

Anharmonic Effects on Charge and Orbital Order

In a recent Letter [1], Mutou and Kontani tried to explain the experimentally observed charge and orbital order (COO) in half-doped manganites (upper left corner in Fig. 1). Some theories for the COO rely on the magnetic CE-type structure as an important ingredient [2]. Experimentally, however, at finite temperatures the COO is also observed without magnetic CE order. It is therefore desirable to obtain the COO without relying on magnetic interactions. Because of incorrect assumptions made in hopping integrals, however, the explanation in Ref. [1] is not valid. We demonstrate this below and show that the observed COO can be stabilized by anharmonic effects which always favor local elongation of oxygen octahedra around Jahn-Teller ions. The ratios of the hopping integrals $t_{ij}^{\alpha\beta}$ in the Hamiltonian $H = \sum_{\langle ij \rangle} t_{ij}^{\alpha\beta} c_{i\alpha}^\dagger c_{j\beta} + U \sum_{i, (\alpha \neq \beta)} n_{i\alpha} n_{i\beta} + V \sum_{\langle ij \rangle} n_{in_j}$, between orbital α on the site i and β on j [1], are known and related by symmetry ($\alpha, \beta = z^2 = 3z^2 - r^2, x^2 - y^2$). If we take $t_{\langle ij \rangle \| z}^{z^2, z^2} = t$, then $t_{\langle ij \rangle \| x, y}^{z^2, z^2} = t/4$, $t_{\langle ij \rangle \| x, y}^{z^2, x^2 - y^2} = \pm \frac{\sqrt{3}}{2}t$, etc. In particular, the hopping integral $t_{\langle ij \rangle \| x, y}^{x^2, y^2} = t/2$, and not zero as is assumed in Ref. [1] (here orbitals $x^2 = 3x^2 - r^2, y^2 = 3y^2 - r^2$). This incorrect simplification has important consequences. If we take the correct values of the hopping integrals, the lowest energy state is not the experimentally observed COO, but the state where $(x^2 - y^2)$ orbitals are occupied at the Mn^{3+} -sites. In Fig. 1 we show the energies of both states, calculated in a mean-field approximation, for $U/t = 8$. One can easily understand this result by comparing energies for $U, V \gg t$: $E_{\text{COO}} = -\frac{5}{6}t^2/V$ and $E_{x^2 - y^2} = -t^2/V$. Thus the conclusion of Ref. [1] that their model reproduces the experimentally observed COO at $x = 1/2$ is based on wrong approximations and is incorrect.

One can however obtain the correct COO without appealing to magnetic interactions. The occupation of the $x^2 - y^2$ orbitals corresponds to locally compressed octahedra and is unfavorable due to the anharmonic effects which always stabilize elongated octahedra. The physical reasons for this are rather simple: concomitant with the occupation of a particular orbital, the local surrounding of the Jahn-Teller ion distorts. The Mn-O distances a , b , and c change to $a \rightarrow a_0 + u_a$, $b \rightarrow b_0 + u_b$, and

$c \rightarrow c_0 + u_c$. For an occupied z^2 orbital we have elongation along the c axis, $u_c = 2\delta$, and a contraction in the other directions $u_a = u_b = -\delta$, $\delta > 0$. If the $x^2 - y^2$ is occupied we have a similar distortion with $\delta < 0$. The loss of elastic energy at such a distortion consists of harmonic and anharmonic contributions, $\sum_l \frac{B}{2} u_l^2 - \frac{\zeta}{3} u_l^3$, with the coefficient $\zeta > 0$ and the sum over the three directions. One immediately sees that the harmonic terms do not discriminate between different orbitals: all states $|\theta\rangle = \cos\frac{\theta}{2}|z^2\rangle + \sin\frac{\theta}{2}|x^2 - y^2\rangle$ have the same energy. However, the anharmonic term always stabilizes local elongation $\delta > 0$ (which may be directed along x , y , or z directions). This can be modeled by adding the term $E_{\text{anh}} = -\zeta \cos 3\theta$ to the energy [3]. For large enough ζ only the states $|z^2\rangle$, $|x^2\rangle$, or $|y^2\rangle$ ($\theta = 0, \pm \frac{2\pi}{3}$) can be occupied. This anharmonic contribution has very general character; it is most probably the reason that among hundreds of known Jahn-Teller systems with localized electrons none has locally compressed octahedra. If the anharmonic term is taken into account states with occupied x^2 and/or y^2 orbitals become preferred and the state with $(x^2 - y^2)$ occupation is destabilized with increasing ζ , $E_{x^2 - y^2} = E_{x^2 - y^2}^o + \zeta$, $E_{\text{COO}} = E_{\text{COO}}^o - \zeta$, so that the experimental COO is lower in energy for $\zeta > t^2/(12V)$. The choice between different OO states made of elongated orbitals is, however, a delicate problem: besides the experimentally observed COO state, one has to consider, for instance, also the state where on all Mn^{3+} sites the x^2 orbitals are occupied. Using the same arguments as in Ref. [1], it is easy to show that the observed COO state is stable at least for $U, V \gg t$.

Thus one can indeed obtain the correct COO in half-doped manganites without invoking magnetic interactions, but only if one includes the strong tendency to stabilize the locally elongated octahedra around localized Jahn-Teller ions. This factor definitely plays an important role also in other situations, e.g., for the stripe phases in the over-doped regime.

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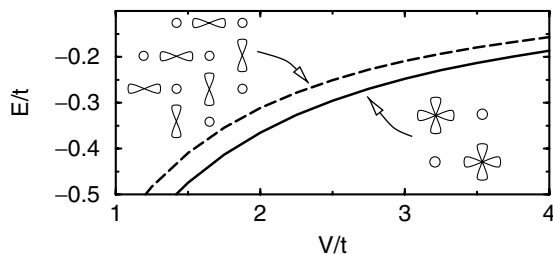


FIG. 1. Mean-field energy of the experimentally observed COO (dashed line) and the $x^2 - y^2$ state (full line).

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