Reentrant charge ordering caused by polaron formation

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Based on a two-dimensional extended Hubbard model with electron-phonon interaction, we have studied the effect of polaron formation on the charge ordering (CO) transition. It is found that for fully ferromagnetically ordered spins the CO state may go through a process of appearance, collapse and reappearance with decreasing temperature. This is entirely due to a temperature-dependent polaron bandwidth. On the other hand, when a paramagnetic spin state is considered, only a simple reentrant behavior of the CO transition is found, which is only partly due to polaron effect. This model is proposed as an explanation of the observed reentrant behavior of the CO transition in the layered manganite LaSr$_2$Mn$_2$O$_7$.

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Electron crystallization was first proposed by Wigner, who considered an electron system in a uniform positive density. It was pointed out that at sufficiently low densities the Coulomb energy of electrons dominates their kinetic energy and then the electrons form a lattice. Such a Wigner lattice is experimentally realized in semiconductor heterostructures.[1]

Wigner’s scenario is also important for solids[2]. Electron or hole crystallization, i.e., charge ordering (CO) is extensively observed in real materials, even at high densities. The Verwey transition in magnetite Fe$_3$O$_4$ is a typical example of a real space ordering of Fe$^{2+}$/Fe$^{3+}$ species[3]. Furthermore hole ordering is found in rare-earth pnictides like Yb$^{3+}$As$_3$ because of intrinsic small hybridization between Yb-4f and As-4p orbitals[4,5]. The compound α’-NaV$_2$O$_5$ which was originally proposed as another inorganic spin-Peierls material is now known to have a CO of V$^{4+}$/V$^{5+}$ at 34K[6]. CO also appears in a variety of colossal magnetoresistance manganites, e.g., in La$_{1-x}$Ca$_x$MnO$_3$ for $x \geq 0.5$[7]. In all the above examples, only one CO transition is observed.

Recently, a melting of the CO state on decreasing the temperature, i.e., reentrant behavior, has been observed in layered manganite LaSr$_2$Mn$_2$O$_7$ by electron and x-ray diffraction[8]. It was proposed that a CO state exists characterized by superlattice reflections appearing at $\sim 210$K, but collapsing again below 100K. Subsequently, more precise measurements have found that surprisingly the superlattice intensities start growing again below about 50K meaning the reappearance of the CO state at lower temperatures[9]. That is to say, in the whole temperature region the CO state goes through a process of appearance, disappearance and reappearance.

It is the purpose of this letter to propose a mechanism which can explain this intricate behaviour. It is known that the essence of CO transition is competition of the inter-site Coulomb energy and kinetic energy of electrons. Therefore a tempting idea is to invoke a temperature-dependent electron bandwidth such that the kinetic energy is small compared to the Coulomb energy at some temperatures (favoring CO state), but dominates at other temperatures (favoring homogeneous state). Such a mechanism can be realized by including electron-phonon interaction, i.e., considering polaron formation since the effective hopping of a polaron is drastically affected by the number of thermally excited phonons. Indeed there is a lot of evidence for polaron formation in manganite materials, for example in La$_{1.2}$Sr$_{1.8}$Mn$_2$O$_7$[10]. Very recently, small polaron ordering was directly observed in the CO phases in La(Ca)MnO$_3$ and Pr(Ca)MnO$_3$[11]. Theoretically the CO transition has already been studied within the polaron context[2], but more profound physics has been ignored. This will be addressed in the following. Rather than directly discussing material aspects we focus on a general interesting problem: how is the CO transition itself affected by a simultaneous polaron formation? The inherent evolution of the ordered polaron state with temperature is presented and rich reentrant behavior is found.

Our model is described by the following Hamiltonian in a two-dimensional square lattice:

$$H = -t \sum_{i,\delta,\sigma} (c_{i+\delta,\sigma}^\dagger c_{i,\sigma} + h.c.) + U \sum_i n_{i\uparrow} n_{i\downarrow} + V_1 \sum_i n_{i\uparrow} n_{i+\delta\downarrow} + V_2 \sum_{i,\eta} n_{i\eta} n_{i+\delta\eta} + J \sum_{i,\delta} (u_{i,\delta} n_{i+\delta\downarrow} - n_{i\downarrow}) + \sum_{i,\delta} \left( \frac{p_{i,\delta}^2}{2m} + \frac{1}{2} m \omega^2 u_{i,\delta}^2 \right),$$

where $c_{i,\sigma}^\dagger (c_{i,\sigma})$ denotes creation (annihilation) operator for an electron at site $i$ with spin $\sigma$, $n_i$ is defined as $n_i = n_{i\uparrow} + n_{i\downarrow}$ with $n_{i\sigma} = c_{i,\sigma}^\dagger c_{i,\sigma}$, $t$ is nearest-neighbouring hopping parameter and $U, V_1, V_2$ represent on-site, n.n. and n.n.n. Coulomb repulsion, respectively. $\delta = \vec{x}, \vec{y}$ are unit vectors along the $x$ and $y$ direction and $\eta = \vec{x} \pm \vec{y}$. The first four terms describe an extended Hubbard model. Here we consider the electron-phonon
interaction in the following way. We assume that between arbitrary two n.n. sites there exists another kind of ion, e.g., oxygen, which vibrates along the bond direction. Such a vibration will be coupled to the electron density difference of two neighboring sites, as shown in the above fifth term \[^{3}\]. Then \( m \) is the oxygen ion mass, \( \omega \) is vibration frequency, \( u_{i,\delta} \) represents the displacement of the oxygen ion located between sites \( i \) and \( i+\delta \). The vibrations have been assumed dispersionless for simplicity. Our electron-phonon coupling is not of an usual on-site form which may be used to model the coupling with the apical oxygen vibrations since experiment on layered manganese \( \text{La}_{0.25}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7 \) showed \[^{10}\] that polaronic distortions are constrained within the perovskite layers \[^{11}\]. For further discussion, we rewrite the electron-phonon interaction in the boson representation:

\[
H_{\text{e-ph}} = g \sum_{i,\delta} (b_{i,\delta} + b_{i,\delta}^\dagger)(n_{i+\delta} - n_i) + \omega \sum_{i,\delta} b_{i,\delta}^\dagger b_{i,\delta} ,
\]

where \( g = f/\sqrt{2m\omega} \). We set \( \hbar = k_B = 1 \) throughout and all energies are in units of \( K \).

The total number of sites is \( N \) and for the electron band we assume quarter-filling. We will be interested in CO with wavevector \( (1/2,1/2) \) and consider different occupancies on the two sublattices A and B of a bipartite lattice. First we treat the electron-phonon interaction with a combined Lang-Firsov (LF) transformation \( U_1 = \exp[-\sum_{i,\delta} g/\omega(b_{i,\delta} - b_{i,\delta}^\dagger)(n_{i+\delta} - n_i)] \[^{13}\] \), and squeezing transformation \( U_2 = \exp[\gamma \sum_{i,\delta} (b_{i,\delta} b_{i,\delta} - b_{i,\delta}^\dagger b_{i,\delta}^\dagger)] \) with \( \gamma \) (>0) a variational parameter \[^{16}\]. Then averaging on equilibrium phonon states \[^{17}\], we obtain the following effective electronic Hamiltonian:

\[
H_{\text{eff}} = \omega (\tau + 1/\tau) N/2 - \tilde{t} \sum_{i,\sigma}(c_{i,\sigma}^\dagger c_{i+\delta,\sigma} + \text{h.c.}) + U \sum_{i} n_{i\uparrow} n_{i\downarrow} + V_1 \sum_{i,\delta} n_{i} n_{i+\delta}
+ V_2 \sum_{i,\eta} n_{i} n_{i+\eta} - g^2/\omega \sum_{i,\delta} (n_i - n_{i+\delta})^2 ,
\]

where \( \omega = \exp(-4\gamma) \) and \( \tilde{t} = t \exp[-5\alpha \tau \coth(\omega/2T)] \) with definition of dimensionless coupling constant \( \alpha = g^2/\omega^2 \). It is obvious that electron-phonon interaction leads to two effects. One is that the bare hopping \( \tilde{t} \) is reduced to \( \tilde{t}_0 \). The narrowing effect which is largely overestimated by the LF method alone in adiabatic limit \( (\omega/\tilde{t} < < 1) \[^{18}\] \) is weakened by the squeezing effect. Our emphasis here is the fact that \( \tilde{t}_0 \) itself increases with decreasing temperature because the phonon occupation decreases until only the contribution coming from zero-point vibrations is left. Such a temperature-dependent renormalized hopping is very important for reentrance of CO transition, as will be seen later. Another effect is phonon-mediated interaction between electrons which favors CO state, as described by the last term above. In our above treatment, the equilibrium positions of vibrating oxygens have been displaced, e.g., \( \langle u_{i,\delta} \rangle \propto \langle n_i - n_{i+\delta} \rangle \), which means the oxygens will be repelled to unoccupied sites once CO forms. In the following we concentrate on the CO transition for Hamiltonian \[^{3}\]. It is complicated if we simultaneously consider charge and spin degrees of freedom. We will therefore treat only cases with explicitly given spin configuration.

First, we consider the fully ferromagnetical (FM) spin ordered case which is equivalent to the case of spinless electrons at half filling for which the Hamiltonian \[^{3}\], up to a constant, is simplified as

\[
H_{\text{eff}} = \omega (\tau + 1/\tau) N/2 - \tilde{t} \sum_{i,\delta}(c_{i,\sigma}^\dagger c_{i+\delta,\sigma} + \text{h.c.}) + (V_1 + 2\alpha \omega) \sum_{i,\delta} n_i n_{i+\delta} + V_2 \sum_{i,\eta} n_i n_{i+\eta} \]

with \( n_i = c_i^\dagger c_i \). In mean-field (MF) treatment and with the assumption \( (n_i) = 1/2 \pm x, i \in A,B \) (\( x \) represents deviation from homogeneous electron distribution), the above Hamiltonian can be diagonalized with energy bands \( \pm \varepsilon_k \)

\[
\varepsilon_k = \sqrt{\tilde{t}_0^2 + (4Vx)^2} \quad \text{with} \quad \tilde{t}_0 = 4\tilde{t} \cos k_1 \cos k_2 \left( -\pi/2 < k_1, k_2 \leq \pi/2 \right) \text{and} \quad V_1 = V_12 + 2\alpha \omega (V_12 = V_1 - V_2 > 0) \text{in the CO phase. It is easy to find that in this case the chemical potential \( \mu = 0 \) for all temperatures, see also Ref. \[^{14}\].}

Note that it is only the difference \( V_12 \) of intersite Coulomb energies that enter the quasiparticle energy. Since \( V_1 \), \( V_2 \) are well screened and of the order 0.3eV in manganites \[^{20}\] the difference \( V_12 \) as estimated from neighbour distances is of the order \( 10^3 \)K. For this reason the CO transition may occur in an observable temperature range. More precisely it is the difference of Madelung energies (with long range Coulomb interactions included) between the charge homogeneous and the CO phases that sets the scale of the transition temperature. Using the density of states for the spectrum \( \varepsilon_k \):

\[
D(\varepsilon) = \frac{N}{2\pi^2} \frac{\varepsilon}{\sqrt{\varepsilon^2 - (4Vx)^2}} K(\sqrt{1 - z^2}) ,
\]

where \( K \) is the complete elliptic function of the first kind and \( z = \sqrt{\varepsilon^2 - (4Vx)^2}/4\tilde{t} \) we finally get the following self-consistent equation for order parameter \( x \)

\[
1 = \frac{2V}{\pi^2} \int_0^1 \frac{\tanh [\sqrt{(Vx)^2/T}]}{(Vx)^2 + T} K(\sqrt{1 - z^2}) dz .
\]

It can be easily proven that this equation always has a solution with nonzero \( x \) at zero temperature no matter what are the values of parameters \( t, \alpha, V_12 \). In the current half-filled spinless case this means that the system must take on CO state at zero temperature. We will refer to this fact later on. For given initial values for \( t, V_12, \omega \) (for example, \( t = 4000, V_12 = 400, \omega = 200 \)), we give
the solution of the above equation in the phase diagram $T$ vs $\alpha$, shown in thick line of Fig. 1. The parameter $\tau$ (or $\gamma$) is determined by minimization of ground state energy of the homogeneous state. Its minor variation with parameter $\alpha$ is ignored since it does not change our qualitative results. An average value $\tau = 0.12$ is adopted.

From the phase diagram it can be clearly seen that there is an intermediate region for $\alpha$ where the system goes through a process of homogeneous state, CO state, homogeneous state and CO state with decreasing temperature. The corresponding variation of the order parameter $x$ with temperature is shown in the inset of Fig. 1 by a solid line. The physical explanation is as follows. At high temperature, the hopping is drastically reduced so that CO state is favored to appear at a relatively high temperature (It is usually quantitatively overestimated due to our simple treatment). On decreasing temperature the effective hopping increases. And most importantly, it increases so fast that its corresponding CO transition temperature decreases even faster than the temperature itself. Therefore the CO state cannot be reached any more and the system returns to the homogeneous state. However, at even lower temperature, the system is sure to recover to CO state since the ground state of the system is charge ordered, as referred above. Actually such a conclusion is strongly favored by other methods beyond MF theory [19,21]. Physically one has a half-filled band of spinless electrons with perfect nesting which has a CO instability for arbitrary small inter-site Coulomb interaction at zero temperature. In this sense it is inevitable that the system finally enters the CO state. We want to emphasize, the multiple reentrant behavior found here is entirely due to a temperature-dependent polaron bandwidth. For comparison, a hypothetical phase diagram without the temperature-dependent factor in hopping $\tilde{t}$, i.e., $\tilde{t} = t \exp(-5\alpha \tau)$ is shown as thin line in Fig. 1. Obviously no reentrance of CO happens now.

The phase diagram with its reentrant behavior is similar for different values of parameters. However it is appropriate to discuss the influence of the optical phonon frequency $\omega$. It is obvious that the renormalized hopping $\tilde{t}$ is nearly unchanged with the temperature in the region about $T < \omega/2$ since the phonons are difficult to excite. This means that the temperature-dependent effective hopping which we emphasized here is mainly observed in the region $T > \omega/2$. Therefore, roughly speaking, if we increase the frequency the reentrant region will as a whole move to higher temperatures. It should be also clearly pointed out that our temperature dependence of the effective hopping $\tilde{t}$ is not quantitatively exact. However the precise form of $\tilde{t}(T)$ is not crucial for the above reentrance behavior as has been checked [22] with a functional dependence of $\tilde{t}(T)$ less pronounced than the exponential behavior given before.

![Fig. 1](image1.png)

FIG. 1. Phase diagram $T$ vs $\alpha$ for the case of fully FM spin order with parameters $t = 4000, V_{12} = 400$, $\omega = 200$. The thin line is a hypothetical CO phase boundary for a constant $\tilde{t} = t \exp(-5\alpha \tau)$ (see text). The inset shows the temperature-dependent order parameter $x$. The dotted line, solid line, dashed line correspond to $\alpha = 0.60, 0.65, 0.68$, respectively. The multiple reentrant behavior is obvious for $\alpha = 0.65$.

Now, we discuss the case including spin and assume a paramagnetic (PM) spin state with $\langle n_{i\uparrow} \rangle = \langle n_{i\downarrow} \rangle = \langle n_i \rangle/2$. For moderate $U$ and with similar steps as before we can obtain self-consistent MF equations for the order parameter $x$ and chemical potential $\mu$:

$$1 = \frac{4V}{\pi^2} \int_0^1 \frac{1}{\sqrt{(\tau z)^2 + (V x)^2}} F_-(z) K(\sqrt{1 - z^2}) \, dz \ , \ (6)$$

$$1 = \frac{8}{\pi^2} \int_0^1 F_+(z) K(\sqrt{1 - z^2}) \, dz \ (7)$$

with functions $F_\pm(z) = 1/(1 + \exp[-(4\sqrt{(\tau z)^2+(V x)^2} + \mu)/T])^{\pm 1}/(1 + \exp[(4\sqrt{(\tau z)^2+(V x)^2} - \mu)/T])$ and the new definition $V = V_0 + 3\alpha \omega$ ($V_0 = V_{12} - U/8$). At zero temperature it is easy to obtain the condition: $V/\tilde{t} > \text{const} \approx 1.2$, under which a solution with nonzero $x$ exists. Obviously $\alpha$ must exceeds a threshold to reach CO state as long as initially $V_0 < 1.2t$. This is a major difference from the fully FM spin ordered case. The numerical solution for Eqs. (6) and (7) is summarized in the phase diagram of Fig. 1 with a thick line (we have set the same value for $\tau$ as before). Due to different zero temperature properties now only possibility of one reen-
trance is found as shown by the solid line in the inset. For comparison, we also give the hypothetical phase diagram with \( t = t \exp(-50\tau) \) by a thin line in Fig. 3. Reentrant behavior is also found. Actually, our hypothetical case is qualitatively equivalent to considering a \( T \) vs \( V_{12} \) (with fixed \( U \)) phase diagram when electron-phonon interaction is not included. Even without electron-phonon interaction, reentrant behavior is also possible in some \( V_{12} \) region in the PM spin case, see also Ref. [23]. However, the quantitative reentrant behavior is much different with and without polaron effect.

It is natural to think about a crossover between the two extreme spin cases, PM and complete FM, i.e. to consider the case of general incomplete FM spin order. Since the fully FM spin order can be considered as a limit of on-site repulsion \( U \rightarrow \infty \), such a crossover has to be treated beyond MF which will be investigated in the future. We predict that even in the intermediate case the multiple reentrant behavior is controlled by the polaron effect. The extended Hubbard model itself is expected to show at most one reentrant transition. This conjecture is obtained from an interpolation between Fig.1 and 2, see the thick and thin phase boundaries respectively.

Finally we give a possible explanation of the experimental observations in manganite LaSr\(_2\)Mn\(_2\)O\(_7\) in the context of our theory. This material is composed of MnO\(_2\) bilayers and there is one \( e_g \) electron every two manganese ions. When double-exchange mechanism is considered, the initial hopping \( t \) should be substituted by \( t(\cos(\theta/2)) \) (\( \theta \): angle between two \( t_{2g} \) spins on n.n. sites), which depends on local spin order. There is strong evidence [24] that in this material in-plane FM spin order has already been well developed within the MnO\(_2\) layers at room temperature, before it exhibits true long range order. This is also concluded from the observation of FM in-plane spin waves even at twice the 3D transition temperature [25]. So a good assumption is considering that the spins (for both \( t_{2g} \) and \( e_g \) electrons) are perfectly aligned in the whole temperature region as far as a single layer is concerned. For the same reason the dependence of \( t \) on the temperature resulting from double-exchange mechanism is ignored. Then we can use our theory with fully FM spin order to explain the CO scenario of LaSr\(_2\)Mn\(_2\)O\(_7\). The reentrant behavior seen in Fig. 3 is qualitatively the same as found experimentally [20]. Moreover the experimental observation of reappearing superlattice intensities at lower temperatures found in Ref. [8] is naturally explained within our theory. We point out, the multiple reentrant behavior is also possible from our theory even if the assumption about perfect FM spin order is relaxed. Of course, full explanation on the experiments needs to consider other factors, especially an orbital degree of freedom [24]. However, we think that polaron formation plays an essential role for the observation of reentrant CO transitions in this material.

In conclusion, in a 2D extended Hubbard model we have found interesting reentrant behavior of CO transition when including the polaron effect. Due to a temperature-dependent polaron bandwidth the CO state may go through a process of appearance, collapse and reappearance on decreasing the temperature in case of fully FM spin order. When a PM spin order is considered, once reentrance of CO transition may happens, which is partly due to polaron effect. The crossover between these two cases is complicated and still has to be investigated.

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