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Ferroelectricity in doped manganites

S.M.Dunaevsky

B.Konstantinov Petersburg Nuclear Physics Institute, Russian Academy of Sciences, Gatchina, Leningrad District, 188300 Russia

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The appearance possibility of spontaneous electric moment P (ferroelectricity) in the antiferromagnetic dielectric state of doped $La_{1-x}Ca_xMnO_3$ manganites is discussed. The tight-binding method and the double-exchange Hamiltonian with infinite on-site Hund interaction are used to calculate the spectrum of e_g electrons in manganites for various magnetic structures composed of ferromagnetic zigzag spin chains that include two to eight spins per one-dimensional unit cell. The carrier concentration x values are found at which the band insulator state can arise in antiferromagnetic $La_{1-x}Ca_xMnO_3$ manganites containing the above chains. In addition to the known spectra of (1×1) and (2×2) chains, the spectrum of a (3×3) zigzag chain is obtained for the first time. A three-dimensional unit cell including this type of chains and comprising 24 manganese atoms permits a correct qualitative description of the atomic and magnetic structures in the $La_{1/3}Ca_{2/3}MnO_3$ manganite. In this magnetic structure (as in the E-phase), the gigantic spontaneous polarization P may arise due to the additional displacement of oxide ions belonging to ferromagnetic chains.

Обсуждается возможность появления спонтанного электрического момента P (сегнетоэлектричества) в антиферромагнитном диэлектрическом состоянии легированных манганитов $La_{1-x}Ca_xMnO_3$. Приближение сильной связи и двойной обменный гамильтониан с бесконечно сильным собственным взаимодействием Хунда применяются для расчета спектра e_g-электронов в манганитах для различных магнитных структур, состоящих из ферромагнитных зигзагообразных спиновых цепей, включающих от двух до восьми спинов на одну одномерную элементарную ячейку. Найдены значения концентрации носителей x, при которых в антиферромагнитных манганитах $La_{1-x}Ca_xMnO_3$, содержащих вышеупомянутые цепи, может возникать зонное изолирующее состояние. В дополнение к известным спектрам цепей (1×1) и (2×2) впервые получен спектр для зигзагообразной цепи (3×3). Трехмерная элементарная ячейка, включающая этот тип цепей и содержащая 24 атома марганца, позволяет корректно качественно описать атомные и магнитные структуры в манганите $La_{1/3}Ca_{2/3}MnO_3$. В этой магнитной структуре (как и в E-фазе) может возникать гигантская спонтанная поляризация P как следствие дополнительного смещения оксидных ионов, принадлежащих ферромагнитным цепям.

1. Introduction

One remarkable property of doped perovskite manganites $R_xA_{1-x}MnO_3$ (R = La, Pr, Nd, Sm; A = Ca, Sr, Ba) is the rich variety of magnetic structures occurring therein. Depending on the chemical composition and doping level, these compounds can either be ferromagnetic (FM) or have different types of antiferromagnetic (AFM) ordering. In addition to simple AFM structures of the G, A and C types, more complex zigzag structures are possible. The most known example is the CE structure found in numerous manganites at half-doping. This structure was predicted theoretically in [1] and experimentally observed first in $La_{0.5}Ca_{0.5}MnO_3$ [2] and then in several other compounds. In the CE structure, the magnetic moments of Mn ions form zigzag FM chains that show an in-plane AFM order. In the normal direction, FM chains are trans-

lated with spins alternating AFM. The unit cell of the *CE* structure contains 16 Mn atoms. In [3, 4], the electron spectra $E(\mathbf{k})$ of the *CE* structure were calculated theoretically within the double exchange model in the approximation of infinitely strong Hund interaction between e_g and t_{2g} electrons, which prohibits hopping of the electrons between chains.

Therefore, the calculation of the spectrum for the three-dimensional (3D) structure is reduced to calculating the spectrum of a 1D zigzag chain with four atoms in its 1D unit cell. The calculations have shown that the manganites possessing the *CE* structure are band insulators, i.e., the lowest two bands in which two electrons can be located are separated from other bands by an energy gap. In the *CE* structure, these bands are fully occupied and the compound is a band insulator. Similar calculations of the spectrum for a 1D zigzag chain with two atoms in its 1D unit cell performed in [5] predicted a new *E*-type of insulating AFM structure, which was found experimentally in $HoMnO_3$ [6]. This magnetic structure is very interesting because upon simultaneous consideration of double exchange and deformation of oxygen octahedrons, a gigantic spontaneous polarization *P* is possible therein due to additional displacement of oxide ions which belonging to ferromagnetic chain [7]. In contrast to the most extensively theoretically studied case of spiral magnetism [8–10], the mechanism responsible for ferroelectricity in the magnetically ordered phase does not rely on the presence of anisotropic Dzyaloshinskii-Moriya interaction. In our case, **P** appears due to a gain in the band energy of e_g electrons. The model proposed explains qualitatively the ferroelectricity (FE) in the *E*-phase of undoped ($x = 0$) orthorhombic manganites ($HoMnO_3$ and others). Since this model is based on the existence of zigzag chains, extremely interesting becomes the task to search for doped manganites which consist of the stepped ferromagnetic chains and allow the arise of a spontaneous electric moment. It is to note that for *CE* structure, the polarization of 2D unit cells within the framework of this model becomes zero.

2. Hamiltonian

As an effective Hamiltonian, we take the Hamiltonian of the double exchange model, which, in the case of one-dimensional FM chains of t_{2g} electron spins localized on Mn ions and infinitely large Hund interaction, reduces to the Hamiltonian of the tight binding model:

$$H = \sum_{i\alpha\sigma} \varepsilon_{i\alpha} d^{+}_{i\alpha} d_{i\alpha} + \sum_{ij\alpha\beta} t^{\alpha\beta}_{ij} d^{+}_{i\alpha} d_{i\beta}. \qquad (1)$$

Here, the indices α and β enumerate e_g atomic orbitals; the indices i and j specify Mn ions; and $d^{+}_{j\alpha}$ and $d_{j\alpha}$ are the formation and annihilation operators, respectively, for an e_g electron in the state α at the site j with spin directed along the localized spins (spin up). The energy of the e_g orbital with spin up is taken as the zero energy ($\varepsilon_{i\alpha} = 0$). The oxygen atoms are located between manganese ions in the chains, and the effective hopping integrals between the local e_g spinor components of adjacent Mn ions are expressed in terms of the hopping integral between the Mn e_g orbital and the *p* orbital of the nearest neighboring oxygen ion (the Slater-Koster parameter $V_{pd\sigma}$) calculated in second-order perturbation theory [11]. Hopping of electrons between the AFM aligned chains is forbidden in the approximation of infinitely strong Hund interaction. We consider the case where the e_g level is degenerate. This case poses the most difficult problems in obtaining a gap in the spectrum.

3. Electron spectrum of zigzag ferromagnetic chains

In the case of a simple square lattice with lattice constant a_0, zigzag chains will be designated as $(n1\times m1\times n2\times m2\times\ldots$, where $n1$, $n2$, ... are the numbers of links in the first, second, and subsequent steps along the *x* axis, respectively; and $m1$, $m2$, ... are similar numbers along the *y* axis.

In [11], we have calculated the electron spectrum of ferromagnetic zigzag chains, which corresponds to the spectrum of three-dimensional AFM structures in the approximation of infinitely strong on-site Hund interaction. By studying various zigzag chains, we have concluded that energy gaps always arise in the 1D spectra of e_g electrons and cause the appearance of the insulating state in the corresponding three-dimensional AFM structures at certain values of the electron concentration *x*. In addition to the known spectra of the (1×1) and (2×2) chains (*E* and *CE* structures), we have calculated for the first time the spectrum of the (3×3) zigzag chain. The 2D unit cells of magnetic structures corresponding to (3×3), (2×1×1×2), and (5×1) chains contain 12 atoms. The electron spectra of this type structures have never

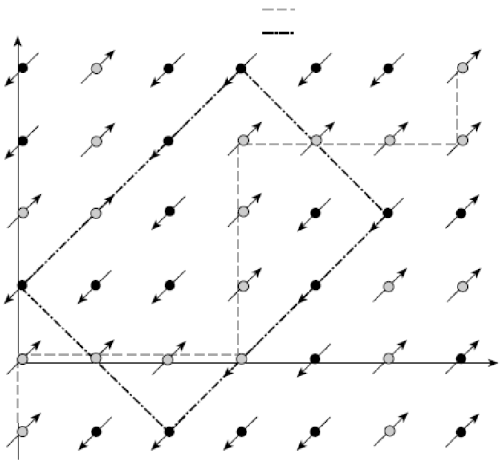

Fig. 1. Magnetic structure consisting of (3×3) zigzag FM chains with (*1*) 6 atoms per 1D unit cell and (*2*) 12 atoms per 2D unit cell. This type of magnetic 2D unit cell was observed in neutron studies of $La_{2/3}Ca_{1/3}MnO_3$.

been calculated previously. Fig. 1 shows a magnetic structure consisting of zigzag (3×3) FM chains with six atoms per 1D unit cell. The dash-dot line shows a 2D unit cell containing 12 atoms. The corresponding 3D unit cell is ($3a \times b \times 2c$) in size, where $a = c = O2a_0$ and $b = 2a_0$.

The spectrum $E(k)$ can be calculated numerically from the secular equation

$$E^{12} - 5E^{10} + 10.5E^8 - E^6 [10 + \cos(k_1 a_0)/2] + 9E^4/16 = 0 \quad (k_1 = 3(k_x + k_y)),$$

and then we find the density of states $\rho(E)$ shown in Fig. 2. The two lower bands and the two upper bands are doubly degenerate, therefore, a magnetic structure consisting of (3×3) chains is an insulator for $x = 1/3$ and 2/3. This type of (canted) magnetic 2D (3D) unit cell was observed in neutron studies of $La_{1/3}Ca_{2/3}MnO_3$ insulator [12].

The (3×3) chain has the lowest energy at $x = 2/3$ among all zigzag chains with six atoms per unit cell, and the corresponding 3D 24-atom unit cell provides a correct qualitative description of the magnetic structure of $La_{1/3}Ca_{2/3}MnO_3$ doped manganite. Further theoretical magnetic structure refinement of this compound is possible within the approach suggested in [13]. Our investigation of the spectrum dependence on the chain geometry has shown that the energy reaches a minimum for the most symmetric chains like (2×2), (3×3), and so on, where the 3D unit cells have a minimum size.

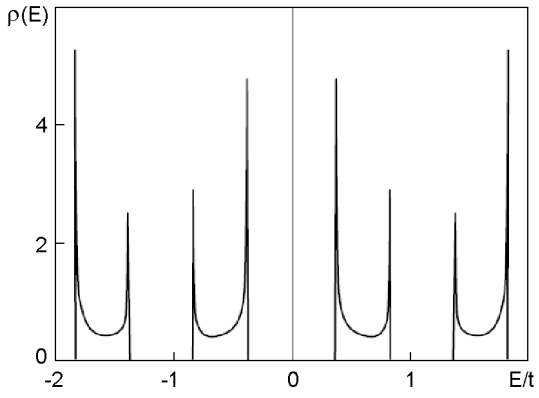

Fig. 2. Density of states for the (3×3) chain.

4. Ferroelectricity in the AF dielectric state of the doped manganites

Of the greatest interest are the calculation results of the magnetic structure which consists of one-dimensional symmetrical FM zigzag (3×3) chains, since upon simultaneous consideration of double exchange and deformation of oxygen octahedrons in this magnetic structure (as in the *E*-phase) the ferroelectricity (gigantic spontaneous polarization *P*) is possible due to the additional displacement of oxide ions that belong to ferromagnetic chain.

The buckling ($GdFeO_3$ type) distortion present in the orthorhombic perovskites plays a crucial role in ferroelectricity generating in our new magnetic phase. The buckling reduces effectively the Hamiltonian symmetry although it is still invariant with respect to the inversion symmetry centers located at each Mn site. The FE polarization emerges only due to the spontaneous symmetry violation caused by the magnetic order (*E*-phase). For *CE* structure, the polarization of 2D unit cells becomes zero. However, for the magnetic structure based on (3×3) chains, the spontaneous polarization vector *P* is again different from zero (Fig. 3). Assuming that displacement of oxide ions here remains unchanged in comparison with *E*-structure, it is easy to show that $P(3\times3) = P(1\times1)/3$ and for the manganite $La_{1/3}Ca_{2/3}MnO_3$, $P = 0.2 - 4\mu C/cm^2$. For the magnetic structure on the basis of (4×4) chains, of the spontaneous polarization vector *P* becomes zero again.

The three-dimensional magnetic structures based on the less symmetrical magnetic structures with the same number of

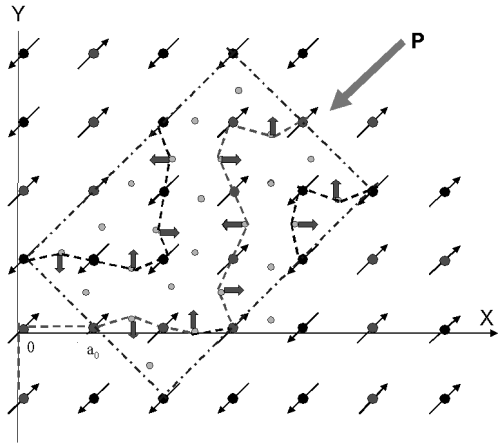

Fig. 3. Oxygen displacements (arrows) and the spontaneous polarization P of our new magnetic structure.

atoms in the one-dimensional unit cell contain a large number of atoms in the 2D unit cell and were not observed during the experiment in the manganites. So, a 2D (3D) unit cell of the magnetic structures which correspond, for example, to the (4×2) and (3×1×1×1) chains contains 24 (48) atoms. Furthermore, their energy exceeds considerably that of magnetic structure based on symmetrical chain (3×3). The latter assertion relates also to the magnetic structures on the basis of chains with the odd number of atoms in 1D unit cell.

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Сегнетоелектрика у легованих манганітах

С.М.Дунаєвський

Обговорюється можливість появи спонтанного електричного моменту P (сегнетоелектрики) в антиферомагнітному діелектричному стані легованих манганітів $La_{1-x}Ca_xMnO_3$. Наближення сильного зв'язку та подвійний обмінний гамільтоніан з нескінченно сильною власною взаємодією Хунда застосовуються для обчислення спектра e_g-електронів у манганітах для різних магнітних структур, які складаються з феромагнітних зигзагоподібних спінових ланцюгів, які включають від двох до восьми спінів на одну одновимірну елементарну комірку. Знайдено значення концентрації носіїв x, при яких в антиферомагнітних манганітах $La_{1-x}Ca_xMnO_3$, що містять вищезгадані ланцюги, може виникати зонний ізолювальний стан. На додаток до відомих спектрів ланцюгів (1×1) та (2×2), вперше одержано спектр для зигзагоподібного ланцюга (3×3). Тривимірна елементарна комірка, яка включає цей тип ланцюгів та містить 24 атоми марганцю, дозволяє коректно якісно описати атомні та магнитні структури у манганіті $La_{1/3}Ca_{2/3}MnO_3$. У цій магнітній структурі (як і в E-фазі) може виникати гігантська спонтанна поляризація P як наслідок додаткового зміщення оксидних іонів, які належать до феромагнітних ланцюгів.