PHYSICAL REVIEW B, VOLUME 63, 140416(R)

Orbital ordering of complex orbitals in doped Mott insulators

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(Received 23 January 2001; published 23 March 2001)

Orbital ordering, often observed in Mott insulators with orbital degeneracy, is usually supposed to disappear with doping, e.g., in the ferromagnetic metallic phase of manganites. We propose that the orbital ordering of a novel type may exist in such a situation: there may occur an orbital ordering of *complex orbitals* (linear superposition of basic orbitals $d_{x^2-y^2}$ and d_{z^2} with complex coefficients). Despite the perfect orbital ordering, such a state still retains cubic symmetry and thus would not induce any structural distortion. This state can resolve many problems in the physics of colossal magnetoresistance manganites and can also exist in other doped Mott insulators with Jahn-Teller ions.

DOI: 10.1103/PhysRevB.63.140416 PACS number(s): 75.30.Vn, 71.70.Ej

Mott insulators often display various types of ordering connected with localized electrons. In particular, in the presence of an orbital degeneracy, very often an orbital ordering occurs besides the magnetic (spin) one. Classical examples are the systems with doubly-degenerate e_g electrons, e.g., $KCuF_3$ or MnF_3.[1] At present special attention is paid to the manganites $La_{1-x}M_xMnO_3$ ($M=$Ca,Sr) with the colossal magnetoresistance (CMR). The undoped material $LaMnO_3$ is a Mott insulator with orbital ordering. What becomes of this ordering in doped materials and which role the orbital degrees of freedom play in the CMR phase, is a matter of active investigation and debate. On the one hand it is usually assumed that the orbital ordering (at least the long-range one) disappears in a ferromagnetic metallic (FM) phase ($0.16<x<0.5$) displaying CMR. This is in particular concluded from the disappearance of lattice distortion typical for the orbitally ordered states. On the other hand, the attempts to explain transport properties in this regime using only electron-spin scattering in the framework of the standard double-exchange model failed,[2] which forced Millis *et al.* to suggest that the orbital degrees of freedom are still important in this regime, e.g., producing Jahn-Teller polarons. Nevertheless the orbitals were still assumed to be disordered in the FM phase below T_c.

Until now, in all the numerous studies of the cooperative Jahn-Teller effect and orbital ordering only one class of solutions was considered: occupied orbitals were always assumed to be certain linear combinations of the basic orbitals $d_{z^2}\sim 1/\sqrt{6}(2z^2-x^2-y^2)$ and $d_{x^2-y^2}\sim 1/\sqrt{2}(x^2-y^2)$ of the form

$$|\theta\rangle=\cos\frac{\theta}{2}|z^2\rangle+\sin\frac{\theta}{2}|x^2-y^2\rangle, \tag{1}$$

i.e., linear superposition with real coefficients. Such orbitals give an asymmetric (quadrupolar) distortion of the electron density at a given site. Consequently, any ordering involving orbitals of the type (1), be it of ''ferro'' or ''antiferro'' type, corresponds to a decrease of the symmetry of charge distribution and is accompanied (or driven) by the corresponding lattice distortion.

There exists, however, yet another possibility: there may exist *an orbital ordering without any lattice distortion*. From the basis set of doubly-degenerate orbitals we can also form a linear superposition of the type (1) but *with complex coefficients*. The simplest example is the normalized functions

$$|\pm\rangle=\frac{1}{\sqrt{2}}(|z^2\rangle\pm i|x^2-y^2\rangle). \tag{2}$$

We can form an orbital ordering with the occupied orbitals of such type, e.g., the ferro-orbital ordering (FOO) with the orbitals $|+\rangle$ at each site or a staggered one $|+\rangle,|-\rangle$. It can be easily checked that the electron charge distribution in this state is perfectly symmetric, it is the same along *x*, *y*, and *z* directions, so that the net symmetry of a crystal would remain cubic. We suggest that just such an ordering is realized in the FM phase of CMR manganites. If true, this would imply that both the spin and orbital degeneracies are lifted in the ground state in these systems which consequently are *perfectly ordered in both the spin and orbital variables* [but with ''strange'' orbitals (2)].

Why have not such states been considered before? Apparently it is connected with two factors. On one hand, in most real materials with Jahn-Teller ions studied up to now there always occurred an orbital ordering accompanied by lattice distortion. On the other hand, in the theoretical description of these phenomena only the operators corresponding to an ordering of conventional type appear in the effective Hamiltonian (see below), so that it seemed that other possibilities are never realized in practice.[3,4] Most probably, indeed only the ''real'' solutions (1) can be realized in stoichiometric compounds with Jahn-Teller ions. The situation, however, may be different in doped materials — and that is what we propose here.

The easiest way to justify the appearance of this ordering is to consider the situation with very strong interaction $U\gg t$. Here we use the traditional description of the strongly interacting electrons by the Hubbard-type model which in case of orbital degeneracy is actually a degenerate Hubbard model; for the ferromagnetic spin ordering considered here it has the form[1]

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$$H=-\sum t_{ij}^{\alpha\beta}c_{i\alpha}^{+}c_{j\beta}+U\sum_{\alpha\neq\beta}n_{i\alpha}n_{i\beta}, \tag{3}$$

where i,j are the site inices and $\alpha,\beta=1,2$ describe the orbital occupation, e.g., $1=z^2$, $2=(x^2-y^2)$. The values of the hopping integrals $t_{i,j}^{\alpha,\beta}$ depend both on the type of orbitals involved and on the direction between sites i,j. Denoting the hopping between z^2 orbitals for a pair along the z direction as t, we have: $t_{z^2,z^2}^{z}=t$, $t_{z^2,z^2}^{x,y}=t/4$, $t_{x^2-y^2,x^2-y^2}^{x,y}=3t/4$, $t_{z^2,x^2-y^2}^{x,y}=\pm\sqrt{3}t/4$, $t_{z^2,x^2}^{x}=t_{x^2,y^2}^{x,y}=t/2$, etc., see e.g., Ref. 1.

It is well known that the electron (or hole) motion in systems with strongly correlated electrons is hindered by an antiferromagnetic background and is much facilitated if the background ordering becomes ferromagnetic (see e.g. Ref. 5): in nondegenerate Hubbard model it gives rise to Nagaoka's ferromagnetism,[6] and in systems with two types of electrons — to ferromagnetism due to double exchange. The energy gain in such a ferromagnetic state as compared to the antiferromagnetic or paramagnetic (disordered) one is of the order of the electron bandwidth, or of the hopping matrix element t per doped charge carrier: $\Delta E=-ctx$ (c is some constant of order 1), whereas the energy loss is of the order of $J(\sim t^2/U)\cdot(1-x)$. Thus, as argued already in Ref. 6, the saturated ferromagnetic state is realized for $x>x_c\sim J/t\sim t/U$ (for $U/t\gg 1$ and $x\ll 1$). For smaller x the inhomogeneous phase separated state with ferromagnetic droplets in an antiferomagnetic matrix can be realized.[7,8]

In exact analogy to this case we should expect that due to the same mechanism a ferro-orbital ordering will be established in very strongly interacting doped Mott insulators with orbital degeneracy. Which particular orbitals would be stabilized at that, may depend on the particular situation; we suggest that it may be the complex orbitals of the type (2).

A convenient way to describe the orbital ordering of double-degenerate e_g orbitals is to introduce pseudospin variables τ_i such that, e.g., the orbital d_{z^2} corresponds to $\tau^z=+\frac{1}{2}$, and the orthogonal orbital $d_{x^2-y^2}$ — to $\tau^z=-\frac{1}{2}$. The orbital states (1) considered until now are parameterized by the angle θ in the (τ^z,τ^x)-plane. Cubic symmetry is reflected in the θ plane in $2\pi/3$ symmetry: the state $\theta=(2\pi/3)$ corresponds to the orbital $|x^2\rangle\sim(2x^2-y^2-z^2)$ and $\theta=-(2\pi/3)$ — to $|y^2\rangle\sim(2y^2-x^2-z^2)$; these are more or less the orbitals occupied in two sublattices in the undoped $LaMnO_3$. The complex orbitals (2) are the eigenstates of the operator τ^y.

When we dope the system with orbital ordering, the motion of the charge carriers would initially (for small x) occur on a background of this orbital ordering. Similar to the hole motion on an antiferromagnetic spin background, the ''antiferro-'' orbital ordering would hinder the motion of a hole and would reduce its bandwidth. One can indeed check that, by making the orbital order ferromagnetic, e.g., occupying the same orbital at each site, for instance $|z^2\rangle$ or $|z^2-y^2\rangle$, we would increase the bandwidth and correspondingly decrease kinetic energy of holes. Indeed, using the values of hopping integrals $t_{\alpha,\beta}^{\langle ij\rangle}$ given above, one obtains for the undoped $LaMnO_3$ (alternation of x^2 and y^2 orbitals) the spectrum

$$\varepsilon(k)=-2[\tfrac{1}{2}t(\cos k_x+\cos k_y)+\tfrac{1}{4}t\cos k_z], \tag{4}$$

so that the minimum energy of the hole (the bottom of the band) will be $\varepsilon_{min}=\varepsilon(k=0)=-2.5t$. If, however, we would make a FOO, e.g., occupying at each site z^2 orbital, the spectrum will be

$$\varepsilon^{z^2\text{-}ferro}(k)=-2t[\tfrac{1}{4}(\cos k_x+\cos k_y)+\cos k_z] \tag{5}$$

and $\varepsilon_{min}^{z^2\text{-}ferro}=-3t$. Thus we indeed see that the energy gain in the FOO state is of order $\sim t$. The same minimum energy is reached also for (x^2-y^2)-ferro. ordering and for FOO with any orbital of the type (1). From Eq. (1) one can easily obtain that

$$t_{\theta,\theta}^{z}=\langle\theta|\hat{t}^z|\theta\rangle=t\cos^2\frac{\theta}{2};\quad t_{\theta,\theta}^{x/y}=\frac{t}{4}\left(\cos\frac{\theta}{2}\pm\sqrt{3}\sin\frac{\theta}{2}\right)^2, \tag{6}$$

and one obtains that the bottom of the spectrum with the hopping integrals given by Eq. (6) does not depend on θ and coincides with the value $-3t$.

But exactly the same ε_{min} is also reached for the τ^y ferromagnetism, where the state (2) is occupied at each site. Using the values of t's presented above, one obtains that $t_{\tau^y,\tau^y}=\frac{1}{2}t$ in all three directions, and

$$\varepsilon^{\tau^y\text{-}ferro}(k)=-t(\cos k_x+\cos k_y+\cos k_z), \tag{7}$$

so that the spectrum is indeed isotropic, and the minimum energy is also equal to $-3t$. [Note that, similarly to the nondegenerate Hubbard model, we can use the simple dispersion relations (4) and (5) only for the electron motion which does not destroy the background ordering. The energy gain in the FOO state is again, similarly to the Nagaoka case[6], $\sim tx$, and the energy loss is $\sim J$.]

As we saw above, for small x different FOO states are equivalent as to the gain in kinetic energy. On the other hand, we can see that τ^y ferro state is favorable as to the loss of the effective exchange energy. Indeed, the effective Hamiltonian describing the orbital interaction for $U\gg t$ and for the ferromagnetic spin ordering which we consider here schematically has the form[1]

$$\mathcal{H}=\sum J_s(\vec{s}_i\vec{s}_j)+J_\tau(\tau_i\tau_j)+J_{s\tau}(\vec{s}_i\vec{s}_j)(\tau_i\tau_j), \tag{8}$$

where the first and the third terms are due to superexchange, $J_{exch}\sim J_s\sim J_{s\tau}\sim t^2/U$, and in the second term also the Jahn-Teller interaction of degenerate orbitals with the lattice contribute, $J_\tau=J_{exch}+J_{\mathrm{JT}}$. The interaction (8) is in general anisotropic with respect to τ operators and usually it does not contain terms with τ^y, but only the orbital operators in combinations $\tau_i^z\tau_j^z$, $\tau_i^x\tau_j^x$, and $\tau_i^z\tau_j^x$ with positive (antiferromagnetic) coefficients J_τ, $J_{s\tau}$.[1] In the ground state of the undoped system a certain spin and orbital order is realized which minimizes the total energy — and it will be an antiferro ordering of real orbitals (1). If, however, we *force* our system to be ferromagnetic both in spins and in orbitals, e.g., as argued above, by doping, in case of $U\gg t$, we strongly

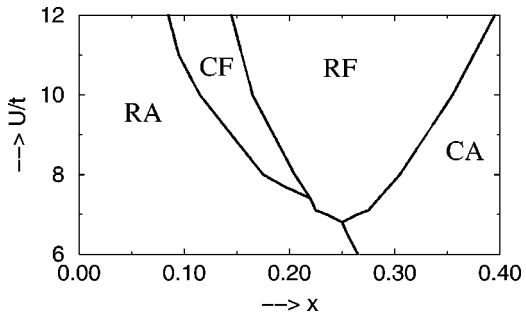

FIG. 1. The regions of stability of different types of orbital ordering for the ferromagnetic spins. The orbitals occupied in the RFOO phase are those with $\theta=\pi$ in Eq. (1), and in the RAOO phase those with alternating $\theta=0,\pi$

increase this exchange energy — and we can minimize this energy loss by choosing FOO of τ^y-type with the orbitals (2).

One can check directly that the superexchange part of the energy is indeed smaller in the τ^y FOO state as compared, e.g., with the FOO state of real orbitals. Thus, taking the standard expression for the exchange integrals $J=2t^2/U$ and calculating exchange constants with the proper values of t [Eq. (6)], we obtain that for the FOO with the real orbitals (1) the energy of the ferromagnetic state in a mean-field approximation is: $E_{real\ FOO}=-\frac{3}{4}(t^2/U)$ for all θ. Similar treatment of the τ^y FOO state shows, however, that the exchange energy in this state is lower.

As the electronic energy of doped charge carriers coincides for the states (1) and (2), and the magnetic energy of the latter is lower, one can conclude that the proposed ferromagnetic state with τ^y FOO [occupation of complex orbitals (2)] will be the best among all possible ferro ordered states — and these, we argue, may be stabilized by the usual Nagaoka mechanism for $U/t\gg 1$.

All these arguments are, strictly speaking, valid only for $U/t\gg 1$ and $x\ll 1$: in this case the holes would occupy the bottom of the band, as we assumed until now. However, for not too large U/t and consequently for larger doping x we should take into account the finite occupation of the band, and the results would depend on the detailed form of the density of states $\rho(\epsilon)$ in different cases. We studied this general situation by calculating the total energy of different possible types of orbital ordering in the mean-field approximation, assuming ferromagnetic spin arrangement. We compared the following types of ordering: ferro-orbital ordering of real orbitals (1) (RFOO); antiferro (staggered) ordering of real orbitals (RAOO) of two types: with the sublattices $(\theta, -\theta)$ and with $(\theta,\pi-\theta)$; ferro ordering of complex orbitals (2) (CFOO), and finally the antiferro ordering of complex orbitals (CAOO) with the sublattices $|+\rangle,|-\rangle$. In each state with real orbitals the energy was minimized with respect to the angle θ. The results of these calculations are presented in Fig. 1.

As we see from these numerical results, there is indeed a possibility of the stabilization of the ordered states with complex orbitals. In accordance with the arguments given above, we indeed see that for very large U/t the ferro-orbital ordering of complex orbitals would be realized. However, due to different density of states some other states may become favorable for not too large U. Thus, for the realistic value of $U/t\sim 8$ the staggered complex orbital ordering is more stable for $x\sim 0.3$–0.5 (for small doping $x\ll 1$ this state is worse than CFOO because the bottom of the corresponding band is not $-3t$, but only $-2t$).[9]

From the point of view of symmetry the proposed τ^y ordering corresponds to the A_{2g}^- (or Γ_2^-) representation of the cubic group.[10] The corresponding order parameter is

$$T_{xyz}=\langle \mathcal{S} l_x l_y l_z\rangle, \tag{9}$$

where $\langle\ \rangle$ is the ground-state average, $\mathcal{S}$ denotes symmetrization and l_x, l_y, and l_z are the corresponding components of the momentum operator $\hat{l}=2$. This follows from the group symmetry, and we checked by direct calculation that it is the lowest nonzero average in our state. One can show that in the basis $|z^2\rangle$, $|x^2-y^2\rangle$ T_{xyz} is indeed proportional to the τ^y-Pauli matrix. From Eq. (9) we see that the order parameter in our state is a magnetic octupole, cf. Refs. 3 and 4. It is in principle possible, although not easy, to observe such ordering experimentally. Probably the most promising would be the resonance experiments like NMR. One can also show that this state should have a piezomagnetism.

It is not apriori clear whether this τ^y-orbital ordering and the ferromagnetic spin ordering would occur at the same temperature. The direct product of corresponding irreducible representations A_2 and T_1 does not contain unit representation A_1,[10] so that there will be in general no linear coupling between these order parameters. However, if the rhombohedral distortion T_{2g}, present in manganites at high temperatures (S. W. Cheong, private communication), would still exist at low temperatures, then there will exist linear coupling of these three types of ordering $(A_2\times T_1\times T_2\in A_1)$ and the octupole orbital ordering and the ferromagnetic spin ordering will occur at the same T_c. This could help to resolve the problem pointed out in Ref. 2, that the change of resistivity through T_c in purely spin case is too small: one would get an extra scattering in a ''para'' phase — an orbital-disorder scattering — in addition to the spin-disorder one.

Summarizing, we suggest in this paper that, similarly to magnetic ordering, doping of orbitally degenerate Mott insulators containing Jahn-Teller ions could stabilize the orbital ordering of special type, the occupied orbitals being ''complex'' — i.e., the linear superpositions of basic orbitals $d_{x^2-y^2}$ and d_{z^2} with complex coefficients. Such orbitals, despite perfect ordering, do not induce any structural distortion. The corresponding order parameter is a magnetic octupole. This idea may explain the main properties of the colossal magnetoresistance manganites in the most interesting ferromagnetic metallic concentration range: in this picture they are perfectly ordered with respect to both spin and orbitals, but with the *complex* orbitals occupied at each site. In particular, this could help to explain the sharp drop of resistivity below T_c, with the crystal structure remaining undistorted. Similar states may in principle exist also in other doped Mott

insulators with Jahn-Teller ions which constitute a large interesting class of magnetic materials with very specific properties.

We are grateful to G. A. Sawatzky and M. V. Mostovoy for useful discussions. We are also grateful to D. Cox who pointed out the possible importance of the rhombohedral distortion in manganites. This work was supported by the Netherlands Foundation FOM, by the European Network OXSEN, and by Project No. INTAS–97 0963.

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