Introduction. The wide variety of phenomena that are observed in transition metal (TM) oxides is caused by the interplay of various degrees of freedom. An intrinsic property of doped TM oxides is the formation of superstructures that are related to the charge, spin, lattice and orbital degrees of freedom. Different types of charge ordering (CO), orbital ordering and magnetic ordering may exist depending on e.g. doping concentration, temperature and pressure. Charge order is usually considered to be an ordering of TM ions with different valence, for instance the alternation of Mn$^{3+/4+}$ in La$_{0.5}$Ca$_{0.5}$MnO$_3$ or Fe$^{2+/3+}$ in Fe$_3$O$_4$. Such a CO state we refer to as a site-centered (or TM-centered) CO, or equivalently, a site-centered charge density wave (SCDW). There is however another possibility for charge ordering —the formation of a bond-centered charge density wave (BCDW). The BCDW is very similar to the state that is observed in Peierls distorted quasi one-dimensional materials. In a TM oxide the BCDW is actually an oxygen-centered charge ordered state as oxygen ions are located on the TM-TM bonds in the typical (e.g. perovskite) crystal structures of these systems. The possibility to have such an oxygen-centered BCDW was studied theoretically for the compounds RNiO$_3$ (with R = Pr, Nd, etc.) [1].

For about the last 50 years it was presumed that in manganites of the type R$_{1-x}$Ca$_x$MnO$_3$ (with R = La, Pr, etc.) only the Mn-centered SCDW occurs. At e.g. $x = 1/2$ this SCDW state has the well-known orbital ordered CE-type magnetic structure, see Fig.1a, an ordering for which there is abundant experimental and theoretical support [2, 3]. However, Daoud-Aladine et al. challenge this canonical picture in their recent study [4]. These authors conclude that in single crystalline Pr$_{0.6}$Ca$_{0.4}$MnO$_3$ another type of superstructure is more consistent with the experimental data. This superstructure is a BCDW, which they refer to as the Zener polaron state (Fig.1b). This state is made out of dimers in which all Mn ions have the same valence (all Mn$^{3+/4+}$), quite different from the canonical SCDW that holds Mn ions with unequal valence. Recently the BCDW state was also found theoretically in Hartee-Fock calculations of the electronic structure [2, 4]. The presence of a BCDW amounts to a drastic change in our understanding of charge ordering —not only for manganites. It may imply that in all cases of charge order in oxides one should have in mind, besides the usual site-centered CO, alternative states with bond-centered superstructures.

In this paper we consider the regions of stability of different superstructures in doped manganites close to half-doping, and show that indeed the bond-centered charge density wave (Zener polaron) state may be favorable in part of the phase diagram. Our results reconcile the conflicting conclusions of Refs. [2] and [4]: the conventional CE state is still better at exactly half-doping $x = 1/2$, but a BCDW is stable at around $x \sim 0.4$, as observed experimentally. The most interesting result of our calculation is the following: in a large part of the phase diagram an intermediate state actually turns out to be most favorable. This state is a superposition of a BCDW (Zener polaron) and a SCDW (of CE-type). As one can easily see, a superposition of Figs.1a and 1b results in a state in which the two Mn ions in one dimer are inequivalent. This produces a dipole moment on each pair, and the resulting state is therefore ferroelectric. The appearance of ferroelectricity in the case of coexistence of a bond-centered CDW (Peierls state) and the site-centered CDW was previously observed in some quasi one-dimensional compounds [5]. But, to the best of our knowledge, such
a state was never discussed in the context of the three-dimensional TM oxides. In this respect it is noteworthy that first measurements of the dielectric constant in these manganites show a strong anomaly at the CO phase transition, which might be related to ferroelectricity 

Qualitative considerations. It is well established that charge and orbital structures are closely related to the magnetic ordering. In all the papers where either the usual SCDW or the BCDW (Zener polarons) are considered, the magnetic structure is taken to be of the CE type (ferromagnetic zig-zag chains stacked antiferromagnetically, Fig.1a). However in the BCDW picture the situation can change drastically due to orbital ordering existing in the structure of Fig.1b (predominantly $d_{xz}$-orbitals on horizontal dimers and $d_{yz}$ on vertical ones, see below). Due to the double exchange mechanism the coupling between spins inside a Zener polaron is definitely strongly ferromagnetic. The high-spin polaron dimers — if we treat them as localized spins — form a triangular lattice, see Fig.1c, with a relatively strong antiferromagnetic coupling between neighboring parallel dimers. A different magnetic coupling can be expected when the dimers are are oriented perpendicular to each other. If these couplings would all be comparable in magnitude and antiferromagnetic, then the angle between neighboring high spin polaron on the triangular lattice would be $120^\circ$ and a tripartite Jaffet-Kittel magnetic structure would be formed, Fig.1c. However from the orbital structure of Zener polaron described above one can immediately conclude that the perpendicular coupling is definitely weaker. We therefore expect that the magnetic structure tends to an "orthogonal" ($\perp$) ordered state with four different spin sublattices as shown in Fig.1b. We should mention that the neutron scattering data for Pr$_{0.6}$Ca$_{0.4}$MnO$_3$ can be equally well described both by the conventional magnetic structure of Fig.1a and by the orthogonal structure of Fig.1b that we propose here. In the overdoped manganites $\text{R}_{1-x}\text{Ca}_x\text{MnO}_3$, with $x = 2/3, 3/4$ a $\perp$ magnetic structure was already observed.

Calculated phase diagram. In our calculations we use a tight binding approach for the band structure of the manganites, where both double exchange and superexchange are incorporated. This approach proved to be quite efficient for overdoped ($x > 0.5$) and half-doped manganites. 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 groundstate energy for different magnetic structures: G-, C- and A- and CE-type antiferromagnetic states, the ferromagnetic (F) phase, and, in addition, for two new phases (with orthogonal ($\perp$) and $120^\circ$ Jaffet-Kittel type magnetic ordering of spin dimers) that we expect to be relevant close to $x \sim 1/2$, based on the arguments above.

The effective hopping matrix elements $t_{ij}^{\alpha \beta}$ depend on the type of the orbitals $\alpha, \beta$ and relative orientation of a pair $i$, $j$, so that $t_{ij}^{x-x} = t_{ij}^{x-y} = t_{ij}^{y-y} = 3/4t$, $t_{ij}^{z-z} = t$ and $t_{ij}^{\perp} = 1/4t$. Besides this, there is the usual dependence of hopping on the angle $\theta$ between neighboring spins: $t_{ij}^{\alpha \beta} = t_{ij}^{\alpha \beta} \cos \theta_{ij}/2$. The antiferromagnetic superexchange energy per bond is $J \cos \theta_{ij}$. With these expressions it is straightforward to calculate the band dispersion and total energy of different phases, cf. 12.

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

From the calculation we know the corresponding wave functions so we can find the orbital occupation on a certain site by projecting the wave function on that particular site. In agreement with the standard picture we obtain that for the CE-structure the edge sites A, A’ in Fig.1a. are occupied by orbitals $d_{xz}$ and $d_{yz}$, respectively. On the corner sites predominantly the $d_{xz}-y^2$ orbital is occupied with about 10% admixture of $d_{yz}$ density. Let us denote the general orbital state as $|\phi\rangle = \cos \phi/2|z^2\rangle + \sin \phi/2|x^2-y^2\rangle$. For an isolated dimer that...
points along the $x$ direction (the equivalent D, D’ sites in Fig.1.b) we then expect $\phi = 2\pi/3$ for both sites in the dimer, which corresponds to occupied $d_{x^2}$ orbitals on both sites. For an isolated dimer along the $y$ direction (C, C’ sites in Fig.1.b.) we then expect $\phi = -2\pi/3$, corresponding to occupied $d_{y^2}$ orbitals. From the calculation of the wave functions for the $\perp$ phase, where there is an interaction between neighboring dimers, we find for the $x$-dimer that $\phi \sim 130^\circ$, which is mainly a $d_{x^2}$-state, as we had for a non-interaction dimer, but with some admixture of $d_{x^2-y^2}$. Correspondingly, for the $y$-dimers we find $\phi \sim -130^\circ$, which amounts to a predominantly $d_{y^2}$-state with some $d_{x^2-y^2}$ character. This admixture is important as it is driving the stability of the $\perp$ phase. The superexchange tends to align the spins of neighboring $x$-and $y$-dimers antiparallel. But in the $\perp$ phase these spins are only orthogonal, so that the hopping between the dimers is possible, although reduced by a factor $1/\sqrt{2}$ from its maximum value. From this hopping between neighboring dimers, which leads to the admixture of $d_{x^2-y^2}$ states into the groundstate wavefunction, the system gains kinetic energy. Note that the hopping amplitude between $d_{x^2}$ orbitals of neighboring $x$-dimers (or between $d_{y^2}$ orbitals of neighboring $y$-dimers, respectively) is much smaller, so that the spins of neighboring dimers of the same kind tend to align themselves fully antiparallel. Thus we conclude that the stability of the $\perp$ state is caused by its orbital order that allows for an optimal compromise between electron delocalization, causing ferromagnetic double exchange, and antiferromagnetic superexchange interactions.

Charge ordering and ferroelectricity. In the CE-phase the edge and the corner sites are crystallographically inequivalent. This results in different total electron occupation numbers on edge and corner sites. Already when the on-site Coulomb interaction $U$ between electrons in different orbitals but on the same site is included, the common picture of a checkerboard SCDW arises in this system, with a valence Mn$^{3.5+\Delta_\perp}$ of the corner sites, Mn$^{3.5-\Delta_\perp}$ of the edge sites and $\Delta_\perp \leq 0.1$ [13]. The CE-structure has a center of inversion symmetry and, consequently, there are no electrical dipoles moments present in the groundstate. This is also the case in the pure $\perp$ structure as both Mn ions in each dimer are equivalent [14]. But there may exist an intermediate state that does have dipole moments: this intermediate state is a superposition of the CE and $\perp$ phase. This state has a magnetic structure in which the spins of $x$-dimers (spins within each dimer are ferromagnetic) are antiparallel to one another, and the $y$-dimers, also antiparallel between themselves, are rotated with a certain angle $\theta$ with respect to the $x$-dimers. The angle $\theta$ characterizes intermediate phase as it determines the amount of mixing between CE and $\perp$ that is present in the groundstate: $\theta = 0$ corresponds to the CE-structure, while $\theta = \pi/2$ corresponds to the $\perp$ one.

![FIG. 3: Charge disproportionation $\Delta q$ and mixing angle $\phi$ (see text) for the $U=t$ in Hartree-Fock approximation in the intermediate $\perp$ and CE phases.](image)

We find that the region of stability of this intermediate phase is larger than that of a pure $\perp$-phase, and extends from the concentrations $x \sim 0.4$ to $x = 0.5$; Fig.2 shows for which values of $x$ and $J/t$ this mixed intermediate phase is stable. The angle $\theta = 0$ for $x = 1/2$, and it increases with decreasing $x$, reaching the value $\theta = \pi/2$ ($\perp$ phase) at $x \sim 0.4$, see Fig.3. The intermediate phase is therefore in general a superposition of the CE and $\perp$ phase, except near the phase boundaries in Fig.2, where the pure phases are stable. In the intermediate phase there exist simultaneously a dimer (Zener polaron) bond-centered CDW and a checkerboard site-centered CDW. This implies that in the intermediate state the valence of the two Mn's in a dimer is different, inversion symmetry is broken and each dimer attains a dipole moment. In this phase the dipole moments of the $x$-dimers point e.g. to the right in Fig.1 and all dipole moments of $y$-dimers point e.g. up (depending on how precisely the inversion symmetry of the system is broken globally) causing each $xy$-plane to acquire a net ferroelectric moment.

We calculate the charge disproportionation $\Delta q$ due to an on-site Coulomb interaction $U$ between the electrons in the Hartree-Fock approximation. In Fig.3. $\Delta q$ 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 $x = 1/2$, which coincides with the transition to a pure CE-phase.

It is experimentally observed that the CDW deformations in neighboring planes are in phase with each other. This implies that there is a net polarization of the electric dipole moments when the system is in the intermediate phase, which leads to a ferroelectric ground state. Of course, in real materials ferroelectric domains may appear. As also the conductivity of these materials is not so low, it may not be easy to observe the predicted ferroelectricity in CO manganites. But already first measurements of the dielectric constant $\varepsilon$ do show a strong peak in $\varepsilon(T)$ at the charge ordering temperature $T_c$. A more detailed experimental study of this phenomenon would certainly be of interest in the present context.

A phenomenological symmetry analysis of possible orderings in $R_{1-x}$Ca$_x$MnO$_3$ was carried out in Ref. [17]. The phases that we find fit exactly into the phe-
nomenclature classification that these authors propose. They conclude that three phases may exist: one with $P2_1/m$ symmetry, which coincides with our SCW CE-structure; another of the Pmm2 type, corresponding to our BCDW orthogonal (Zener polaron) state, and a structure with Pm-symmetry that corresponds to our ferroelectric intermediate phase. Experimental structural refinements do show that the actual symmetry of the low-temperature phase of $Pr_{1-x}Ca_xMnO_3$ is $Pm[2]$, i.e. it is in the intermediate phase. Our calculations provide the microscopic basis for this phenomenological treatment and shows that, indeed, all three phases are stable in a doping region close to $x \sim 0.4$. Apparently, with increasing $x$ $Pr_{1-x}Ca_xMnO_3$ goes from the $\perp$ or intermediate phase to the CE-phase at around $x = 1/2$, and then to the C-phase for overdoped samples. The $(LaCa)MnO_3$-system is, due to a larger hopping $t$, apparently below the $\perp$ phase in Fig 2: with increasing doping it goes from $F$ to CE and then to the C-phase. In our phase diagram the A-phase appears between the metallic F and “insulating” $\perp$ and CE-phases [13], whereas experimentally the A-phase usually exists only for $x \gtrsim 0.5$ [13]; the reason for this discrepancy is not clear at present.

We should remark that we only considered different homogeneous states. It is known, however, that in many correlated electron models for the manganites the doped systems may be unstable with respect to phase separation (PS) [20]. Also in our analysis we find for the intermediate phase a convex dependence of the energy on the electron density, i.e. there is the tendency for PS into a pure CE and a pure $\perp$ phase with their appropriate electron densities. However, the inclusion of the long-range Coulomb interaction in model calculations of the electronic properties prevents large-scale PS. Such a long-range interaction has to be taken into account in the case of PS, in order to guarantee the total charge neutrality of the system. These Coulomb interactions allow only for the formation of weak inhomogeneities with smooth boundaries, which implies that the properties of the resulting PS state are similar to the properties of the homogeneous state. Nevertheless, the question of what the detailed properties of such an inhomogeneous state would be, is an interesting problem and deserves further investigation.

**Conclusions.** We have shown that in manganites with doping concentrations close to $x = 1/2$ a novel type of magnetic order can appear besides the well known CE-type ordering. In this ($\perp$) phase the neighboring 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 $x = 1/2$ [1]. 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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