

Charge ordering in doped manganese oxides: Lattice dynamics and magnetic structure

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Based on the Hamiltonian of small polarons with strong nearest-neighbor repulsion, we have investigated the charge-ordering phenomena observed in half-doped manganites $R_{1/2}A_{1/2}MnO_3$. We have explored possible consequences of the charge-ordering phase in the half-doped manganites. First, we have studied the renormalization of the sound velocity around T_{CO} , considering the acoustic phonons coupled to the electrons participating in the charge ordering. Second, we have found an antiferromagnetic phase induced by the charge ordering, and discussed its role in connection with the specific CE-type antiferromagnetic structure observed in half-doped manganites. [S0163-1829(97)50722-3]

Since the discovery of colossal magnetoresistance (CMR) compounds $R_{1-x}A_xMnO_3$ ($R=La, Pr, Nd$; $A=Ca, Ba, Sr, Pb$),¹ there have been extensive experimental and theoretical efforts to find the origin of the anomalous magnetotransport phenomena. Despite such intense studies, however, a complete understanding of unusual physical properties in perovskite manganites is still lacking. Undoped $RMnO_3$ is an antiferromagnetic (AFM) insulator, but with carrier doping of divalent A elements in R sites, the system becomes a ferromagnetic (FM) metal with the observed CMR for $0.2 < x < 0.5$. Qualitative explanation is given by the double exchange (DE) mechanism.² At higher doping ($x \geq 0.5$), the ground state becomes again an AFM insulator.^{3,4} A phase boundary between the FM metallic and the AFM insulating ground states exists in a narrow range around $x=0.5$.⁵ In addition, another intriguing phase, the charge ordered (CO) state has been found to exist in insulating $R_{1/2}A_{1/2}MnO_3$ [$RA=LaCa$ (Ref. 6), $PrSr$ (Ref. 7), $PrCa$ (Ref. 8), $NdSr$ (Ref. 9)]. A direct evidence of the CO state is provided by the electron diffraction for $La_{1/2}Ca_{1/2}MnO_3$.¹⁰

The CO state is characterized by the real space ordering of Mn^{3+}/Mn^{4+} in mixed valent $R_{1/2}A_{1/2}MnO_3$. The CO state is expected to become stable when the repulsive Coulomb interaction between carriers dominates over the kinetic energy of carriers.¹¹ In this respect, the electron lattice of the CO state may be viewed as the generalized Wigner crystal. Furthermore, the carriers to form the CO state are believed to be manifested in some types of polarons, which arise from the strong electron-phonon interaction, possibly, the Jahn-Teller effect.¹² In fact, ordering of such polarons are occasionally observed in $3d$ transition metal oxides. The Verwey transition in Fe_3O_4 (Ref. 13) is a typical example of the real space ordering of mixed valent Fe^{2+} and Fe^{3+} species. Also the formation of a polaron lattice has been reported in $La_{2-x}Sr_xNiO_4$ ($x=1/3$ and $1/2$).¹⁴

Recently, Ramirez *et al.*⁵ observed in $La_{1-x}Ca_xMnO_3$ ($0.63 \leq x \leq 0.67$) that the CO transition is accompanied by a dramatic increase ($\geq 10\%$) in the sound velocity, implying a strong electron-phonon coupling. Another interesting aspect

of the CO state is its relevance to the observed magnetic phases. In the half-doped $LaCa$ (Refs. 6 and 10) and $PrSr$ (Ref. 7) manganites, the CO state has been realized with FM-AFM transition. On the other hand, in $PrCa$ (Ref. 8) manganites, it has been found in the paramagnetic (PM) state followed by the AFM transition thereafter. However, the common feature is that the AFM structure of the specific CE-type³ is observed in the CO state of manganites, suggesting a nontrivial effect of the CO state on the magnetic phase. The other noteworthy observation is the transport phenomena of the CO phase in the presence of the magnetic field. The high magnetic field induces the melting of the electron lattice of the CO phase to give rise to a huge negative magnetoresistance (MR).¹⁵

In this paper, we have studied the CO transition in half-doped manganites in the context of an order-disorder transition in interacting small polarons. The model seems quite plausible, in view of the fact that the transport behaviors in half-doped CMR compounds are qualitatively similar to the small polaron conduction in Fe_3O_4 .¹⁶ We have then investigated interesting physical consequences associated with the CO state. First, we have studied the CO effects on the lattice dynamics, taking into account the acoustic phonons coupled to the CO states. Second, considering the spin interaction in terms of the DE, we have studied the magnetic structure resulting from the CO state. It is found that the CO transition produces a large sound velocity renormalization around T_{CO} , and that the CO state favors the specific AFM structure apparently very similar to the CE-type AFM structure of half-doped manganites.

To describe the charge-ordering phenomena in the mixed valence systems with $Mn^{3+}:Mn^{4+}=1:1$, we start with the following Hamiltonian of repulsively interacting small polarons:

$$\mathcal{H}_c = V \sum_{\langle ij \rangle} c_i^\dagger c_i c_j^\dagger c_j + t \left\langle \cos \frac{\theta}{2} \right\rangle \sum_{\langle ij \rangle} c_i^\dagger c_j, \quad (1)$$

where $\langle ij \rangle$ denotes the nearest-neighbor pair. Here, V and t represent, respectively, the nearest-neighbor polaron interaction and the hopping parameter, both of which are renormalized by the strong electron-phonon interaction.¹⁷ As the carrier concentration increases, the interaction between carriers will play a more decisive role in the system. The second term in \mathcal{H}_c is the DE interaction with the single band, and the thermodynamic average $\langle \cos\theta/2 \rangle$ is determined by underlying spin structures. We assume that electrons are strongly trapped into small polarons so that there is no significant overlap of orbitals. Then the DE term can be treated as a small perturbation ($V \gg t \langle \cos\theta/2 \rangle$). This assumption is consistent in that the ordering of mixed valent $\text{Mn}^{3+}/\text{Mn}^{4+}$ atoms weakens the DE interaction, as the degeneracy in the ground state ($\text{Mn}^{3+}-\text{O}^{2-}-\text{Mn}^{4+}$ and $\text{Mn}^{4+}-\text{O}^{2-}-\text{Mn}^{3+}$) is lifted.¹⁸ We also consider spinless electrons, since the strong on-site interaction U (~ 10 eV) prohibits the doubly occupied states. Therefore the most important physics in our consideration is the nearest-neighbor repulsion between small polarons.

In the lowest order approximation, we can neglect the DE term in the above Hamiltonian, which then can be transformed into the spin one-half AFM Ising model,

$$\mathcal{H}_c = \frac{V}{4} \sum_{\langle ij \rangle} \sigma_i \sigma_j, \quad (2)$$

where we have used the pseudospin operator ($c_i^\dagger c_i = \frac{1}{2} + \frac{1}{2} \sigma_i$).¹⁹ The AFM transition of the above Ising model should be interpreted as the CO transition, and the sublattice magnetization $\langle \sigma_i \rangle$ will correspond to the order parameter of a given charge order-disorder transition. The spontaneous magnetization will occur below the transition temperature T_N . In the mean-field approximation, T_N is given by $zV/4$ (z : coordination number) which corresponds to the CO transition temperature T_{CO} . Thus below T_{CO} , the real space ordering of $\text{Mn}^{3+}/\text{Mn}^{4+}$ species takes place, minimizing the repulsion between localized small polarons.

Another notable thing in the original Hamiltonian, Eq. (1), is that the CO state becomes unstable when $V \leq t \langle \cos\theta/2 \rangle$. Since both V and $t \langle \cos\theta/2 \rangle$ critically depend on the spin structure and the electron-phonon interaction of the system, such a situation could happen by controlling external thermodynamic variables, e.g., magnetic field or pressure. The subtle balance between two parameters, V and $t \langle \cos\theta/2 \rangle$, will actually determine the stable ground state.²⁰ The melting of the CO state induced by the magnetic field could be understood in this framework. This part will be left for future study.

To investigate lattice dynamics near the CO transition, we consider the extended Hamiltonian \mathcal{H}_{cp} , incorporating the electron-acoustic phonon coupling,

$$\begin{aligned} \mathcal{H}_{cp} = & \frac{V}{4} \sum_{\langle ij \rangle} \sigma_i \sigma_j + \frac{1}{2} \sum_{\vec{k}} (P_{\vec{k}}^* P_{\vec{k}} + \omega_0^2(k) Q_{\vec{k}}^* Q_{\vec{k}}) \\ & + \frac{1}{\sqrt{N}} \sum_{\vec{i}} \sum_{\vec{k}} \omega_0(k) g(k) \sigma_i Q_{\vec{k}} e^{i\vec{k} \cdot \vec{R}_i}, \end{aligned} \quad (3)$$

where $P_{\vec{k}}$ and $Q_{\vec{k}}$ are the momentum and the amplitude of the local vibrational mode, and the final term represents the

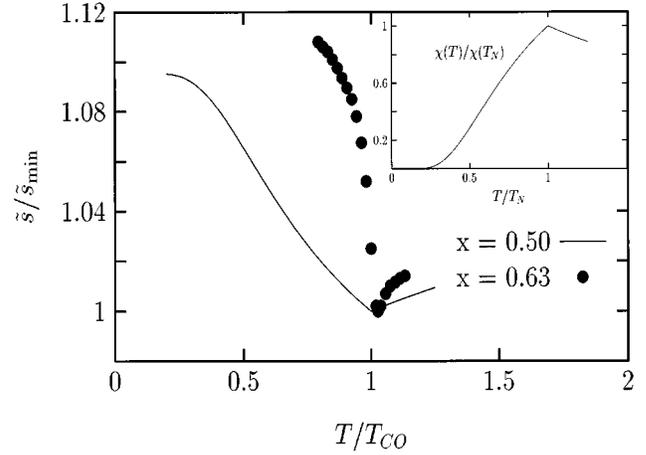


FIG. 1. The behavior of the renormalized sound velocity \tilde{s} around the charge ordering ($x=0.5$). In the inset, the AFM spin susceptibility $\chi_{\sigma\sigma}(T)$ of the Ising model is plotted. To help in understanding, the comparison of present results with those of Ramirez *et al.* ($x=0.63$) (full dots) are also provided (Ref. 5). In this plot, we used $g^2(0)=0.8z\tilde{V}$ for the parameter of the electron-phonon coupling strength.

electron-phonon interaction of local deformation type. We have adopted the pseudospin operator here too. By employing the canonical transformation, $\tilde{Q}_{\vec{k}} = Q_{\vec{k}} + [g(k)/\omega_0(k)]\sigma_{\vec{k}}$, the electron-phonon coupling term can be decoupled. Then introducing the generalized susceptibility function,¹⁹ one can obtain the following renormalized phonon frequency, $\tilde{\omega}(k) = \omega_0(k)/\sqrt{1 + g^2(k)\chi_{\sigma\sigma}(\vec{k})}$, where $\chi_{\sigma\sigma}(\vec{k})$ is an AFM spin susceptibility of the wave vector \vec{k} .

Since we are dealing with the acoustic phonon with $\omega_0(k) = sk$, the renormalized sound velocity \tilde{s} in the limit of $k \rightarrow 0$ is given by

$$\tilde{s} = s/\sqrt{1 + g^2(0)\chi_{\sigma\sigma}(T)}. \quad (4)$$

Here $\chi_{\sigma\sigma}(T)$ corresponds to the uniform AFM spin susceptibility of the Ising model with the exchange interaction $\frac{1}{4}\tilde{V} = \frac{1}{4}\sum_{\vec{k}} (V_{\vec{k}} - 2g^2(k))e^{-i\vec{k} \cdot \vec{\tau}}$ ($\vec{\tau}$: nearest-neighbor vector). Note that, as the electron-phonon coupling is turned on, the AFM Néel temperature becomes reduced to $T_N = z\tilde{V}/4 (= T_{CO})$. By using the uniform AFM spin susceptibility in the mean-field approximation,²¹ the behavior of sound velocity \tilde{s} as a function of T can be obtained (see Fig. 1). Due to a cusp maximum in the AFM susceptibility, there appears a cusp minimum in the sound velocity at T_{CO} . The sound velocity is softened smoothly above T_{CO} , but becomes substantially hardened below T_{CO} . Quite interestingly, the behavior of the above sound velocity around T_{CO} is qualitatively very similar to the observation of Ramirez *et al.*⁵ (denoted by full dots in Fig. 1) for $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($0.63 \leq x \leq 0.67$). It is noteworthy to compare the present sound velocity results with those in other charge-ordered materials such as $\text{La}_{1.67}\text{Sr}_{0.33}\text{NiO}_4$ ($T_{CO} \sim 240$ K).²² The sound velocity just near T_{CO} in this compound is very similar to the present calculation, but as T decreases far below T_{CO} , it

becomes again softened. That seems due to the residual charge hopping or other possible effects in nickelates. On the contrary, in the manganese oxides, the residual hopping is not available because the DE is suppressed by the CO.

The hardening of the sound velocity has been also reported for the low doping compound ($\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$) of the FM metallic phase below the FM transition temperature, T_C .^{5,23} But the hardenings of the sound velocity in two cases have different origins. In the low doping case, the renormalization of the sound velocity occurs due to T -dependent electron screening coming from the DE interaction, and so the hardening is enhanced by the external magnetic field which greatly influences the DE interaction.²⁴ On the contrary, in the high doping case, the present study reveals that the ordering of localized polarons is responsible for the renormalization. Accordingly, the sound velocity in the CO state will not be susceptible to the external magnetic field, because the DE interaction is not involved in the ordering and the accompanying renormalization. It is thus expected that the behavior of the sound velocity under the magnetic field would be very different between two cases. Different behaviors for the above two cases were indeed observed in the experiment of Ramirez *et al.*⁵ Meanwhile, the stronger magnetic field will destabilize the CO state and definitely modify the behavior of the sound velocity in the CO state, which needs further experimental investigations.

Now let us examine the magnetic structure in the CO state. Collecting relevant spin interactions, we have

$$\mathcal{H}_m = V \sum_{\langle ij \rangle} n_i n_j + t \sum_{\langle ij \rangle} \cos \frac{\theta_{ij}}{2} c_i^\dagger c_j + J_s \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (5)$$

where the last term is the AFM superexchange between local spins. Although the DE interaction does not contribute to realizing the CO state, it is the lowest order in the local spin interaction which yields a direct connection between the spin and the CO ordering. One can get the coupling between e_g electrons and t_{2g} local spins by expressing the DE, $\mathcal{H}_{DE} \approx (t/\sqrt{2}) \sum_{\langle ij \rangle} (1 + \mathbf{S}_i \cdot \mathbf{S}_j / 2S^2) c_i^\dagger c_j$. This approximation will be valid when T is not too close to 0 K.²⁵ Then by using the mean-field approximation; $\mathcal{H}_{DE} \approx (t/2\sqrt{2}S^2) \sum_{\langle ij \rangle} \langle c_i^\dagger c_j \rangle \mathbf{S}_i \cdot \mathbf{S}_j$, one can study effects of electron orderings on the local spins.²⁶

Defining $J' = (t/2\sqrt{2}S^2) \langle c_i^\dagger c_{i+\vec{\tau}} \rangle$ ($\vec{\tau} = \pm a\hat{x}, \pm a\hat{y}, \pm a\hat{z}$) as the spin exchange coming from \mathcal{H}_{DE} , we investigate how differently the exchange J' behaves between the disordered (uniform) phase and the ordered phase (CO). The exchange J'_1 in the disordered phase ($T > T_{CO}$) corresponds to $(t/2\sqrt{2}S^2)(1/N) \sum_{\vec{k}} \langle c_k^\dagger c_{\vec{k}} \rangle e^{i\vec{k} \cdot \vec{\tau}}$ (N : number of sites), which is nothing but the conventional FM interaction coming from the DE. The situation, however, becomes quite distinct in the ordered phase ($T < T_{CO}$). Below T_{CO} , the charge modulation starts to occur as a result of the CO, and so one can express $\langle c_i^\dagger c_{i+\vec{\tau}} \rangle$ as

$$\begin{aligned} \langle c_i^\dagger c_{i+\vec{\tau}} \rangle &= \frac{1}{N} \sum_{\vec{k}} \langle c_k^\dagger c_{\vec{k}} \rangle e^{i\vec{k} \cdot \vec{\tau}} \\ &+ \frac{1}{N} \sum_{\vec{Q} \in \Lambda} \sum_{\vec{k}} \langle c_k^\dagger c_{\vec{k}+\vec{Q}} \rangle e^{i\vec{k} \cdot \vec{\tau}} e^{i\vec{Q} \cdot \vec{R}_i} e^{i\vec{Q} \cdot \vec{\tau}}, \quad (6) \end{aligned}$$

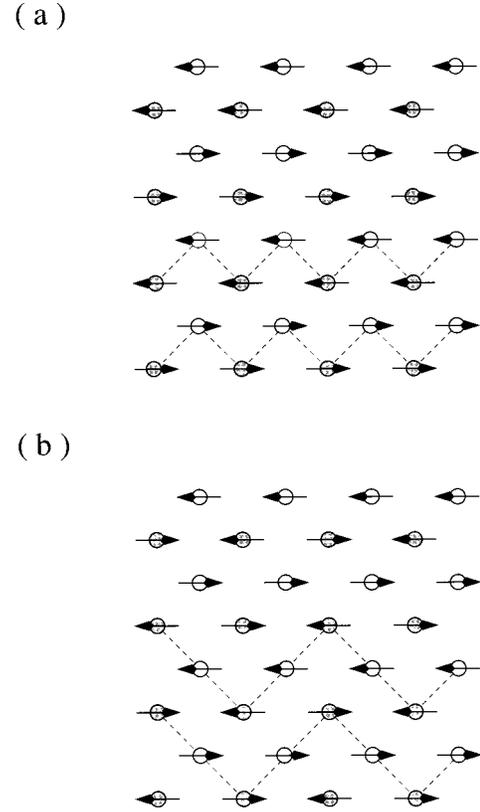


FIG. 2. (a) The AFM spin structure (a - b plane) induced by the additional exchange J'_2 in the CO phase. White and grey circles denote Mn^{3+} and Mn^{4+} , respectively. (b) The real spin ground state (CE-type) observed in the half-doped manganites (Ref. 3). In both cases, the spin structures are given by zig-zag shaped ferromagnetic chains coupled antiferromagnetically.

where the second term results from the CO state, and $\langle c_k^\dagger c_{\vec{k}+\vec{Q}} \rangle$ is related to the CO order parameter with the charge modulation vector \vec{Q} . If the carriers in the CO phase are located in every other sites, the vector \vec{Q} belongs to the set of $\Lambda = \{(\pi/a)(\pm 1, \pm 1, \pm 1)\}$. As a result, the exchange J' is given by $J' = J'_1 + J'_2$ with

$$J'_2 = -\frac{t}{2\sqrt{2}S^2} \frac{1}{N} \left[\sum_{\vec{Q} \in \Lambda} \sum_{\vec{k}} \langle c_k^\dagger c_{\vec{k}+\vec{Q}} \rangle e^{i\vec{k} \cdot \vec{\tau}} \right] e^{i\vec{Q} \cdot \vec{R}_i}, \quad (7)$$

for a given $\vec{\tau}$ ($e^{i\vec{Q} \cdot \vec{\tau}} = -1$) and the lattice site vector $\vec{R}_i = a(l\hat{x} + m\hat{y} + n\hat{z})$. Note that J'_2 gives the AFM exchange interaction. The strength of J'_2 in the CO phase is expected to be comparable to those of J'_1 and J_s , because J'_2 is somehow related to the order parameter $\langle \sigma_i \rangle$ which increases rapidly below T_{CO} . The phase factor $e^{i\vec{Q} \cdot \vec{R}_i} (= e^{i\pi(l+m+n)})$ in the spin exchange J'_2 of Eq. (7) is of particular interest, because it gives rise to an unusual AFM spin structure. Even though the explicit value of J'_2 is hard to evaluate, the schematic spin structure arising from J'_2 can be obtained as in Fig. 2(a) which shows the structure in a - b plane. It is seen that the spin structure is rather complicated with zig-zag shaped ferromagnetic chains which are mutually coupled in an antiferromagnetic way. Most remarkable is that this spin structure

is very similar to the real spin structure of CE-type AFM [see Fig. 2(b)] observed in half-doped manganites.³ This comparison illustrates that the AFM exchange (J'_2) induced by the CO may be essential in realizing the CE-type spin structure through the competition with other exchanges such as the FM-DE (J'_1), and the already existing AFM superexchange ($J_s \sim 10$ meV).

The above arguments reflect that the DE interaction still plays an essential role in the magnetism of the highly doped manganites, and in this manner, one can understand consistently magnetic properties of both metallic FM states ($0.2 < x < 0.5$) and the AFM ordered electron lattices ($x \geq 0.5$) within the same framework. Finally it should be pointed out that the CO transition is likely to be accompanied by the orbital ordering and the lattice distortion.¹⁸ The latter phenomenon can be described in the present scheme by following the procedure by Bari.²⁷ The former, however, is not considered in the present model, since the nondegenerate single band is assumed for the DE interaction. Nonetheless, the orbital ordering may play an important role in determining the observed magnetic structure.^{18,28} A generalized

model including both the charge-ordering and the orbital-ordering interaction will certainly provide a more realistic magnetic structure.

To summarize, we have described the CO phase in $R_{1/2}A_{1/2}MnO_3$ in the context of the order-disorder transition of repulsively interacting small polarons. We have found that the drastic renormalization of the sound velocity in the CO transition arises from the strong coupling of acoustic phonons to the CO states. Further, we have found interesting implications of the effect of the CO state on the magnetic structure, which may be essential for the observed specific CE-type AFM structure in the CO phase of half-doped manganites.

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