Orbital ordering in undoped manganites using Jahn-Teller interaction

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Abstract : To understand the orbital ordering of LaMnO\textsubscript{3} in the ground state, we study it in the A-type spin antiferromagnetic state. We calculate the two-dimensional response functions associated with the Jahn-Teller \( Q_2 \) and \( Q_3 \) distortions and find that they diverge at the wavevector \((\pi, \pi)\). Furthermore, the \( Q_2 \) response function diverges faster which indicates that perhaps the ordering of the orbitals at low temperatures is dominated by the \( Q_2 \) distortion. We calculate the ground state energy for the cases when only one of the \( Q_2 \) and \( Q_3 \) modes is excited cooperatively and find that the \( Q_2 \) excited state yields lower energy.

Keywords : Orbital density wave, Jahn-Teller interaction.

PACS No. : 71.45.Lr, 71.38.-k, 75.10.-b

1. Introduction

Undoped manganites like LaMnO\textsubscript{3} are the parent systems for the colossal magnetoresistive materials. It is well known that orbital ordering occurs around 780 K resulting in a C-type orbital structure with two kinds of orbitals alternating on adjacent sites in the \( xy \) plane while like orbitals are stacked in the \( z \) direction \[1\]. As the temperature is further lowered to 140 K an A-type spin antiferromagnetic order sets in wherein the spins are ferromagnetically aligned in the \( xy \) plane with the spin coupling in the \( z \) direction being antiferromagnetic \[2\]. To explain the observed order several studies have been reported. These studies fall into two classes, with one class based on Jahn-Teller (JT) interaction \[3–6\] being the main cause while the other class corresponds to Coulombic interaction \[7–10\] being the dominant cause for the observed order. However, it must be pointed out that the electron-phonon based studies do not point to a transparent mechanism.

The purpose of the present paper is to use the framework developed earlier by one of us (Ref. \[11\]) and analyze the orbital ordering by using a generalized Peierls instability approach. However, as compared to the one-dimensional Peierls charge density wave (CDW) approach, our higher dimensional orbital density wave (ODW) analysis is more complicated on account of there being two \( e_g \) orbitals (with inter-orbital hopping) and two response functions corresponding to the JT \( Q_2 \) and \( Q_3 \) distortions. We begin by assuming that the A-type antiferromagnetic ordering has already set in. Thus, on account of strong Hund’s coupling, the transport is restricted to spin polarized electrons in two dimensions only. We assume that the \( Mn \) sites are fixed and that only the oxygen atoms between the \( Mn \) sites can move along the axis joining the neighboring \( Mn \) sites. We find that the non-interacting response functions \( \chi_{2,3} \) corresponding to the \( Q_{2,3} \) modes diverge at wavevector \( \vec{Q} = (\pi, \pi) \). Thus one can expect local minima in energy for states corresponding to ODW being excited at wavevector \( \vec{Q} \) by the cooperative \( Q_2 \) and \( Q_3 \) modes. We find that \( \chi_2(\pi, \pi) \) diverges faster than \( \chi_3(\pi, \pi) \) and as expected the energy for the \( Q_2 \) related ODW state has lower energy than the \( Q_3 \) related ODW state.

2. Mean-field approach to ODW

We will now consider manganite systems with two \( e_g \) orbitals per site and ignore spin. The Hamiltonian consists of the kinetic term, the ionic term, and the electron-ion interaction term. The kinetic term in momentum space is given by

\[
H_1 = \sum_{\vec{r}} \text{B}_\rho^\dagger \cdot \text{T} \cdot \text{B}_\rho,
\]  \hspace{1cm} (1)

where \( \text{B}_\rho^\dagger = (b_1^\dagger b_2^\dagger) \) with \( b_1 \) and \( b_2 \) corresponding to the destruction operators for electrons with the orthonormal wavefunctions \( \psi_{x^2−y^2} \) and \( \psi_{3z^2−r^2} \) respectively. Furthermore, \( \text{T} \) is a hermitian matrix with \( \text{T}_{1,1} = -1.5t[\cos p_x + \cos p_y] \), \( \text{T}_{2,2} = -0.5t[\cos p_x + \cos p_y] \), and \( \text{T}_{1,2} = 0.5\sqrt{3}t[\cos p_x - \cos p_y] \). The eigenvalues of the
kinetic energy are given by $\lambda_n^F = -\cos p_x - \cos p_y - (-1)^n \sqrt{\cos^2 p_x + \cos^2 p_y} - \cos p_x \cos p_y$ with $n = 1, 2$.

The Fermi sea corresponding to the lower eigen energy value $\lambda_2^F$ is given by the union of the region $-\pi/2 \leq k_x \leq \pi/2$ (with all values of $k_y$ allowed) and the region $-\pi/2 \leq k_y \leq \pi/2$ (with all values of $k_x$ allowed). Whereas the Fermi sea corresponding to the higher eigen energy value $\lambda_1^F$ is given by the intersection of the region $-\pi/2 \leq k_x \leq \pi/2$ and the region $-\pi/2 \leq k_y \leq \pi/2$.

Since the number of electrons is equal to the number of sites, the total area occupied by both Fermi seas is equal to the area of the Brillouin zone ($4\pi^2$). Furthermore, the Fermi surface corresponds to $\lambda_n^F = 0$.

Using mean-field approximation we get, after averaging the Hamiltonian over phonon coordinates, the following effective Hamiltonian (see Ref. [11] for details):

$$
\bar{H} = H_1 - 2\frac{A^2}{\omega_0} \sum_j \left[ \langle b_{1j}^\dagger b_{2j} + b_{2j}^\dagger b_{1j} \rangle \langle b_{1j} b_{2j} + b_{2j} b_{1j} \rangle + \langle b_{1j}^\dagger b_{1j} - b_{2j}^\dagger b_{2j} \rangle \langle b_{1j}^\dagger b_{1j} - b_{2j}^\dagger b_{2j} \rangle \right] + \frac{A^2}{\omega_0} \sum_j \left[ \langle b_{1j} b_{2j} + b_{2j} b_{1j} \rangle^2 + \langle b_{1j}^\dagger b_{1j} - b_{2j}^\dagger b_{2j} \rangle^2 \right], \tag{2}
$$

where $\langle .. \rangle$ implies averaging over the phonon coordinates, $A\sqrt{2M\omega_0}$ is the electron-JT coupling constant, $2A\langle b_{1j}^\dagger b_{2j} + b_{2j}^\dagger b_{1j} \rangle = -\omega_0 \sqrt{2M\omega_0} \langle Q_{2j} \rangle$, and $2A\langle b_{1j}^\dagger b_{1j} - b_{2j}^\dagger b_{2j} \rangle = -\omega_0 \sqrt{2M\omega_0} \langle Q_{3j} \rangle$.

We will now determine the wavevector for long range cooperative ordering of the $Q_{2,3}$ modes. For this we must figure out the values of $q$ that make the susceptibilities $\chi_{2,3}(q,q)$ diverge. The expressions for $\chi_{2,3}(q)$ are given as

$$
\chi_{i}(q) = -2 \sum_{k,n} \frac{\langle c_{k+n}^\dagger c_k^\dagger \rangle}{\lambda_{k+q} + \lambda_k - \lambda_2^F} \sin^2 \left[ \frac{\theta_{k+q} + \theta_k + l\pi}{2} \right] + 2 \sum_{k} \frac{\langle c_{k+q}^\dagger c_{k}^\dagger \rangle - \langle c_{k}^\dagger c_{k}^\dagger \rangle}{\lambda_{k+q} + \lambda_k - \lambda_2^F} \cos^2 \left[ \frac{\theta_{k+q} + \theta_k + l\pi}{2} \right], \tag{3}
$$

where $\langle c_{k}^\dagger c_{k}^\dagger \rangle = \langle b_{1k}^\dagger b_{2k}^\dagger \rangle \cdot M, M$ is the diagonalizing matrix for the kinetic matrix $T$ with $M_{1,1} = \sin(\theta_{k}/2)$, $M_{2,2} = -\sin(\theta_{k}/2)$, and $M_{1,2} = \cos(\theta_{k}/2)$. At 0 K the second term on the right hand side of both $\chi_2$ and $\chi_3$ produces a divergence at $\bar{Q}$ because of the fact that $\lambda_1^{k+\bar{Q}} = -\lambda_k^F$ and that the Fermi energy is zero. Furthermore the ratio of $\chi_2/\chi_3$ at 0 K and wavevector $\bar{Q}$ is expected to be 3.

### 3. Results and discussion

In Fig. 1 we plot $\chi_{2,3}(\bar{Q})$ as a function of temperature (with hopping term $t$ set equal to 0.1 eV) and notice that they diverge as $T \to 0$ with $\chi_2$ diverging faster than $\chi_3$. In Fig. 2 we plot $\chi_{2,3}(q,q)$ as a function of $q$ (with $0 \leq q \leq \pi$) at fixed temperature $T = 0.01$ K and hopping term $t = 0.1$ eV and find that they both peak sharply close to $\bar{Q}$ with $\chi_2$ peaking faster. Then based on the fact that the phonon mode goes soft at wavevector $\bar{Q}$ we compute the ground state energy when only either $Q_{2}$ mode or $Q_{3}$ mode gets excited cooperatively in the system. The order parameters are given by $\langle b_{1j}^\dagger b_{2j} + b_{2j}^\dagger b_{1j} \rangle = c_2 \cos(\bar{Q} \cdot \bar{R}_j)$ and $\langle b_{1j}^\dagger b_{1j} - b_{2j}^\dagger b_{2j} \rangle = c_3 \cos(\bar{Q} \cdot \bar{R}_j)$ with $-1 \leq c_{2,3} \leq 1$ and $\bar{R}_j$ being the position vector. Here it should be pointed out that the order parameter $\langle b_{1j}^\dagger b_{2j} + b_{2j}^\dagger b_{1j} \rangle$ corresponds to the density difference of electrons in the two orbitals $\psi_X \equiv (\psi_{x^2+y^2} - \psi_{3z^2-r^2})/\sqrt{2}$ and $\psi_Y \equiv$
\[-(\psi_{x^2-y^2} + \psi_{3z^2-r^2})/\sqrt{2}\] (see Ref. [5]). From the symmetry of the \(\psi_X\) and \(\psi_Y\) orbitals it follows that at each site the total charge is unity. The unit cell needed to compute the ground state energy consists of two adjacent sites with the Brillouin zone being given by \(-\pi \leq (k_x + k_y) \leq \pi\) and \(-\pi \leq (k_x - k_y) \leq \pi\). We diagonalize a \(4 \times 4\) matrix at each momentum and integrate the lowest two eigen energies over the Brillouin zone to obtain the ground state energy. The results of

\[
\begin{align*}
\text{Figure 3.} & \quad \text{Dependence on dimensionless polaronic energy} \\
& \quad (A^2/\omega_0 t) \text{ of dimensionless ground state energy per site} \ (E/t) \ 	ext{for cooperative} \ Q_2 \ 	ext{and} \ Q_3 \ 	ext{modes.}
\end{align*}
\]

\[
\begin{align*}
\text{Figure 4.} & \quad \text{Variation of coefficients} \ c_{2,3} \ \text{of ODW order parameters for} \ Q_2 \ \text{and} \ Q_3 \ \text{distortions as a function of the dimensionless polaronic energy} \ (A^2/\omega_0 t).
\end{align*}
\]

our calculations are shown in Figs. 3 and 4. From Fig. 3 we see that the ground state energy corresponds to the \(Q_2\) mode with the difference in energy between the \(Q_2\) only state and the \(Q_3\) only state peaking at intermediate values of the dimensionless polaronic energy \((A^2/\omega_0 t)\). For zero values and infinite values of the polaronic energy both modes yield the same energy because zero value implies no phononic coupling effect while infinite value corresponds to localized polarons. Thus for large values of the polaronic energy, the ground state energy is only slightly smaller than the polaronic energy. Furthermore, from Fig. 4 we also see that as the polaronic energy increases the values of \(c_{2,3}\) increase and become unity around \(A^2/\omega_0 t \sim 2\) implying that for the \(Q_3\) \((Q_2)\) mode \(\psi_{x^2-y^2}\) \((\psi_X)\) orbital is occupied fully at one site with the \(\psi_{3z^2-r^2}\) \((\psi_Y)\) orbital being fully occupied at the adjacent sites.

In conclusion, we have studied orbital ordering for the ground state of the undoped manganite systems. We find that the two-dimensional orbital ordering, in the ferromagnetic planes of the observed A-type antiferromagnetic state, is governed by the wavevector \(\vec{Q}\) with \(Q_2\) JT mode being cooperatively excited in the system.

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