Orbital ordering in LaMnO$_3$: Electron-lattice versus electron-electron interactions

Wei-Guo Yin, Dmitri Volja, and Wei Ku

1 Physics Department, Brookhaven National Laboratory, Upton, NY 11973
2 Physics Department, State University of New York, Stony Brook, NY 11790

(Dated: Received September 2, 2005)

The relative importance of electron-lattice (e-l) and electron-electron (e-e) interactions in ordering orbitals in LaMnO$_3$ is systematically examined within the LDA+$U$ approximation of density functional theory. A realistic effective Hamiltonian is derived from novel Wannier state analysis of the electronic structure. Surprisingly, e-l interaction ($\simeq 0.9$ eV) alone is found insufficient to stabilize the orbital ordered state. On the other hand, e-e interaction ($\simeq 1.7$ eV) not only induces orbital ordering, but also greatly facilitates the Jahn-Teller distortion via enhanced localization. Further experimental means to quantify the competition between these two mechanisms are proposed.

PACS numbers: 75.47.Lx, 71.70.-d, 71.70.Ej, 75.30.Fv

Study of perovskite manganites has been one of the main focuses of recent research in condensed matter physics, not only because of their great potentials in technological applications related to colossal magnetoresistance (CMR) in La$_{1-x}$Ca$_x$MnO$_3$, but also because these strongly correlated electron materials (SCEM) are ideally instrumental to the understanding of the complex interplay of the charge, spin, orbital, and lattice degrees of freedom that leads to abundant fascinating phenomena, including long range order in all the above channels [1].

The unusual orbital degree of freedom in the manganites, which is the focus of our study, originates from the singly occupied degenerate $e_g$ states ($d_{z^2}$ and $d_{x^2-y^2}$) of the Mn$^{3+}$ 3d electrons in the high-spin configuration ($t_{2g}^3e_g^1$) due to the ligand-field splitting and strong Hund’s coupling. This orbital degeneracy makes the Mn$^{3+}$ ion Jahn-Teller (JT) active: the degeneracy can be split via biaxial distortion of the surrounding oxygen octahedron.

Currently, one of the critical questions on the manganites is the interplay of electron-lattice (e-l) and e-e electron-electron (e-e) interactions [2, 3, 4, 5, 6, 7, 8]. Indeed, carrier mobility [3] and magnetism [2, 5], both essential to the unresolved mechanism of CMR in the manganites [9, 10, 11, 12], respond to these two interactions in a substantially different manner (despite some other aspects [2] reacting similarly). However, even for the simplest parent compound, LaMnO$_3$ (which presents prototype orbital order (OO) and strongest JT-distortion in the family), various spectral measurements to date [13, 14, 15, 16, 17, 18] have left two possible mechanisms of the OO in dispute: the cooperative JT e-l effect [16] and the e-e superexchange effect [20]. To our knowledge, there is no clear experimental evidence to support one over the other, due to lack of “signatures” in distinguishing these two mechanisms. This leads to great confusions in the field: for example, whether a new type of elementary excitations called orbiton has been observed in Raman scattering spectroscopy [17, 18], and more generally which interaction dominates localization of the $e_g$ electrons and thus facilitates the CMR effects upon doping LaMnO$_3$ [4, 11]. It is thus important and timely to discern the real roles of e-l and e-e interactions.

In this Letter, the electronic structure of the prototype LaMnO$_3$ is systematically analyzed, aiming to quantify the relative importance of e-e and e-l interactions in ordering the orbitals. A realistic effective Hamiltonian for the low energy $e_g$ states is derived from a novel Wannier function-based scheme for general SCEM, with the key effective e-e interaction $U_{ee} \simeq 1.7$ eV, JT splitting $\Delta_\text{JT} \simeq 0.9$ eV, and octahedral-tilting induced tetragonal crystal field $E_\text{G} \simeq 0.12$ eV. Surprisingly, e-l interaction alone is found insufficient to stabilize OO. On the other hand, e-e interaction not only induces OO, but also greatly facilitates the JT distortion by strongly localizing the electrons. The present results provide new insight into OO in LaMnO$_3$, and place stringent constraints on any realistic theories of excitations and CMR in the manganites. Furthermore, our analysis indicates certain competition between mechanisms, allowing direct experimental determination of their relative strengths.

Aiming at a careful determination of the relevant mechanisms without assuming a particular dominant interaction, the following novel three-step scheme designed for general SCEM is employed, with each step leading to additional insights into essential interactions and more accurate evaluation of their strengths: (i) A systematic analysis of the electronic structure within the LDA+$U$ method [22, 23] against various constraints (e.g.: lattice distortion), giving a rough estimate of the relevant e-l and e-e effects; (ii) Construction of the low-energy Wannier states [14, 21], leading to signatures of competition between e-l and e-e interactions, additional tetragonal field effects, and a local representation of the LDA+$U$ Hamiltonian, $H^{\text{LDA}+U}$; (iii) Determination of the effective many-body Hamiltonian via a self-consistent mapping to $H^{\text{LDA}+U}$, providing a quantitative evaluation of the interactions and deep microscopic insights.

(i) Analysis of the LDA+$U$ results. The results of our systematic study of the electronic structure of LaMnO$_3$ are summarized in Fig. 1 where the total energy gain per
formulation (f.u.), $E_{JT}$, as a function of cooperative JT distortion vectors $Q_i$ (defined in the caption) is shown for a wide range of $U$ \cite{22,24}. Notice that for realistic $U = 8$ eV, the crystal structure is stabilized at $Q^* = 0.4$ Å [Fig. 4(a)] and $\theta_Q = 109^\circ$ [Fig. 4(b)], in excellent agreement with experiments \cite{27}, supporting the good quality of the LDA+U approximation for this system.

Surprisingly, e-I interaction alone is found insufficient to stabilize the orbital ordered insulating phase: for $U = 0$ eV, the system stabilizes in a metallic state at $Q = Q^*$ with small $E_{JT} = -27$ meV, despite being weakly insulating at $Q = Q^*$ with a small gap of 0.1 eV \cite{22}. On the other hand, $E_{JT}$ dramatically increases in magnitude to $-215$ meV as $U$ increases to 8 eV, indicating that the electron localization induced by the e-e interaction greatly facilitates the JT instability—in fact, OO can be stabilized even without JT distortion \cite{22}. Indeed, as shown in Fig. 4(a), fitting the data points to the JT picture ($E_{JT} \simeq -\frac{1}{2} g Q + \frac{1}{2} K Q^2$ \cite{13}) is excellent for $U > 4$ eV but unsatisfactory for small $U$, suggesting that only with $U > 4$ eV the $e_g$ electrons are well localized as assumed in the JT picture. For realistic $U = 8$ eV, the JT splitting ($\sim 4E_{JT}$ at $Q^*$) is thus $\Delta_{JT} \sim 0.9$ eV, comparable to $\sim 0.8$ eV extrapolated from spectral ellipsometry \cite{13,16}.

It is extremely important to distinguish carefully the JT distortion from other lattice distortions, namely octahedral tilting and its associated octahedral distortion of GdFeO$_3$-type. The latter is found negligible in LaMnO$_3$, as our study of LaFeO$_3$ (a JT-inactive counterpart of LaMnO$_3$ \cite{26}) produces negligible octahedral distortion with total energy gain of merely $-3$ meV. In contrast, octahedral tilting is found to give large energy gain of $-403$ meV/f.u. Clearly, a correct assessment of $E_{JT}$ should exclude such a JT-distortion-unrelated contribution. Therefore, our systematic study was performed with the experimental octahedral tilting angle ($\phi_{tilt}=16^\circ$, nearly unchanged upon JT distortion \cite{22,27}).

In addition to localizing $e_g$ states, e-e interaction plays other crucial roles, as clearly demonstrated in the LDA+U (8 eV) band structure (Fig. 2 left panel): The $\sim 2.6$ eV splitting between the spin-majority occupied and unoccupied $e_g$ bands near the Fermi energy is too large to be accounted for with the estimated JT splitting ($\sim 0.9$ eV), indicating an effective on-site repulsion $U_{eff} \sim 1.7$ eV. Note that the $U_{eff}$ relevant to OO is to be distinguished from the “bare” $U$ acting between atomic Mn 3$d$ states, as $U_{eff}$ acts only between the low-energy $e_g$ Wannier states (WSs, discussed below), and thus includes effects of additional screening and slight delocalization via hybridization that weaken the “bare” repulsion. Also note that the considerable amount of $e_g$-character near the bottom of the oxygen 2$p$ bands ($[-8,-6]$ eV) is not very relevant to OO, as such feature has its origin in strong hybridization with the oxygen 2$p$ orbitals, independent of ordering of the orbitals. Though it does imply the charge-transfer nature of the manganites in general.

(ii) Construction of WSs. To proceed with more quantitative evaluation of the above effects and to identify other relevant mechanisms, a well-defined local (Wannier) representation of the low-energy $e_g$ states is necessary for further theoretical formulation. To this end, our previously developed energy-resolved symmetry-specific WS construction \cite{14,21} is extended to allow mixed symmetry with a constraint search for maximal localization \cite{29}. The resulting orbital ordered occupied ($[-2.5,0]$ eV) and unoccupied WSs ($[0,2.5]$ eV) are illustrated in Fig. 2 (middle panel), from which the staggered ordering of the orbitals is apparent, as well as the considerable weight at the oxygen sites due to strong p-d hybridization. Also given in Fig. 2 are band dispersions (solid lines) corresponding to these WSs, obtained by diagonalizing the
This competition makes \( \theta \) was confirmed by our LDA+ above transformation between the above two sets of WSs, \( \sum_{i} n_{i}^\uparrow n_{i}^\downarrow \) with experimental \( \theta \) relative importance of leading mechanisms for OO. As it will become more apparent with \( g \) is the JT coupling constant and \( K(Q) = \frac{g}{2} \sum_{i} T_{i} \cdot B_{i} + E_{0} \). Here the effective field \( B_{i} = (B_{i}^x, B_{i}^y) \). \( B_{i}^z = 2U_{\text{eff}}(T_{i}^z) + E_{z}^Q \), where \( B_{i}^z = 2U_{\text{eff}}(T_{i}^z) + gQ_{i}^z \), and \( B_{i}^\pm = \pm \sqrt{2} gQ_{i}^x \). \( B_{i}^\pm \) with \( (T_{i}^z) = T_{i}^x \) and \( (T_{i}^x) = e^{iQ_{i}^x}T_{i}^x \). Remarkably, even \( \Theta \) favors \( \theta_{Q} = 0 \) instead. Notice also from Fig. 3(a) that \( \Theta \) grows as \( Q \) increases, reflecting a sizeable e-I interaction. Nevertheless, even at optimal (experimental) \( Q \), \( \Theta \) is still way below \( \theta_{Q} \), confirming that the JT effect is far from being dominant.

(iii) Mapping the Effective Hamiltonian. Based on the above systematic analysis, the concrete physics of the low-energy spin-majority \( e_{g} \) states can be described by an effective Hamiltonian including \( U_{\text{eff}}, \Delta_{\text{JT}} \), and \( E_{z} \):

\[
\begin{align*}
H_{\text{eff}} &= \sum_{(ij)} t_{ij}^\gamma d_{ij}^\gamma d_{ij}^{\gamma^\prime} + U_{\text{eff}} \sum_{i} n_{i}^\uparrow n_{i}^\downarrow + \sum_{i} T_{i} \cdot B_{i} + E_{0}.
\end{align*}
\]

where \( \gamma \) and \( \gamma^\prime \) refer to the conventional WSs, denoting \( | \uparrow \rangle = |3z^2-r^2 \rangle \) and \( | \downarrow \rangle = |y^2-x^2 \rangle \), and \( t_{ij}^\gamma = \frac{3t}{4} \), \( t_{ij}^{\gamma^\prime} = \frac{t}{4} \), and \( t_{ij}^{\gamma} = t_{ij}^{\gamma^\prime} = \frac{3t}{4} \) (the \( \pm \) sign distinguishes hopping along the \( x \) and \( y \) directions), while out-of-plane hoppings are strongly suppressed in the A-type antiferromagnetic ground state due to the double-exchange effect. To properly map out these parameters from the LDA+ results, an unambiguous approach is developed in this study. Employing the fact that strong local e-e interaction is approximated in LDA+ in an effective HF manner, a proper connection can be made on the same WS basis by matching \( H_{i=1}^{\text{LDA+}} \) with the self-consistent HF expression of \( H_{\text{eff}} \)
TABLE I: Contribution of the energy terms in Eq. (2) to $\Delta_0$ and $\Delta_{Q^*}$ (see text), in unit of meV per formula unit.

| Term | Total | $U_{\text{eff}}$ | $g$ | $K$ | $E_{\text{res}}$ | $t$ |
|------|-------|-----------------|----|----|----------------|----|
| $\Delta_0$ | −50 | −173 | 0 | 0 | −9 | 132 |
| $\Delta_{Q^*}$ | −215 | −129 | −356 | 96 | 16 | 158 |

as $\Delta_{Q^*}$ (second row), consists of considerable further contribution from e-e interaction (−129 meV). Without the e-e interaction, the JT coupling (−356 meV) alone is insufficient to overcome the energy cost of lattice (96 meV) and kinetic (290 meV) energy. That is, e-e interaction, whose contribution is enhanced due to increased JT coupling, serves as a hidden driving force for octahedral distortion. Overall, $U_{\text{eff}}$ is more important to OO in LaMnO$_3$ than the JT coupling, while their effects on cooperative octahedral distortion are comparable.

The present results place stringent constraints on any realistic theories of the manganites and interpretations of their excitation spectra, for example, current controversy on the recently observed 120 − 160 meV Raman shifts of incident photons resonant at $E_{\text{res}} \simeq 2$ eV [12, 13]. On the one hand, the excitations were interpreted as orbital waves, or ‘orbitons’, derived from the pseudo-spin superexchange model in the large $U_{\text{eff}}$ limit of Eq. (2). With the orbiton spectrum gap $\sim 2.5J_{\text{orb}} + \Delta_{\text{JT}}$ [3, 4, 30] and superexchange coupling constant $J_{\text{orb}} \simeq 40−50$ meV ($\propto \alpha^2/\langle Q \rangle$), this scenario requires small $\Delta_{\text{JT}} \lesssim 50$ meV [14, 15]. On the other hand, in the JT scenario the Raman shifts were attributed to two-phonon processes (single phonon frequency $\sim 60−80$ meV) induced by a phonon assisted on-site $d^4 \rightarrow d^3$ transition, requiring large $\Delta_{\text{JT}} \simeq E_{\text{res}} \simeq 2$ eV [14, 15]. In contrast, our quantitative results ($\Delta_{\text{JT}} \simeq 0.9$ eV and $U_{\text{eff}} \simeq 1.7$ eV) show that the spin-majority $e_g$ states are in the intermediate e-e interaction regime with comparable JT coupling. Thus, a more reasonable picture would be two-phonon processes mediated by optically active inter-site $d^4d^1 \rightarrow d^3d^3$ transition with $E_{\text{res}} \simeq 2$ eV [14, 15]. Direct experimental verification of our results includes probing, e.g., on-site $d$-$d$ transition (−0.9 eV) via inelastic X-ray scattering, or $\theta_F$ via nuclear magnetic resonance.

In summary, we have quantified the relative importance of e-e and e-1 interactions in ordering orbitals in LaMnO$_3$ using a new theoretical approach. A realistic effective Hamiltonian resulting from this quantitative method reproduces consistently both LDA+$U$ energies and wavefunctions. Intermediate e-e interaction ($U_{\text{eff}} \simeq 1.7$ eV) is found to play a crucial role in inducing OO and localizing the electrons, which in turn enhances the JT interaction ($\Delta_{\text{JT}} \simeq 0.9$ eV) and stabilizes JT distortion. Furthermore, a clear “signature” of competition between e-e and e-1 interactions is given via the orbital mixing angle $\theta_F < \theta_Q$. Experimental means to directly clarify the relative strengths of the leading mechanisms are suggested. The developed general theoretical scheme can be applied to other strongly correlated materials.

We are grateful to P. Allen, E. Dagotto, S. Grenier, J. Hill, A. J. Millis, A. Moreo, G. Sawatzky, D. Singh, and J. Thomas for helpful discussions. W.Y. thanks M. Lufaso and P. Woodward for providing SPuDS [26] and T. Chatterji for providing structural data [27]. Brookhaven National Laboratory is supported by U.S. Department of Energy under Contract No. DE-AC02-98CH1-886. This work is partially supported by DOE-CMSN.

[1] E. Dagotto, Nanoscale Phase Separation and Colossal Magnetoresistance (Springer Series in Solid State Sciences vol. 136, Springer, 2003).
[2] T. Hotta, A. L. Malvezezi, and E. Dagotto, Phys. Rev. B 62, 9432 (2000).
[3] W.-G. Yin, H. Q. Lin, and C. D. Gong, Phys. Rev. Lett. 87, 047204 (2001).
[4] J. Bala and A. M. Oleś, Phys. Rev. B 62, R6085 (2000).
[5] M. V. Mostovoy and D. I. Khomskii, Phys. Rev. Lett. 92, 167201 (2004).
[6] K. H. Ahn and A. J. Millis, Phys. Rev. B 61, 13545 (2000).
[7] S. Okamoto, S. Ishihara, and S. Maekawa, Phys. Rev. B 65, 144403 (2002).
[8] R. Tyer, W. M. Temmerman, Z. Szotek, G. Banach, A. Svane, L. Petit, and G. A. Gehring, Europhys. Lett. 65, 519 (2004).
[9] A. J. Millis, Nature (London) 392, 147 (1998).
[10] C. M. Varma, Phys. Rev. B 54, 7328 (1996).
[11] A. S. Alexandrov, and A. M. Bratkovsky, Phys. Rev. Lett. 84, 2043 (2000).
[12] T. V. Ramakrishnan, H. R. Krishnamurthy, S. R. Hassan, and G. Venketeswara Pai, Phys. Rev. Lett. 92, 157203 (2004).
[13] Y. Murakami, J. P. Hill, D. Gibbs, M. Blume, I. Koyama, M. Tanaka, H. Kawata, T. Arima, Y. Tokura, K. Hirot, at al., Phys. Rev. Lett. 81, 582 (1998).
[14] S. Grenier, J. P. Hill, V. Kryukuhin, W. Ku, Y.-J. Kim, K. J. Thomas, S.-W. Cheong, Y. Tokura, Y. Tomioka, D. Casa, et al., Phys. Rev. Lett. 94, 047203 (2005).
[15] N. N. Kovaleva, A. V. Boris, C. Bernhard, A. Kulakov, A. Pimenov, A. M. Balbashov, G. Khaliullin, and B. Keimer, Phys. Rev. Lett. 93, 147204 (2004).
[16] R. Rauer, M. Rübbhausen, and K. Dörr, to be published.
[17] R. Krüger, B. Schulz, S. Naler, R. Rauer, B. Dufelmenn, J. Bäckström, K. H. Kim, S.-W. Cheong, V. Perebeinos, and M. Rübbhausen, Phys. Rev. Lett. 92, 097203 (2004).
[18] E. Saïtoh, S. Okamoto, K. T. Takahashi, K. Tobe, K. Yamamoto, T. Kimura, S. Ishihara, S. Maekawa, and Y. Tokura, Nature (London) 410, 180 (2001).
[19] J. Kanamori, J. Appl. Phys. 31, 14S (1960).
[20] K. Kugel and D. Khomskii, Sov. Phys. JETP 37, 725 (1973).
[21] W. Ku, H. Rosner, W. E. Pickett, and R. T. Scalettar, Phys. Rev. Lett. 89, 167204 (2002).
[22] V. I. Anisimov, F. Aryasetiawan, and A. I. Lichtenstein, J. Phys.: Condens. Matter 9, 767 (1997).
[23] LDA+$U$ ($U=8$ eV, $J=0.11U$) was shown to appropriately
describe the (\(\pi, \pi, 0\)) orbital and (0, 0, \(\pi\)) magnetic structures of LaMnO\(_3\), see I. S. Elfimov and V. I. Anisimov and G. A. Sawatzky, Phys. Rev. Lett. 82, 4264 (1999).

[24] All our LDA+U results were obtained with the linearized augmented plane wave method \[25\] for the A-type antiferromagnetic phase with experimental volume and fixed \(J=0.11U\). Hypothetic crystal structures were prepared with SPuDS \[26\].

[25] P. Blaha et al., Comput. Phys. Commun. 147, 71 (2002).
[26] M. W. Lufaso and P. M. Woodward, Acta Cryst. B 60, 10 (2004).

[27] T. Chatterji, F. Fauth, B. Ouladdiaf, P. Mandal, and B. Ghosh, Phys. Rev. B 68, 052406 (2003).
[28] W. E. Pickett and D. J. Singh, Phys. Rev. B 53, 1146 (1996).
[29] W. Ku et al., to be published.
[30] J. van den Brink, Phys. Rev. Lett. 87, 217202 (2001).
[31] P. B. Allen and V. Perebeinos, Phys. Rev. Lett. 83, 4828 (1999).