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Charge order and phase segregation in overdoped bilayer manganites

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Abstract

There have been recent reports of charge ordering around $x = 0.5$ in the bilayer manganites like $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$. At $x = 0.5$, there appears to be a coexistence region of layered A-type antiferromagnetic order and charge order. There are also reports of orbital order in this region without any Jahn–Teller effect. Based on physical grounds, this region is investigated from a model that incorporates the two e_g orbitals at each Mn site and a near-neighbour Coulomb repulsion. It is shown that there indeed both charge and orbital order close to the half-doped region coincident with a layered magnetic structure. Although the orbital order is known to drive the magnetic order, the layered magnetic structure is also favoured in this system by the lack of coherent transport across the planes and the reduced dimensionality of the lattice. The anisotropic hopping across the e_g orbitals and the underlying layered structure largely determine the orbital arrangements in this region, while the charge order is primarily due to the long-range interactions.

1. Introduction

Bilayer manganites such as $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$, the $n = 2$ member of the Ruddelsden–Popper series $(\text{R}, \text{A})_{n+1}\text{Mn}_n\text{O}_{3n+1}$ (where R and A are rare-earth and alkaline-earth ions, respectively), show [1] a distinct lack of symmetry in the nature of their ground states across $x = 0.5$ just as their 3D counterparts. These systems have started drawing attention after colossal magnetoresistance (CMR) has been reported in them [2]. These layered systems not only show large magnetoresistance and a sequence of magnetic phases [3, 4]; they are very rich in their charge, magnetic and orbital structures. Most of the studies in the bilayer system so far have focused on the Mn^{3+} richer region of $x < 0.5$. The Mn^{4+} -rich region ($x > 0.5$) is now being explored carefully both experimentally [1, 5, 6] and theoretically [7, 8], and a

succession of magnetic phases $A \rightarrow C \rightarrow G$ has been confirmed. The situation very close to and around $x = 0.5$ is somewhat poorly understood at present. It emerged recently that there is a coexistence between the charge ordered and layered A-type spin ordered state [5, 9] there, giving way to C-type (or its polytype [1]) magnetic order at larger Mn^{4+} concentration. Both A-type (ferromagnetic (FM) layers coupled antiferromagnetically) and C-type (ferromagnetic chains coupled antiferromagnetically) phases have been found to be orbitally ordered [1, 10].

There are strong indications from several experimental groups that, at and around $x = 0.5$, a charge ordered state coexists with an A-type antiferromagnetic (AFM) phase. Both neutron scattering [11, 12] and muon spin rotation corroborate this view. A discontinuity in the muon precession frequency at $x = 0.52$ has been observed by Coldea *et al* [5]. Recently Wilkins *et al* [13] have reported that although there is clear evidence of both charge and orbital order in $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ at $x = 0.5$, there is no detectable signature for any Jahn–Teller (JT) distortion in their resonant x-ray diffraction study. JT distortion of the MnO_6 octahedra begins to appear beyond $x = 0.55$ [6]. There is, though, a reasonably large (tetragonal) static distortion—the crystallographic c/a ratio reaches a minimum [1] around the same composition, enhancing the AF super-exchange along the c direction. This is expected to favour the A-type spin order in that region. Unlike in the 3D manganites, there is no significant buckling of the bonds during distortion.

It is now generally believed that the various magnetic structures owe their origin to a large degree to the underlying orbital order [7, 14]. Models have been proposed [15, 16] for the manganites that incorporate the e_g orbitals and the anisotropic hopping between them. The use of such models to the bilayer manganites (like $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$) has only had limited success [8] though; the A-phase is overestimated owing to the low dimensionality of the lattice. A much improved magnetic and orbital phase diagram was later obtained [7] from a model that included the JT distortion as well as the proper choice of orbital degrees of freedom. The A-type AFM instability is indeed quite strong in the layered system [1], extending from $x = 0.42$ to 0.66 and at low temperatures. The FM region of the phase diagram of some of the 3D manganites around $x = 0.5$ is absent here, taken over by the A-type AFM phase. Having only two layers separated by large distance from the adjoining bilayer in the c -direction impedes a long-range charge transport in that direction leading to stronger AFM correlations along the c -direction thereby contributing to an enhanced A-type instability. Beyond $x = 0.66$, it is replaced by C-type (and its polytype) order. The A and C phases are orbitally ordered and there is a connection between the preferred orbital order and the observed magnetic order.

However, the presence of charge order and its relation to the underlying magnetic phases have not been investigated in any of the previous theoretical studies [7, 8] in bilayer systems. The question of charge order and possible phase separation in the overdoped bilayer systems, therefore, still remains an open issue with increasing evidence in favour of such coexistence coming from the experiments. We attempt to address it in the following, starting from a model that incorporates the essential physical attributes of this region.

2. The model

A quite general model for the bilayer manganites has been used [7] to delineate the different orbital and magnetic structures for $x > 0.5$. It incorporates the degenerate e_g manifold and the physics of double exchange (DE) along with electron–electron interactions. This model can be adapted to investigate the charge order by including a longer-range Coulomb term in the interaction part. Such a term has been known [21, 22] to give rise to coexisting charge ordered state in the 3D manganites at $x = 0.5$.

$$H = J_{\text{AF}} \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j - J_{\text{H}} \sum_i \mathbf{S}_i \cdot \mathbf{s}_i - \sum_{\langle ij \rangle \sigma, \alpha, \beta} t_{i,j}^{\alpha\beta} c_{i,\alpha,\sigma}^\dagger c_{j,\beta,\sigma} + H_{\text{int}}. \quad (1)$$

As usual, the charge and spin dynamics of the conventional DE model [19] operate here too, with additional degrees of freedom coming from the degenerate e_g orbitals (α, β stand for the e_g orbitals) and hopping across them, which is determined by their symmetry. In the reasonably large Hund's coupling limit, which is relevant for the studies on manganites, the DE mechanism implies that an electron can hop onto a site if core spins at that site (as well as the spin of any e_g electron there) are parallel to its spin. Mobility reduces drastically with increasing J_H if they are antiparallel. In equation (1) \mathbf{S}_i and \mathbf{s}_i are the t_{2g} and e_g spins at site i and J_H and J_{AF} are the Hund and super-exchange (SE) coupling, respectively. $H_{\text{int}} = U' \sum_{i\sigma\sigma'} \hat{n}_{i1\sigma} \hat{n}_{i2\sigma'} + V \sum_i \hat{n}_i \hat{n}_j$ contains the on-site inter-orbital and the near-neighbour Coulomb repulsion term. The intra-orbital term can be ignored as J_H in manganites is fairly large, preventing double occupancy in any given Mn 3d orbital [17]. The exchange interaction between two bilayers is known to be at least 100 times weaker [18] than the intra-bilayer exchange. Two bilayers are also well separated in a unit cell and intervened by the rare-earth ions. One can, therefore, use only one bilayer for a reasonable description of the system [8]. In general, in manganites, there is a strong JT coupling and that is included in the Hamiltonian. As we mentioned above, in the bilayer systems (e.g. in $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$), the JT coupling is weak and does not play a major role [6, 13] in the region $x < 0.6$. In the absence of electron-lattice coupling, the kinetic energy (KE) of electrons in the e_g band and the Hund's coupling between t_{2g} and e_g spins compete with the antiferromagnetic SE interaction, leading to a variety of magnetic and orbital structures. Considering that there are two e_g orbitals, the nominal band filling is $\frac{1-x}{4}$.

Typical values of the interaction and band parameters for the bilayer systems are in the same range as in the 3D manganites. As in their 3D counterparts, the Hund coupling and Coulomb correlations are the largest scale of energy [17] in the problem. We neglect the inter-orbital Coulomb term in the following discussion of charge order. The inter-orbital Coulomb term does not have strong effect in the doping range x less than or around 0.5, primarily because of the low filling $((1-x)/4)$ making two orbitals at the same site less likely to be occupied simultaneously. As we see below, the magnetic order also prefers preferential occupancies in one of the two e_g orbitals in both A and C phases and the U' term only enhances that (discussed later).

Treating the t_{2g} spins semiclassically [19], the SE contribution to the ground state energy becomes $E_{\text{SE}} = \frac{J_{\text{AF}} S_0^2}{2} (2 \cos \theta_{xy} + \cos \theta_z)$, where θ_{xy} and θ_z are the angles between the near-neighbour t_{2g} spins in the xy plane and z -direction respectively. In the ferromagnetic state, $\theta_{xy} = \theta_z = 0$, while in the A phase $\theta_{xy} = 0$ and $\theta_z = \pi$.

In the limit of infinite J_H , the e_g electron quantization axis at each site i is rotated in the local coordinate frame to make it parallel to \mathbf{S}_i . This is accomplished quite easily by the spin-1/2 rotation matrix $\exp(i\frac{\phi_i}{2}\sigma_z) \exp(i\frac{\theta_i}{2}\sigma_y) \exp(-i\frac{\phi_i}{2}\sigma_z)$ operating on a two-component spinor. Allowing the core spins at each site to cant in the xz -plane and neglecting the phase term (the Berry phase) appearing from the transformation, it is straightforward to show [19] that the effective hopping matrix elements are $t_{xy} = t \cos(\theta_{xy}/2)$ and $t_z = t \cos(\theta_z/2)$. In this level of approximation, the diagonalization of the KE part of H reduces to solving the 2×2 matrix equation $|\epsilon_{\alpha\beta} - \omega \delta_{\alpha\beta}| = 0$ for a system of spinless fermions. The matrix elements are obtained from the standard table of overlap integrals [20] involving $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals on neighbouring sites of a square lattice, and the dispersions are

$$\begin{aligned} \epsilon_{11} &= -2t_{xy}(\cos k_x + \cos k_y) \\ \epsilon_{12} = t_{21} &= -\frac{2}{\sqrt{3}}t_{xy}(\cos k_x - \cos k_y) \\ \epsilon_{22} &= -\frac{2}{3}t_{xy}(\cos k_x + \cos k_y) - \frac{8}{3}t_z \cos k_z. \end{aligned}$$

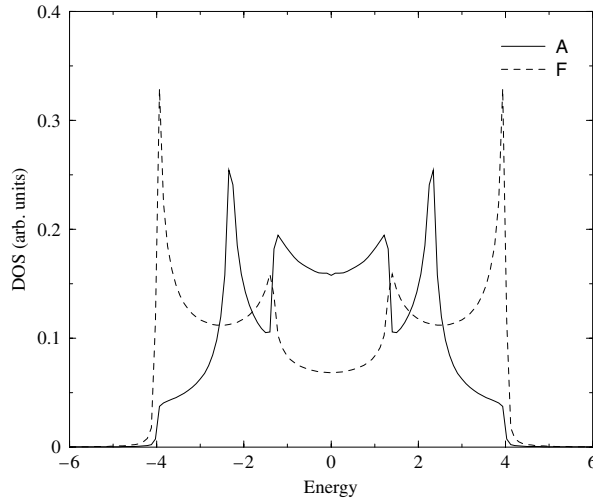


Figure 1. Density of states in pure FM and A phase.

Using the form of t_{xy} and t_z in terms of θ_{xy} and θ_z in the $J_H \rightarrow \infty$ approximation, the two energy bands are obtained by the diagonalization of the above matrix. In the uncanted A and C phases, the dispersions for A and C phases become two and one dimensional, respectively. In the pure FM phase, the density of states (DOS) is three dimensional. However, in the bilayer system, owing to the absence of dispersion in the z -direction, the DOS in both the FM and A phases shows two-dimensional character, as shown in figure 1. There being only two k -points in the z -direction, the DOS for the C phase has two delta functions centred at $\pm \frac{8t_z}{3}$. In all the calculations that follow, all energies are measured in terms of the overlap between the $d_{3z^2-r^2}$ orbitals along the z -direction $t^z = t$, which has a typical value about 0.25 eV in manganites.

3. Charge and orbital ordering

In order to look for charge ordering in the bilayer manganites, we treat the nearest-neighbour Coulomb interaction $V \sum_{\langle ij \rangle} \hat{n}_i \hat{n}_j$ in the mean-field approximation, $\langle \hat{n}_i \rangle = n + C_0 \exp(iQ \cdot r_i)$, where C_0 is the charge order parameter and n is the average number of electrons per site. We take the usual staggered ordering $Q = (\pi, \pi, \pi)$. The charge order parameter C_0 is then calculated self-consistently. The mean-field approximation is known to work quite well [8, 16, 17] for the ground state properties in the manganites. In the infinite J_H limit, the electronic part of the Hamiltonian is a 4×4 matrix $\sum_{\mathbf{k}, \alpha\beta} \epsilon_{\mathbf{k}\alpha\beta} \tilde{c}_{\mathbf{k}\alpha}^\dagger \tilde{c}_{\mathbf{k}\beta} - \Delta \sum_{\mathbf{k}, \alpha} \tilde{c}_{\mathbf{k}\alpha}^\dagger \tilde{c}_{\mathbf{k}+\mathbf{Q}\alpha}$ (where \tilde{c} represents the locally rotated e_g electron operators described earlier), and this is diagonalized at each of the \mathbf{k} points on a momentum grid.

The bands obtained thereof are filled up to a chemical potential and the order parameter $\Delta = zVC_0$ (z is the number of nearest neighbours) calculated along with the filling. The process is repeated until self-consistency is achieved as is customary in the mean-field theory. Charge order (CO) is indeed observed in a region $x \geq 0.5$ when V reaches a critical value, similar to the 3D manganites [21, 22]. But unlike in the 3D case, we do not observe any FM phase coexisting with the CO in this region. As reported in previous work [8, 23], A-phase instability is quite strong in the layered manganites owing to the 2D structure of its DOS, and even for $V = 0$, there is no F phase for $x \geq 0.5$ [7]. The A–CO coexistence region extends in a region above $x = 0.5$ (discussed later). In this limit of infinite J_H , the value of V for

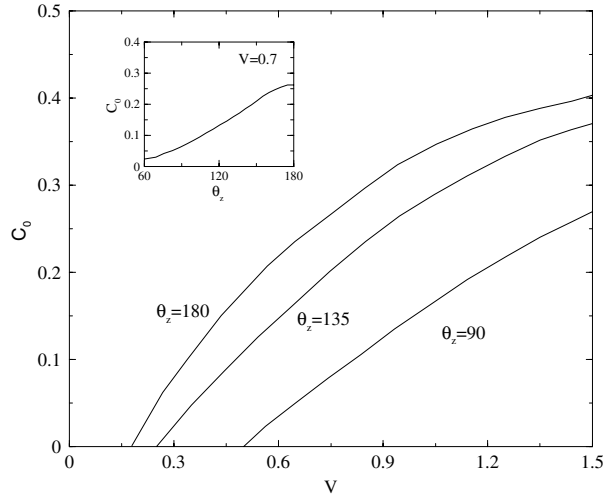


Figure 2. Charge order parameter as a function of V for three different angles θ_z in the limit $J_H \rightarrow \infty$. In the inset is shown the variation of charge order parameter with θ_z for a fixed $V = 0.7$.

which the CO phase appears depends strongly on the canting angle θ_z away from the A phase (towards an FM phase). In figure 2 is shown the dependence of the CO order parameter on V at three different angles ($\theta_z = 180^\circ$ being the pure A phase). The inset shows how C_0 varies with canting at a typical $V = 0.7$. In the infinite Hund's coupling limit, the only way an electron gains KE in an AF configuration of background spins is via the canting of them [24], thereby generating an effective non-zero hopping across. This has been observed [16] in the 3D manganites as well close to its G-C phase boundary (for $x \simeq 1$). As we observe here, a CO phase does not coexist with an F phase (which is energetically unfavourable to an A phase in this region) and therefore the increased canting requires larger V to bring about the charge ordering. At a fixed V , therefore, the CO order parameter reduces with increased canting away from A phase.

The appropriate limit for any of the manganites is, of course, a large but finite value of the Hund's coupling as is generally believed. In this limit, we can treat the core spins semi-classically again, and the spin degrees of freedom for the e_g electrons are reintroduced. In order to take care of this, the second term in the Hamiltonian (1) would have to be treated now in various possible ground states. We choose $\mathbf{S}_i = \mathbf{S}_0 \exp(i\mathbf{q} \cdot \mathbf{r}_i)$ to represent a homogeneous spin configuration, where \mathbf{q} determines different spin arrangements for the t_{2g} spins [21]. The second term in equation (1) becomes $-J_H S_0 \sum_{\mathbf{k}\alpha\sigma} \sigma c_{\mathbf{k}\alpha\sigma}^\dagger c_{\mathbf{k}+\mathbf{q}\alpha\sigma}$. The near-neighbour Coulomb term is treated in the mean-field approximation as above. In this semi-classical approximation for the t_{2g} spins the Hamiltonian (1) reduces, then, to a 16×16 matrix [21] at each \mathbf{k} point.

This mean-field Hamiltonian is again diagonalized at each \mathbf{k} -point on the momentum grid. The ground state energy is calculated for different magnetic structures. The CO order parameter is also determined self-consistently. Four different magnetic structures are relevant for the experimental phase diagram (with q values in the parentheses): A-type $(0, 0, \pi)$, the usual C-phase $(\pi, \pi, 0)$, with FM chains along the c -direction, and the 3D AFM G-type (π, π, π) . There is also the C'-type polytype structure [1, 7], with $\mathbf{q} = (\pi, 0, \pi)$. This is same as a C-type, only its FM ordering is along the y -direction as reported by Ling *et al.* The magnetic structure with minimum ground state energy and the CO order parameter are determined for each set of parameters (x, J_H, J_{AF}) for the range of doping $(0.5 < x \leq 1)$.

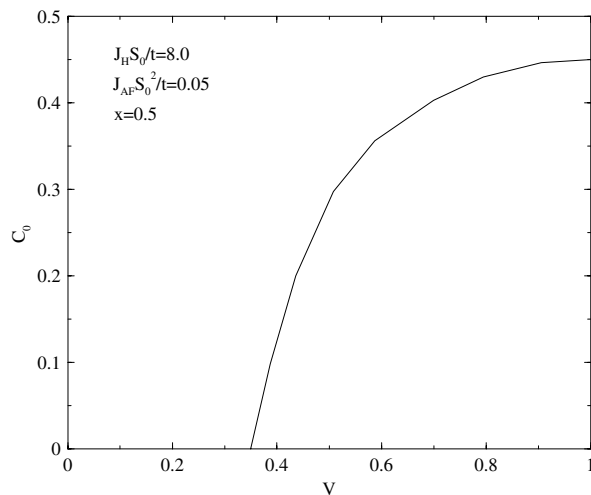


Figure 3. Charge order parameter as a function of V at $x = 0.5$.

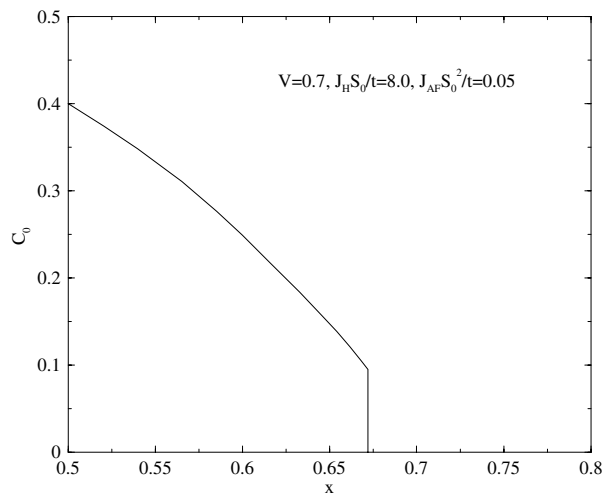


Figure 4. Variation of charge order as x is changed from 0.5 for a fixed $V = 0.7$. The jump in the order parameter indicates the A-CO to A boundary.

Charge order is observed in the region $0.67 > x \geq 0.5$. Figure 3 shows the CO order parameter as a function of V for $x = 0.5$. The underlying spin order in this region is found to be A-type, and there is an A-CO to A transition at around $x = 0.67$ for $V = 0.7$. There is a jump in the CO order parameter as a function of x , shown in figure 4, indicating a first-order transition. The coexistence region of CO and A is a manifestation of this first-order transition. Based on the observed variation of these different charge and spin ordered states, we obtained a phase diagram in the x - J_H plane for $V = 0.7$.

The observed phase diagram, shown in figure 5, is markedly similar to the one obtained by Ling and co-workers. In addition it also has the charge ordered phase coexisting with the A phase in the region close to $x = 0.5$. As reported by Coldea *et al* [5], there is indeed a

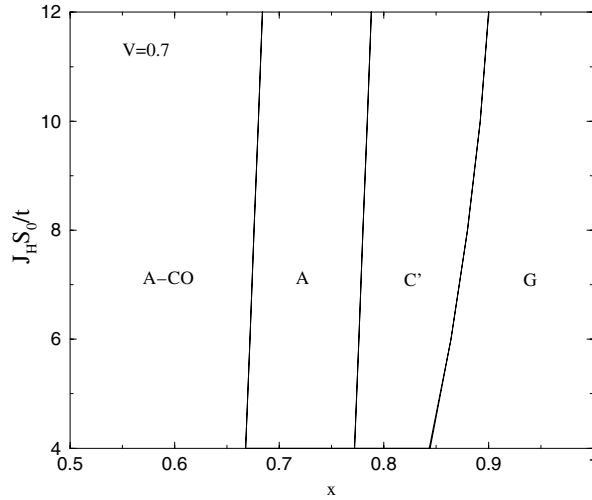


Figure 5. Phase diagram, in the $J_H S_0$ versus filling x plane. The terms A, C', G, CO, etc are explained in the text.

region of A–CO coexistence between $x = 0.5$ and 0.65 . We note that we have also tried a charge order with wavevector $\mathbf{Q} = (\pi, \pi, 0)$ instead of the fully staggered one and observed that energetically it is very close to the staggered one. This is primarily due to the absence of coherent charge transport in the c -direction making a charge uniform state in that direction nearly degenerate with a charge ordered one. We note in passing that we did not observe the well known CE phase [25] in our calculation, even at $x = 0.5$. This is similar to the findings in the $V = 0$ case studied earlier [7, 8]. The region of no long-range-order (LRO) just above the A–CO coexistence reported by both Ling *et al* and Coldea *et al* is beyond the scope of the treatments here. It is at this point useful to note that a region of two-phase coexistence is not very stable against long-range Coulomb interactions, and in real systems one would probably observe a microscopically phase-separated mixture of one phase in another. The region of no LRO could well be such a region, around the A–CO to A transition, and with the competing C' phase energetically very close by.

In the absence of CO the phases A and C' are both orbitally ordered [1, 7], and we look for this in the presence of the near-neighbour Coulomb term also. We do indeed find very similar orbital occupancies here too. There is a predominant occupancy in the $d_{x^2-y^2}$ orbital over the $d_{3z^2-r^2}$ orbital, indicating orbital ordering. The occupancies in the two orbitals add up to the total electron density ($\frac{1-x}{4}$). In figure 6(a) the corresponding orbital occupancies are shown as a function of filling. The orbitally ordered state is shown in the adjacent figure 6(b). The effect of charge ordering is seen to be small (figure 6(a)), reducing the orbital order (measured, for example, by the imbalance in the orbital occupancies) in the A–CO phase from its value in the absence of CO. There is no effect in orbital occupancies at the A–CO to A boundary: they smoothly continue into the pure A phase. The presence of orbital order here is not contingent upon the underlying lattice distortion or JT effects. This conforms to the recent observation of Wilkins *et al* [13] that, even without JT distortion, there is a pronounced orbital order. In the region of C' phase, the orbital order is identical (predominantly $d_{3y^2-r^2}$ over $d_{z^2-x^2}$) to the one reported earlier [7] for the undistorted bilayer system and is not shown here. We have looked into the effect of an inter-orbital repulsion term on the phase diagram and charge ordering and, except for a slight enhancement of the orbital order, found it to have little effect on the

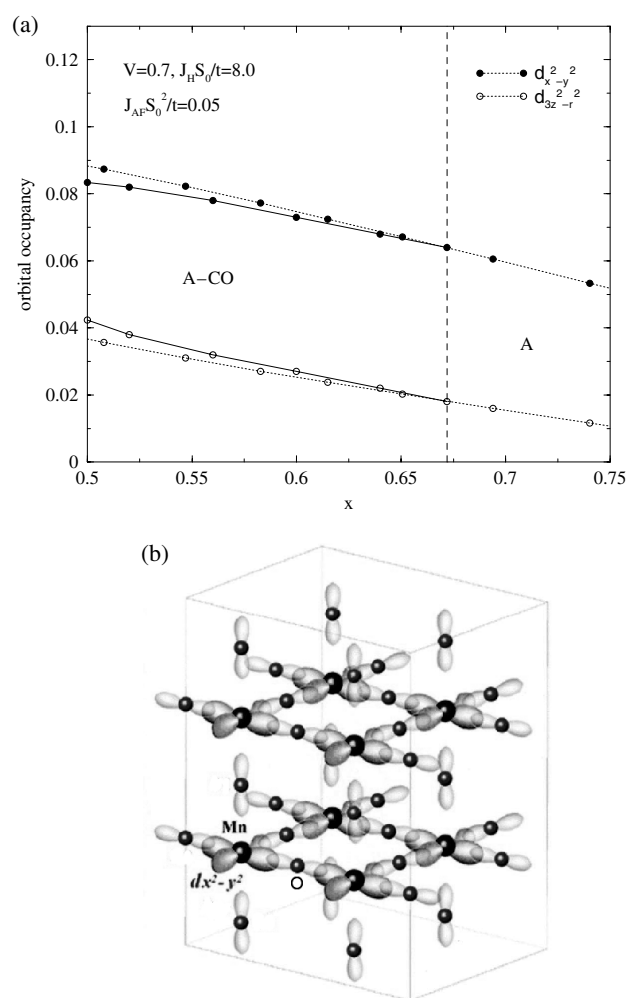


Figure 6. (a) Orbital occupancies in the A-CO and A phases. The upper curves are for $d_{x^2-y^2}$ while the lower ones are for the $d_{3z^2-r^2}$ orbitals. The occupancies add up to the electron density $\frac{1-x}{4}$. The dotted lines are for comparison with $V = 0$ situation where no CO is present. (b) The corresponding planar Mn $d_{x^2-y^2}$ order in the bilayer manganites is shown along with the O atoms with their $2p_\sigma$ orbitals bridging the Mn orbitals.

phase diagram. The intra-orbital Coulomb term is known to have very little effect [17] in the mean-field theory in the region of large J_H , and we have not considered it in the above.

4. Conclusion

Motivated by the observation of charge ordering in the region $x \geq 0.5$ in the bilayer systems, we have investigated it with a model that has been quite useful in understanding the overdoped manganites. We find the charge order from our calculation in the same region where it has been seen experimentally. There is also a region of phase separation abutting the experimentally observed no long-range order region. We observe orbital order even in the absence of JT

distortion as reported recently in the same region of doping. It would be interesting to see more experiments on the region of no long-range order in the phase diagram. The possibility of canting of spins is yet not ruled out, and we have seen trends for it for very large Hund's coupling in our calculations.

Acknowledgments

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