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Bond centered vs. site-centered charge ordering: ferroelectricity in oxides

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Abstract

We show that in manganites close to half-doping, novel non-bipartite magnetic phases appear due to the interplay between double exchange, superexchange and orbital ordering. In considerable part of the phase diagram the ground state has a magnetic order that is intermediate between the canonical magnetic CE phase and a state that we identify as the recently observed Zener polaron state. The intermediate phase shows a type of charge ordering that breaks inversion symmetry and is therefore predicted to be ferroelectric.

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Keywords: Manganites; Orbital ordering; Ferroelectricity

1. Introduction

One of the intrinsic property of doped transition metal oxides is the formation of superstructures that are related to the spin, charge and orbital degrees of freedom. Charge ordering is usually considered as an ordering or alternation of the valency of transition metals. Further we will refer it as site-centered charge density wave (SCDW). However there exists another possibility for charge ordering, namely, formation of a bond centered charge density wave (BCDW). It is an analog of the Peierls distorted quasi-one-dimensional materials.

For more than 50 years the accepted picture of charge ordering in manganites of the type $R_{1-x}Ca_xMnO_3$ (with R = La, Pr, etc.) was BCDW ordering [1]. However in the recent work by Daoud-Aladine et al. [2], it was put under question. The authors conclude that the experimental data for single-crystalline $Pr_{0.6}Ca_{0.4}MnO_3$ are more consistent with the BCDW structure (see

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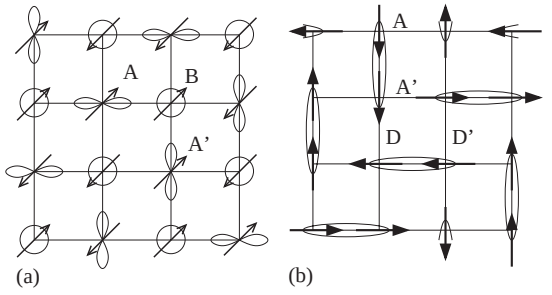

Fig. 1. Two types of magnetic/orbital superstructures: (a) CE phase; (b) Orthogonal (⊥) phase.

Fig. 1). Below we consider parameters which stabilize different superstructures and we show, that indeed, there is a region with a stable BCDW phase. Surprisingly, the resulting state turns out to be ferroelectric.

2. Calculations

In our calculations we use tight-binding approach for the band structure of manganites, where both double exchange and superexchange are incorporated [3]. In the double-exchange framework with strong on-site Hund's rule coupling the motion of e_g-electrons is largely determined by the underlying magnetic structure. In this approach, the stability of various magnetic and orbital structures is determined by the competition of the band energy of the e_g-electrons, favoring ferromagnetism, and superexchange interaction J between localized (t_{2g}) spins, favoring antiferromagnetism. The double degeneracy of conduction electrons significantly modifies the conventional picture and leads to the stabilization of more complicated magnetic structures, besides the simple ferromagnetic (F) or antiferromagnetic (G) ones. We calculate the ground state energy for different magnetic structures: G-, C-, A- and CE-type antiferromagnetic states, the ferromagnetic (F) phase, and, in addition, for two new phases (with orthogonal (⊥) and 120° Jaffet–Kittel type magnetic ordering of spin dimers) that we expect to be relevantly close to $x \sim \frac{1}{2}$, based on the arguments above.

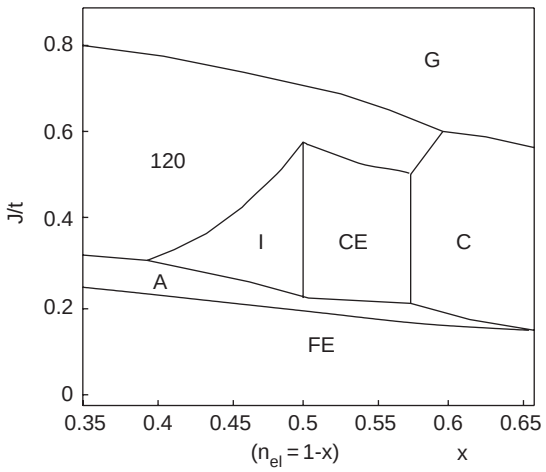

Fig. 2. Phase diagram of manganites for doping concentrations close to 1/2. F: ferromagnetic, G: antiferromagnetic (AF), A: F planes coupled AFM, C: F chains coupled AF, CE: F zig-zag chains coupled AF, 120: Jaffet–Kittel state and I: intermediate orthogonal phase. The electron density is $n_{el} = 1 - x$.

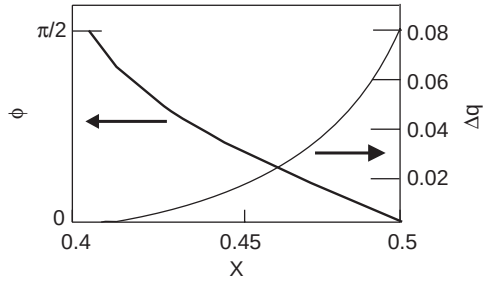

Fig. 3. Charge disproportionation Δq and mixing angle ϕ (see text) for the $U = t$ in Hartree–Fock approximation in the intermediate ⊥ and CE phases.

In Fig. 2. we show the resulting phase diagram as a function of doping x and antiferromagnetic coupling J. For $x \gtrsim \frac{1}{2}$ we find mainly the magnetic CE, C, A and F phase to be stable, in accordance with previous results [3,4]. For $x \lesssim 0.5$, we also find a large region where the BCDW magnetic 120° state is stable. Most interestingly, we also find a finite region of the ⊥ phase. This phase is stable for doping concentration of around $x \sim 0.4$, which agrees with the fact that at this concentration the Zener polaron state was found [2].

It turned out that the I phase in Fig. 2 is not a pure Zener polarons phase (BCDW) but the phase which interpolates between BCDW and SCDW. We calculate the charge disproportionation Δq due to the on-site Coulomb interaction U between the electrons in the Hartree–Fock approximation. In Fig. 3. Δq is shown as a function of doping. Charge ordering starts at $x \sim 0.4$ where the intermediate phase appears, and has its maximum at $x = \frac{1}{2}$, which coincides with the transition to a pure CE-phase. The coexistence of dimers (BCDW) with unequal charges at two ends (SCDW) makes this state ferroelectric.

3. Conclusions

We have shown that in manganites with doping concentrations close to $x = \frac{1}{2}$ a novel noncollinear type of magnetic order can appear besides the well known CE-type ordering. In this ($\perp$) phase the neighbouring spins are, depending on the direction of the bond, either oriented parallel, antiparallel or perpendicular to each other. Due to double exchange and orbital ordering, parallel spins form strong dimer-like bonds, which we identify as the Zener polaron state that was recently observed experimentally close to $x = \frac{1}{2}$ [2]. In considerable part of the phase diagram an intermediate phase, which is a superposition of a CE-type and orthogonal state, is stable. We predict that in this charge ordered intermediate state inversion symmetry is spontaneously broken and ferroelectric moments appear. This may be the first example of the appearance of ferroelectricity due to charge ordering in transition metal oxides.

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