossal magnetoresistance phenomena in samples with Sr dopant densities in the \[0.2 \leq x \leq 0.4\] regime \[3\] brought a revival of the interest to these systems.

The Mn\(^{+3}\) ion in the hole-undoped compound LaMnO\(_3\) has the high-spin \(d^4\) electron configuration \(t_{2g}^3e_{g}^1\). The \(t_{2g}\) orbitals hybridize with O2p orbitals much more weakly than the \(e_g\) orbitals and can be regarded as forming the localized spin \((S=3/2)\). In contrast to that, \(e_g\) orbitals, which have lobes directed to the neighboring oxygen atoms, hybridize strongly with O2p producing in the result rather broad bands. The strong exchange interaction with \(t_{2g}\) subshell leads to the splitting of the \(e_g\) band into unoccupied \(e_{g\downarrow}\) and half-occupied \(e_{g\uparrow}\) subbands. The half filled \(e_{g\uparrow}\) subband is a typical example of the Jahn-Teller system, and, indeed, LaMnO\(_3\) has an orthorhombic crystal structure \[4\] with distorted (elongated) MnO\(_6\) octahedra. This cooperative Jahn-Teller effect is usually considered responsible for the opening of the gap in the half-filled \(e_{g\uparrow}\) band and an insulator ground state of LaMnO\(_3\).

The orthorhombic crystal structure of LaMnO\(_3\) (\(Pbnm\) space group) can be described as a perovskite with two types of distortion from a cubic structure: 1) Tilting (rotation) of the MnO\(_6\) octahedra, so that Mn-O-Mn angles become less than 180°, and 2) Jahn-Teller distortion of the octahedra, with one long Mn-O bond and two short bonds. With doping by Sr the orthorhombicity (the deviation of the values of the lattice parameters \(b\) and \(c/\sqrt{2}\) from \(a\)) becomes smaller and for \(x \geq 0.175\) the stable crystal structure at room temperature becomes rombohedral, where only tilting of oxygen octahedra is present but all three Mn-O bonds are equal. Around the same value of the doping \(x\), \(La_{1-x}Sr_xMnO_3\) becomes metallic.

For Sr doping with \(0.2 \leq x \leq 0.4\), \(La_{1-x}Sr_xMnO_3\) is a ferromagnetic metal at low temperatures. However, as the temperature increases and approaches the Curie temperature \(T_c\) a sudden increase of the resistivity is observed \[3\]. As the temperature dependence of the resistivity \(\rho(T)\) has typically semiconducting behavior (\(d\rho/dT < 0\)) above \(T_c\), this increase in resistivity at around \(T_c\) is usually described as a metal-insulator transition. The colossal magnetoresistance effect happens when the temperature is close to \(T_c\): the external magnetic
field leads to suppression of the resistivity increase or to shifting the metal-insulator transition to higher temperatures resulting in a very large negative value of \([\rho(H) - \rho(0)]/\rho(0)\).

The crucial point in the understanding of the effect of the colossal magnetoresistance is the nature of the metal-insulator transition with the temperature variation across \(T_c\). It was shown \([5]\) that the double exchange mechanism alone is not enough to explain such transition. Millis et al. \([6]\) suggested local Jahn-Teller distortions (Jahn-Teller polarons) as a main mechanism causing localization. Their idea is that a \(E_{JT}/W\) ratio (\(E_{JT}\) is self-trapping Jahn-Teller polaron energy and \(W\) is effective band width) is close to the critical value in \(La_{1-x}Sr_xMnO_3\) and as \(W\) decreases with destroying the ferromagnetic order above \(T_c\) (the effective hopping takes the maximum value for a parallel spin alignment), this ratio becomes larger than the critical value to result in polaron localization. Varma \([7]\) argues that \(LaMnO_3\) is not an insulator due to the Jahn-Teller distortion but is a Mott insulator and the Jahn-Teller distortion occurs parasitically. He explains localisation of the holes in the paramagnetic phase by spin polaron mechanism.

By replacing \(La\) with other trivalent ions with smaller ionic radius, the \(Mn-O-Mn\) bond angle becomes smaller and the \(e_g\) band width \(W\) is reduced to enhance the tendency to the carrier localization and lattice distortion. Variety of dramatic phenomena have been observed in \((Pr, Nd, Sm)(Sr, Ca)MnO_3\) systems. As one of such examples, we study \(Pr_{1/2}Ca_{1/2}MnO_3\) in the present paper. This system has a very peculiar phase diagram \([8,9]\). At low temperature, it is an antiferromagenetic insulator with a charge ordering of \(Mn^{3+}\) and \(Mn^{4+}\) accompanied by an orbital ordering: the orbital ordering and spin ordering is of CE-type. Between \(T_N (\simeq 180 \text{ K})\) and \(T_{co} (\simeq 240 \text{ K})\), there is no long-range magnetic ordering but the system remains to be insulating because of the persisitence of the charge ordering. Above \(T_{co}\), it is a paramagnetic insulator.

The local spin density approximation (LSDA) \([10]\) was used by several groups for theoretical investigation of the electronic structure of \(La_{1-x}Sr_xMnO_3\) \([11,12]\). Those calculations have confirmed the importance of the Jahn-Teller distortion for correct description by the LSDA of the insulating antiferromagnetic ground state of the undoped \(LaMnO_3\), because
The calculations with an undistorted cubic perovskite crystal structure produce a half-filled metallic \( e_g \) band. However, in order to address the charge and orbital order observed in doped manganites it is necessary to go beyond LSDA by including the intra d-shell Coulomb interaction (LSDA+U method \([14,15]\)). Recently such an approach was used for treating the charge ordering in magnetite \( \text{Fe}_3\text{O}_4 \), where LSDA gives a metallic uniform solution. The LSDA+U calculation gave a charge ordered insulator as the ground state of this compound \([17]\). In this paper we describe the results of the electronic structure calculation for \( \text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3 \) for \( x = 0 \) and \( 0.5 \) in the LSDA+U approximation.

II. COMPUTATIONAL METHOD

The problem of the charge ordering cannot be treated properly by the standard LSDA because of the non-vanishing self-interaction. In contrast to the Hartree-Fock approximation, where the self-interaction is explicitly excluded for every orbital, in the LSDA it is canceled to a good approximation in the total energy, but rather poorly in the local one-electron potentials, which are orbital-independent. The spurious self-interaction present in the LSDA leads to an increase in the Coulomb interaction when the distribution of the electron charge deviates from the uniform one. This effect can be illustrated in the following way. If we consider the system having less than one electron per site in the partially filled electronic subshell (for example \( e_g \)-electrons in \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \)) then the potential which this electron feels at some site must not depend on the orbital occupancy of this particular site, as the electron does not interact with itself. However, as the LSDA potential is a functional of the electron density only, increasing the electron density at one site and decreasing it at another one, with a formation of the charge ordering, will lead to an increase of the potential at the first site and a decrease at the second one. As a result, in the self-consistency loops, the charge distribution will return to the uniform density. In order to cure this deficiency, it is necessary to remove the self-interaction. The LSDA+U method \([14,15]\) is one of the practical methods to solve the self-interaction problem.
Let us introduce the d-orbitals occupation matrix defined by:

\[
\sigma_{mm'} = -\frac{1}{\pi} \int_{E_F}^{E} \text{Im} G_{\text{inlm},\text{inlm}'}(E) dE,
\]

where \(G_{\text{inlm},\text{inlm}'}(E) = \langle \text{inlm}\sigma \mid (E - \hat{H})^{-1} \mid \text{inlm}'\sigma \rangle\) are the elements of the Green function matrix (\(i\): index of atom site, \(nl\): main and orbital quantum numbers (for example 3\(d\)), \(m\): index of a particular \(d\)-orbital and \(\sigma\): spin projection index). In terms of the elements of this occupation matrix \(\{\sigma\}\), the LSDA+U functional [16] is defined as follows:

\[
E_{\text{LSDA+U}}[\rho^\sigma(r), \{\sigma\}] = E_{\text{LSDA}}[\rho^\sigma(r)] + E_{\text{U}}[\{\sigma\}] - E_{\text{dc}}[\{\sigma\}]
\]

(2)

Where \(\rho^\sigma(r)\) is the charge density for spin-\(\sigma\) electrons and \(E_{\text{LSDA}}[\rho^\sigma(r)]\) is the standard LSDA (Local Spin-Density Approximation) functional. \(E_{\text{U}}[\{\sigma\}]\) is the Hartree-Fock type electron-electron interaction energy given by

\[
E_{\text{U}}[\{\sigma\}] = \frac{1}{2} \sum_{\{m\},\sigma} \{ \langle m, m'' | V_{ee} | m', m''' \rangle \sigma_{mm'} \sigma_{m'm''} - \langle m, m'' | V_{ee} | m', m''' \rangle \sigma_{m'm''} \sigma_{mm'} - \langle m, m'' | V_{ee} | m', m'' | V_{ee} | m', m'' \rangle \sigma_{mm'} \sigma_{m'm''} \}
\]

(3)

where \(V_{ee}\) is the screened Coulomb interaction among the \(nl\) electrons. Finally, the last term in Eq.(4) corrects for double counting and is given by

\[
E_{\text{dc}}[\{\sigma\}] = \frac{1}{2} UN(N - 1) - \frac{1}{2} J N^\uparrow(N^\uparrow - 1) + N^\downarrow(N^\downarrow - 1),
\]

(4)

where \(N^\sigma = Tr(n^\sigma_{mm'})\) and \(N = N^\uparrow + N^\downarrow\). \(U\) and \(J\) are screened Coulomb and exchange parameters [18,19].

In addition to the usual LSDA potential, the variation of the functional (2) gives an effective single-particle potential to be used in the single-particle Hamiltonian:

\[
\hat{H} = \hat{H}_{\text{LSDA}} + \sum_{mm'} | \text{inlm}\sigma \rangle V^\sigma_{mm'} \langle \text{inlm}'\sigma |
\]

(5)
The matrix elements of the screened Coulomb interaction $V_{ee}$ can be expressed in terms of complex spherical harmonics and effective Slater integrals $F^k$ as

$$
\langle m, m'' | V_{ee} | m', m''' \rangle = \sum_k a_k(m, m', m'', m''') F^k,
$$

where $0 \leq k \leq 2l$ and

$$
a_k(m, m', m'', m''') = \frac{4\pi}{2k + 1} \sum_{q=-k}^k \langle lm | Y_{kq} | lm' \rangle \langle lm'' | Y_{kq}^* | lm''' \rangle.
$$

For d-electrons one needs $F^0$, $F^2$ and $F^4$ and these can be linked to the Coulomb- and Stoner parameters $U$ and $J$ obtained by the LSDA-supercell procedures via $U = F^0$ and $J = (F^2 + F^4)/14$ with the ratio $F^2/F^4$ being to a good accuracy a constant $\sim 0.625$ for the 3d elements.

The LSDA+U approximation was realized in the framework of the linear muffin-tin orbital method in the atomic sphere approximation (LMTO-ASA). The values of $U=7.9$ eV and $J=0.9$ eV were used as obtained from the constrained LSDA supercell calculations.

**III. RESULTS AND DISCUSSION**

As a first step the electronic structure of the undoped PrMnO$_3$ was calculated. This compound has practically the same properties as LaMnO$_3$. The only difference is that due to the smaller ionic radius of Pr ion compared with that of La ion, the tilting of the oxygen octahedra in orthorombic $Pbnm$ crystal structure is stronger, resulting in smaller effective $e_g - e_g$ hopping between Mn atoms and narrower band width.
The crystal structure of the doped Pr$_{1-x}$Ca$_x$MnO$_3$ does not show transition to the rombohedral symmetry, as it is the case for La$_{1-x}$Sr$_x$MnO$_3$, preserving the orthorombic $Pbnm$ space group [8]. However the values of the lattice parameters $a$, $b$ and $c/\sqrt{2}$ for $x=0.5$ are so close that it can be called a pseudocubic structure. In this structure only the tilting of the oxygen octahedra is present, but octahedra themselves are not Jahn-Teller distorted as in the undoped crystal structure. In order to study effects of the orbital polarization purely due to the intrashell d-d Coulomb interaction without any influence of the Jahn-Teller lattice distortion the calculation for the undoped PrMnO$_3$ was performed with the crystal structure parameters corresponding to Pr$_{1/2}$Ca$_{1/2}$MnO$_3$.

Kugel and Khomskii [23] demonstrated for a wide range of Jahn-Teller magnetic compounds that the exchange mechanism (caused by an interplay between on-site Coulomb interaction $U$ and intersite hopping $t$) by itself, without taking Jahn-Teller distortions into consideration, is able to give a correct picture of the spin and orbital ordering. In this case the change in the lattice structure (the structural transition) is a secondary effect. One may say that the system shows the ”Jahn-Teller ordering” without the ”Jahn-Teller interaction”. Actually an exchange mechanism acts jointly with the Jahn-Teller and the quadrupole mechanisms. It is quite difficult to determine just which mechanism will be predominant in each specific case due to complexity of the real compound. One of the possible ways to answer this question in the frame of *ab-initio* band structure calculations is to use a crystal structure excluding distortions caused by the Jahn-Teller interaction.

Such kind of approach was used for the cooperative Jahn-Teller system KCuF$_3$ [10]. It also has the perovskite crystal structure, but there is no tilting of the CuF$_6$ octahedra and all Cu-F-Cu angles are equal to 180°. Divalent copper ion in this compound has a $d^9$ configuration ($t_{2g}^3 \cdot t_{2g}^3 \cdot e_{g}^2 \cdot e_{g}^1$) known to be a Jahn-Teller ion, and, indeed, the Jahn-Teller distortion is observed in the form of the elongated CuF$_6$ octahedra with long axes alternatively along $a$ and $b$ axes in the $ab$-plane. Kugel and Khomskii [23] showed that a simple Hubbard model type calculation in a mean-field approximation without taking into account the electron-phonon interaction could predict the orbital ordering (alternating $3x^2 - r^2$ and
$3y^2 - r^2$ Cu3d-orbitals for electrons or $x^2 - z^2$ and $y^2 - z^2$ orbitals for holes) corresponding to the symmetry of the experimentally observed lattice distortions.

The LSDA+U functional (eq.2) has a definite important improvement upon the LSDA: explicit cancellation of the self-interaction and the proper description of the lowering of Coulomb interaction energy with development of the orbital polarization. The functional (eq.2) is also rotationally invariant (the total energy does not change with the unitary transformation of the d-orbital basis set $|m >$), meaning that if the local coordinate system (and, correspondingly d-orbital basis set $|m >$) was chosen inappropriately for describing the resulting orbital polarization, the unitary transformation which diagonalizes the non-diagonal occupation matrix $n^\sigma_{mm'}$ (eq.1) will give a proper orbital basis set.

The LSDA+U calculation for KCuF$_3$ [16] in cubic perovskite crystal structure gave results fully confirming Kugel-Khomskii’s prediction - alternating $3x^2 - r^2$ and $3y^2 - r^2$ orbital order. Moreover, it was not just the lowest total energy configuration among many possible stationary configurations as in the model calculation [23], but the only one stable solution. The lattice relaxation to minimize the total energy is in good agreement with experimental data. Note that the standard LSDA did not show the lattice instability with respect to the Jahn-Teller distortion in KCuF$_3$. We would like to emphasize that the orbital polarization caused by the d-d Coulomb interactions practically did not change with the lattice distortion [24].

The use of the crystal structure parameters corresponding to Pr$_{1/2}$Ca$_{1/2}$MnO$_3$ (with undistorted oxygen octahedra) for PrMnO$_3$ may correspond to the use of the cubic perovskite crystal structure for KCuF$_3$. However, for PrMnO$_3$, we have to take into account the tilting of MnO$_6$ octahedra (present in Pr$_{1/2}$Ca$_{1/2}$MnO$_3$ structure), which is essential for the proper description of the reduction in the effective $e_g - e_g$ hopping due to the bending of the Mn-O-Mn bond. The LSDA+U calculation with the experimental A-type antiferromagnetic spin alignment resulted in a non-diagonal occupation matrix for spin density (for the $e_g$ subspace ($3z^2 - r^2$ and $x^2 - y^2$ orbitals) of one particular Mn atom):
\[ n_{mm'}^\uparrow - n_{mm'}^\downarrow = \begin{pmatrix} 0.31 & 0.22 \\ 0.22 & 0.58 \end{pmatrix} \] (8)

The diagonalization of this matrix gives two new \(e_g\) orbitals: \(\phi_1 = 3y^2 - r^2\) with occupancy 0.71 and \(\phi_2 = z^2 - x^2\) with occupancy 0.18. For the second type of Mn atom \(\phi_1\) and \(\phi_2\) orbitals can be obtained by transposition of \(x\) and \(y\).

The resulting orbital order can be presented graphically by plotting the angle distribution of the \(e_g\)-electron spin density:

\[ \rho(\theta, \phi) = \sum_{mm'} (n_{mm'}^\uparrow - n_{mm'}^\downarrow) Y_m(\theta, \phi) Y_{m'}(\theta, \phi) \] (9)

As a Mn\(^{+3}\) ion has formally only one electron in partially filled \(e_g\) subshell, the \(e_g\)-spin density must correspond to the density of this electron (Fig.1).

The plot of Fig.1 and the form of the \(\phi_1\) and \(\phi_2\) orbitals diagonalizing the spin density occupation matrix show that the orbital order obtained in our LSDA+U calculations for PrMnO\(_3\) is of the same symmetry as the one in KCuF\(_3\). The "parasitical" lattice distortion, which one could expect from such orbital ordering: elongation of MnO\(_6\) octahedra in the direction of the lobes of \(\phi_1\) orbitals, will reproduce the experimentally observed Jahn-Teller lattice distortion.

The orbital polarization is far from being 100\%, the difference in the occupancy of \(\phi_1\) and \(\phi_2\) orbitals is only 0.53. The reason for this is the strong hybridization of \(e_g\)-orbitals with oxygen 2p-orbitals. In Fig.2, the total and partial densities of states (DOS) for PrMnO\(_3\) are shown (for \(e_g\)-electrons DOS projected on \(\phi_1\) and \(\phi_2\) orbitals are also presented).

The electronic structure obtained in our LSDA+U calculation is semiconducting with a band gap of 0.5 eV. Note that the standard LSDA needs the Jahn-Teller distorted crystal structure to reproduce the non-metallic ground state. The \(e_g\) band is split by this gap into two subbands: the occupied one with the predominantly \(\phi_1\) character, and the empty one with the \(\phi_2\) character. However there is significant admixture of \(\phi_2\) in the occupied subband and \(\phi_1\) in the empty one.
After checking that our calculation scheme gives a proper orbital order in the undoped PrMnO$_3$, we applied it to Pr$_{1/2}$Ca$_{1/2}$MnO$_3$. In order to treat the experimentally observed CE-type of antiferromagnetism it was necessary to quadruple the $Pbnm$-type unit cell and the supercell had 16 formula units. The distribution of the Pr and Ca atoms in the lattice was chosen according to a model where all Pr ions have only Ca as their nearest neighbors in the lanthanide sub lattice. We did not impose any symmetry restrictions in our calculation, the integration in the reciprocal space being performed for the whole Brillouin zone, and the self-consistency iteration was started from a uniform distribution of $e_g$-electrons over both $e_g$-orbitals of all Mn atoms.

The result of the self-consistent calculation was a charge and orbital ordered insulator. The $e_g$-electron spin-density-plot calculated by eq.9 is presented in Fig.3. This is in a striking agreement with the orbital order derived in [8] from the neutron diffraction measurements (Fig.4). The unexpected result is that the total number of d-electrons at all types of Mn sites are nearly equal (4.99 and 5.01), so that formally Mn$^{4+}$ ions (in the Fig.3 the ones with symmetric in-plane density distribution) and Mn$^{3+}$ ions (the ones with the density strongly anisotropic) have nearly the same number of 3d-electrons. However the difference in the magnetic moment values is more pronounced: $3.34\mu_B$ for Mn$^{4+}$ and $3.44\mu_B$ for Mn$^{3+}$.

**IV. CONCLUSION**

The results of our LSDA+U calculations for Pr$_{1-x}$Ca$_x$MnO$_3$ demonstrate that taking into account the Coulomb interaction inside the d-shell of Mn together with the intersite hopping is enough to reproduce not only the orbital order present in the undoped manganites, but also the localization and ordering of the holes in the doped materials. Naturally the lattice relaxation (Jahn-Teller and polaron lattice distortions) will significantly renormalize the total energies, gap values, charge disproportion and magnetic moments. However it seems that the symmetry of the ordered state can be obtained without explicitly including the electron-lattice interactions. This is in clear contrast to the standard LSDA where energy
band splitting and orbital polarization appear only as results of the Jahn-Teller crystal structure distortion.

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[24] The LSDA works much better in LaMnO$_3$ and perhaps also in PrMnO$_3$ than in KCuF$_3$. In the latter case, the LSDA does not give even a stable antiferromagnetic state. However, in LaMnO$_3$ and PrMnO$_3$, the antiferromagnetic state can be obtained by LSDA. Our recent calculation (H. Sawada, et al.) for LaMnO$_3$ reproduces about 50% of the experimental Jahn-Teller distortion by the theoretical structural optimization for experimental lattice parameters.

**Figure captions**

Fig. 1. The calculated angle distribution of the $e_g\uparrow$-electron spin density in PrMnO$_3$. 
Fig. 2. The total and partial densities of states (DOS) from the result of LSDA+U calculation of PrMnO$_3$. a) Total DOS per unit cell (4 formula units); b) Partial $e_g$ DOS of Mn. Solid lines are for the $\phi_1$-projected DOS, and dashed lines for the $\phi_2$-projected DOS with $\phi_1$ and $\phi_2$-orbitals diagonalizing the occupation matrix.; c) and d) Partial DOS for two types of oxygen orbitals.

Fig. 3. The calculated angle distribution of the $e_g^\uparrow$-electron spin density in Pr$_{1/2}$Ca$_{1/2}$MnO$_3$.

Fig. 4. The scheme of the spin, charge and orbital order in Pr$_{1/2}$Ca$_{1/2}$MnO$_3$ deduced from the neutron diffractive data [8]. The open circles with the lobe of the $e_g$ electron density distribution denote Mn$^{3+}$ and the filled circles Mn$^{4+}$. The arrows denote the magnetic moments.
