Hydrostatic pressure effect on the orbital character and magnetic properties of bilayer manganites

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We have investigated theoretically the hydrostatic pressure effect on the electronic and magnetic properties of the doped bilayer manganites $La_{2-2x}Sr_{1+2x}Mn_2O_7$ ($0.30 \leqslant x \leqslant 0.48$). The key observation is the anisotropic variations of lattice parameters of the separate bilayers under the hydrostatic pressure, which in turn leads to the different changes between the intra- and interlayer hopping amplitudes of electrons and an additional energy level splitting of the two e_g orbits x^2-y^2 and $3z^2-r^2$ of Mn ions. It was found that these two factors from pressure have opposite effects on the orbital occupation properties of the system and the competition between them can cause very different behaviors depending on the doping concentrations. Our results of magnetic and orbital order variations at different doping levels are consistent with recent experiments.

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I. INTRODUCTION

In manganites, the coupling of several degrees of freedom (including spin, charge, orbital, and lattice) can result in many possible ground states which are near in energy[1–5] and thus the system is extremely sensitive to the tuning of the external parameters,[1–3,6] such as magnetic field and pressure. The interplay among these different degrees of freedom can also result in rich electronic and magnetic properties, among which colossal magnetoresistance[1,7] is of particular importance since it has numerous promising applications in magnetic sensor and memory related devices. As another example, we will investigate here the hydrostatic pressure effect[8–11] on the bilayer manganites.

Bilayer manganites[7,12–16] are characterized by their intrinsic double-layered structures and these manganite bilayers are weakly coupled through insulating rocksalt-type rare-earth and alkaline-earth ion oxide layers,[14–16] which makes the motion of their carriers highly anisotropic and nearly two dimensional (2D). As is known,[12–14,16,17] the separate bilayers are the essential units of the bilayer manganites and are decisive to the system properties. Recently, the properties of the prototypical bilayer manganites $La_{2-2x}Sr_{1+2x}Mn_2O_7$ (LSMO-327)[7,12,14] have been intensively studied in experiments. At the doping concentration $x=0.48$, it was reported in Ref. 8 that under the application of a hydrostatic pressure, the orbital state changed from planarlike to a three-dimensional (3D) fluctuating state, and at the same time, the magnetic order changed from antiferromagnetic (AF) to ferromagnetic (F) between the two layers of a single bilayer; on the other hand, at a lower doping $x=0.30$, earlier study[9] showed that the hydrostatic pressure made the sample more 2D like.

In this paper, we will extend our previous model on the $LaMnO_3$ (Ref. 18) to study the hydrostatic pressure effect on the LSMO-327 systems in order to provide a mechanism which can explain the two experiments consistently. The exchange interaction between two neighboring bilayers is much weaker than the intrabilayer one;[16,19] thus, we can solve the system properties in a single bilayer. Due to the intrinsic anisotropy in the layered structures of LSMO-327,[14,15] the application of an isotropic hydrostatic pressure[8,9,20,21] on the system can lead to anisotropic lattice parameter variations, i.e., the planar (layer plane) lattice size changes little, whereas in the perpendicular direction (z axis) the lattice parameter has a considerable variation. This, in turn, gives rise to two competing consequences with regard to the electron occupation among the two e_g orbits of Mn ions. The first is the relative change between the intralayer and interlayer hopping energies of electrons within the single bilayer.[8] The second is an additional energy level splitting between the two e_g orbits[20] like the Jahn-Teller effect due to the decrease of octahedra symmetry. Taking these two ingredients into account on the same foot, our self-consistent mean field calculations show that for the $x=0.48$ system, the magnetic coupling between the two layers changes from AF to F with the increase of the pressure. Meanwhile, the occupation number of the $3z^2-r^2$ orbit increases, while that of the x^2-y^2 orbit decreases with the pressure increasing. These are both in agreement with the recent experiment.[8] As is known, the transport properties of manganites are closely related to their orbital occupations[8,9,15,20] and magnetic structures.[1,22] The x^2-y^2 orbit facilitates planar transport, while the $3z^2-r^2$ orbit favors transport along the z axis. The transport is either facilitated or blocked depending on F or AF type of magnetic coupling along a certain direction. In this sense, we can relate our calculated orbital and magnetic state changes to the observed transport property changes. The result for $x=0.48$ is then also in agreement with the experimentally observed more 3D behavior[8] after pressure is applied. Under the same parameters, the result of the orbital occupation variation for $x=0.30$ is contrary to the case of $x=0.48$: the interlayer magnetic coupling remains F, which also agrees with the experimental measurement, more 2D behavior of the sample upon the application of pressure.[9]

The rest of the paper is organized as follows. In Sec. II, we introduce the lattice model and adopt a mean field method to reduce the Hamiltonian. In Sec. III, we present numerical results and discuss the pressure effect on orbital occupation and magnetic structure of LSMO-327. A brief summary is given in Sec. IV.

II. MODEL

The layer plane of LSMO-327 is labeled as the xy plane and the direction perpendicular to the layer is set as the z axis. We adopt the following Hamiltonian to describe the system:

$$H = -\sum_{i,\gamma\delta}\sum_{n=\pm x,y} t_n^{\gamma\delta}\cos\left(\frac{\theta_{i,xy}}{2}\right)(a_{i\gamma}^{\dagger}a_{i+n,\delta}+b_{i\gamma}^{\dagger}b_{i+n,\delta}) - \sum_{i,\gamma\delta} t_z^{\gamma\delta}\cos\left(\frac{\theta_{i,z}}{2}\right)(a_{i\gamma}^{\dagger}b_{i\delta}+b_{i\delta}^{\dagger}a_{i\gamma}) + \lambda\sum_{i;\alpha=a,b}(Q_{1i}^{(\alpha)}\rho_i^{(\alpha)} + Q_{2i}^{(\alpha)}\tau_{xi}^{(\alpha)} + Q_{3i}^{(\alpha)}\tau_{zi}^{(\alpha)}) + \frac{1}{2}\sum_{i;\alpha=a,b}(\beta Q_{1i}^{(\alpha)2} + Q_{2i}^{(\alpha)2} + Q_{3i}^{(\alpha)2}) + J_{AF}\sum_i \vec{S}_i^{(a)}\cdot\vec{S}_i^{(b)} + \Delta\sum_{i;\alpha=a,b}(n_{i2}^{(\alpha)} - n_{i1}^{(\alpha)}). \quad (1)$$

$a_{i\gamma}^{\dagger}$ ($a_{i\gamma}$) and $b_{i\gamma}^{\dagger}$ ($b_{i\gamma}$) denote the creation (annihilation) operators of electrons of each layer of the bilayer system, respectively, i is the site index, and γ represents one of the two e_g orbits of Mn ions, i.e., $|1\rangle=|x^2-y^2\rangle$ or $|2\rangle=|3z^2-r^2\rangle$ adopted in the paper. The first and second terms of the Hamiltonian describe the intralayer and interlayer double-exchange hopping of e_g electrons, respectively. The third and fourth terms are the static electron-phonon interaction and the lattice distortion energy, respectively. β is the ratio between the spring constants of the breathing mode and the Jahn-Teller modes and will be taken as 2 in all calculations. The fifth term accounts for the interlayer AF couplings between local t_{2g} spins. The intralayer AF couplings of local t_{2g} spins are neglected because they are of no consequences to our calculations involving only in-plane ferromagnetic couplings between the t_{2g} spins. The last term denotes the energy level splitting between the two e_g orbits induced by the hydrostatic pressure, which could be absorbed into the electron-phonon interaction part; in other words, the pressure can also give rise to a similar Jahn-Teller effect by changing the symmetry of octahedra. The magnitude of Δ varies with pressure.[20]

In the Hamiltonian above, the spin index has been suppressed by assuming the infinite Hund coupling approximation,[1,18] $J_H/t\to\infty$, and the itinerant electron spins keep parallel to the local t_{2g} spins that are reflected in the hopping term by $\theta_{i,xy(z)}$. The hopping amplitudes are written in matrix form as[1,18,23]

$$[t_{\pm x}^{\gamma\delta}] = t_1\begin{bmatrix} 1 & -1/\sqrt{3} \\ -1/\sqrt{3} & 1/3 \end{bmatrix}, \quad [t_{\pm y}^{\gamma\delta}] = t_2\begin{bmatrix} 1 & 1/\sqrt{3} \\ 1/\sqrt{3} & 1/3 \end{bmatrix}, \quad [t_{\pm z}^{\gamma\delta}] = t_3\begin{bmatrix} 0 & 0 \\ 0 & 4/3 \end{bmatrix}. \quad (2)$$

In the bilayer manganites with tetragonal lattice structure, $t_1=t_2\neq t_3$ is generally assumed in the calculation. When the external hydrostatic pressure is applied on the system, the in-plane and out-of-plane lattice parameters change differently.[8–11,20,21] According to the experimental measurements, the out-of-plane lattice parameter (c) varies more apparently than that of the in-plane ones (a and b),[8,9] so we can make an approximation by assuming that only the out-of-plane lattice parameter varies with the external pressure while the in-plane variation is neglected in our consideration, i.e., the hydrostatic pressure is nearly equivalent to a uniaxial pressure applied along the z axis in bilayer manganites.[20] $t_1=t_2$ is taken as the energy unit. The anisotropic lattice parameter variations will lead to two consequences. One is the change of t_3/t_1 and the other is the change of Δ. $\delta t=\delta t_3-\delta t_1=\delta t_3=t_3-t_3^0$ is introduced to denote the first change, the hopping energy variation, where δt_1 is zero as regards above arguments and t_3^0 denotes the hopping constant in the absence of the pressure. The relationship between the bare hopping amplitudes and the lattice parameters in transition metal compounds is known as[24] $t_i\sim 1/a_i^{3.5}$, where a_i is the lattice parameter along the hopping direction associated with t_i. When the hydrostatic pressure is applied to make the lattice parameter along the z axis more shorter, the variation $\delta t>0$, Δ accounts for the additional energy level splitting between the two e_g orbits arising from the local MnO_6 octahedra deformations, the orbit x^2-y^2 is more favorable than the orbit $3z^2-r^2$ for electron occupancy,[24] and then $\Delta>0$.[20] It is assumed that $\Delta=\xi\delta t$ ($\xi>0$), which can be regarded as keeping only the leading lowest order term of an polynomial expansion of Δ in terms of the small parameter δt. This term can also be rewritten as $\Delta=\xi(t_3-t_1)+\xi(t_1-t_3^0)$, where the second term $\xi(t_1-t_3^0)$ depending on the specific material[15,25] corresponds to a constant shift between the two orbits. It only slightly influences the initial orbital occupation numbers and has little effect on the pressure behavior of the materials, so we can neglect it and take $\Delta\simeq\xi(t_3-t_1)$ in our following calculations.

Employing a mean field approximation[1,18] to the static electron-phonon interaction and lattice distortion parts of Eq. (1), we obtain

$$H_{MF} = -\sum_{i,\gamma\delta}\sum_{n=\pm x,y} t_n^{\gamma\delta}\cos\left(\frac{\theta_{i,xy}}{2}\right)(a_{i\gamma}^{\dagger}a_{i+n,\delta}+b_{i\gamma}^{\dagger}b_{i+n,\delta}) - \sum_{i,\gamma\delta} t_z^{\gamma\delta}\cos\left(\frac{\theta_{i,z}}{2}\right)(a_{i\gamma}^{\dagger}b_{i\delta}+b_{i\delta}^{\dagger}a_{i\gamma}) - \lambda^2\sum_{i,\alpha}\left(\frac{\langle\rho_i^{(\alpha)}\rangle\rho_i^{(\alpha)}}{\beta} + \langle\tau_{xi}^{(\alpha)}\rangle\tau_{xi}^{(\alpha)} + \langle\tau_{zi}^{(\alpha)}\rangle\tau_{zi}^{(\alpha)}\right) + \frac{\lambda^2}{2}\sum_{i,\alpha}\left(\frac{\langle\rho_i^{(\alpha)}\rangle^2}{\beta} + \langle\tau_{xi}^{(\alpha)}\rangle^2 + \langle\tau_{zi}^{(\alpha)}\rangle^2\right) + J_{AF}\sum_i \vec{S}_i^{(a)}\cdot\vec{S}_i^{(b)} + \xi(t_3-t_1)\sum_{i;\alpha=a,b}(n_{i2}^{(\alpha)} - n_{i1}^{(\alpha)}). \quad (3)$$

Then, the Fourier transformation of the e_g electron part is performed and the calculation can proceed in the wave-vector space as in Ref. 18; several mean field parameters need to be computed in a self-consistent manner to determine the mean field ground state of the system. Two magnetic configurations, AF and F magnetic couplings between the two F layers inside a single bilayer, are taken into account in our self-consistent calculations.

III. RESULTS AND DISCUSSION

In the same series of materials, such as LSMO-327 for different doping concentrations, the same model parameters are generally taken. According to the classification of manganites in terms of their bandwidths,[1] LSMO-327 is a typical wide bandwidth manganite which is accounted for by a big t_1 in our model. So, in terms of t_1, both the electron-phonon coupling and the antiferromagnetic coupling between t_{2g} spins should be small. Here, we adopt $\lambda^2/t_1=1$ and $J_{AF}S^2/t_1=0.112$, referring to earlier works.[1,18] ξ is tuned to produce the correct behaviors for our systems and is taken as 0.63 for LSMO-327. From low-temperature experimental observation $d(t_3/t_1)/dP>0$,[8,9] t_3/t_1 and P (pressure) have the same trend of variation and the former parameter can somewhat reflect qualitatively the pressure effect.

The orbital occupation variations presented in this paper are in the case of F-type interlayer magnetic coupling between the two ferromagnetic planes of the single bilayer. It is clear in Fig. 1(a) that for $x=0.48$ with the increase of t_3/t_1 (increase of pressure P), the occupation number of the x^2-y^2 orbit decreases, while that of the $3z^2-r^2$ orbit increases. The x^2-y^2 orbit is lying in the xy plane, while the $3z^2-r^2$ orbit is distributed mainly along the z axis. So, the charge density transfers from intralayer to interlayer in the bilayer system, which agrees with the experimental result[8] from the maximum entropy method analysis on the synchrotron radiation x-ray powder data. In Fig. 1(b), the magnetic coupling between the two ferromagnetic layers will change from AF type to F type at $\sim t_3/t_1=1.08$, which is in agreement with the experimental observation.[8,24]

In perovskite manganites, the transport properties are strongly influenced by the e_g-orbital state and the magnetic structure.[15,20,22,26] Usually, the x^2-y^2 orbit facilitates conduction in the xy plane,[20] while the $3z^2-r^2$ orbit favors conduction along the z direction.[8] The electron conduction along a certain direction is either blocked or facilitated depending on the AF or F type of t_{2g} local spin arrangement in that direction, which has been taken into account by the double-exchange mechanism.[1,22] In the $x=0.48$ system, it is clear from our calculations that the pressure can lead to both a change from AF to F coupling between the two F layers and a more $3z^2-r^2$-like orbital character, so that the hopping of the e_g electrons along the z direction is enhanced as well as the 3D character of system.[8] In the light of this connection, we have also calculated the orbital occupation variation for the $x=0.30$ system, as shown in Fig. 1(a). With the increase of pressure (t_3/t_1), the orbital character of the $x=0.30$ system, will become more x^2-y^2-like; however, the magnetic coupling between the two layers will remain F as shown in Fig. 1(c). These two factors will imply a more 2D conduction of the material while at the same time keeping the basic characters of the conduction invariant with pressure, which are both in qualitative agreement with the experiment.[9] With these results, it is natural to expect the existence of some doping level between 0.48 and 0.30 at which neither $3z^2-r^2$ nor x^2-y^2 character is enhanced by the application of pressure. The intermediate doping concentration is found to be about 0.38, the orbital occupation variation of which is also shown in Fig. 1(a).

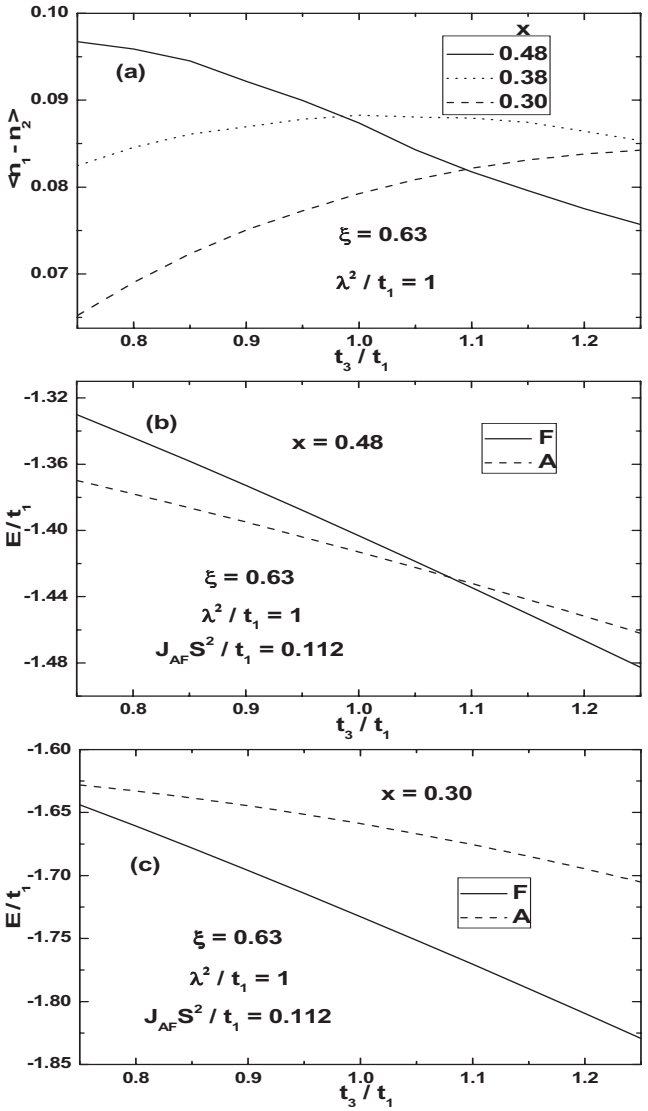

FIG. 1. (a) Occupation number differences of the two e_g orbits as a function of t_3/t_1 (P) for doping concentrations at $x=0.48$, 0.38, and 0.30 under the given parameters. The variations of the averaged single site energies of the states with AF and F magnetic couplings between the two F layers as a function of t_3/t_1 (P) for $x=0.48$ and $x=0.30$ are shown in (b) and (c), respectively.

The above different orbital occupation variation behaviors at different doping concentrations can be understood qualitatively as follows. With the increase of t_3/t_1 (or equivalently the pressure), the difference in hopping energies will favor the $3z^2-r^2$ orbit, while the energy level splitting term will favor the x^2-y^2 orbit. In LSMO-327, with the doping concentration increasing, the carrier density and hence the double-exchange hopping of e_g electrons increase as well, and the influence of the difference in hopping energies enhances. On the other hand, the influence of the energy level splitting term proportional to the e_g electron density decreases with the increase of the doping concentration. So, the $3z^2-r^2$ orbit will be more favored by pressure as compared to the x^2-y^2 orbit at higher doping concentration for the same material series. This is what the experiments[8,9,11] and our calculations indicate.

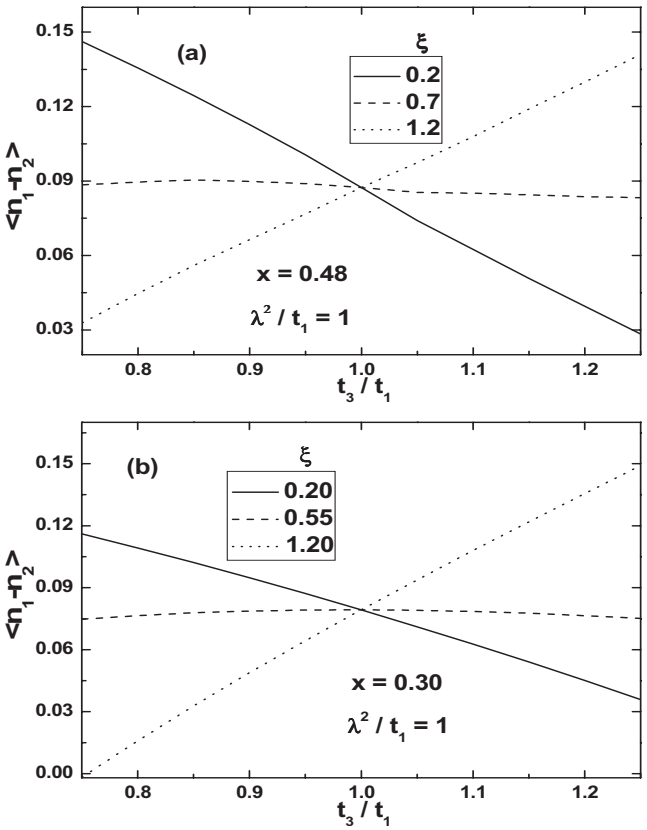

FIG. 2. Different possible pressure induced behaviors of the orbital occupation difference corresponding to the same doping concentration but for different ξ at (a) $x=0.48$ and (b) $x=0.30$.

We now turn to discuss by varying ξ the effect of changing the relative strength of the two factors introduced by the anisotropic lattice parameter changes under pressure. Three typical behaviors for $x=0.48$ and $x=0.30$ under $\lambda^2/t_1=1$ are shown in Figs. 2(a) and 2(b), respectively. As is shown, even for the same doping concentration, widely different behaviors can happen depending on the different choices of ξ. In Fig. 2, only when $0.55<\xi<0.7$ can the opposite behaviors in orbital occupations occur upon the application of pressure for different doping between 0.30 and 0.48. Because ξ is introduced as a material specific parameter, it should change when substitutions of the rare-earth ions (e.g., Nd for La) or alkaline-earth ions (e.g., Ca for Sr) are made.[4,6,10,26] Because Δ arises from local deformations of the MnO_6 octahedrons, it should change little with the introduction of the above substitutions. From earlier studies, the bandwidth or equivalently the hopping amplitudes (e.g., t_1) generally decrease with such substitutions.[1] The increase of ξ with substitutions such as Nd for La or Ca for Sr is thus expected. Because the orbital occupation variation is dominated by ξ, no qualitative change occurs when incorporating changes in other parameters. In this sense, we can relate the results in Fig. 2 with the changes from one material series to another. Comparing with the discussion on LSMO-327, we could expect the increase of the intermediate doping concentration separating different orbital variation behaviors of a certain material series compared with LSMO-327, and hence the possible existence of one or several material series in which the application of pressure always makes the material more 2D-like in the whole range of x between 0.30 and 0.48. The magnetic Compton scattering[27,28] experiments which can directly measure the orbital occupancy of manganites can be used to check our predictions. For this purpose, the earlier experiments[27,28] performed at zero pressure should be extended to measure the orbital occupation variations with pressure.

Though our calculations are restricted to the bilayer manganites, we believe that our mechanism can be extended to apply to other similar systems. The essential point of our mechanism is the competition of two factors arising from the intrinsic anisotropy of the layered structure. Thus, the pressure effects in other transition metal oxides with similar layered structures should also be explainable within our mechanism.

IV. SUMMARY

In summary, we have established a consistent theoretical framework for the hydrostatic pressure tuning of the orbital character and magnetic states in the bilayer manganites. We have shown that the anisotropic lattice parameter changes are essential to the problem. They can induce both a difference between intralayer and interlayer hopping amplitudes as well as an energy level splitting of the two e_g orbits. The two factors compete with each other when pressure increases. Different pressure induced behaviors are shown to appear with both the change of doping concentration and the change of relative strength of the two factors. Comparison with experiments shows qualitative agreement.

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