**Jahn-Teller distortion and charge, orbital, and magnetic order in NaMn$_7$O$_{12}$**

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(Rceived 14 February 2014; published 28 May 2014)

With the use of band structure calculations we demonstrate that previously reported [A. Prodi et al., Nat. Mater. 3, 48 (2004)] experimental crystal and magnetic structures for NaMn$_7$O$_{12}$ are inconsistent with each other. The optimization of the crystal lattice allows us to predict another crystal structure for the low temperature phase, which is qualitatively different from the one presented before. The AFM-CE type of magnetic order stabilizes the structure with elongated, not compressed, Mn$_{16}^+$O$_6$ octahedra, excluding NaMn$_7$O$_{12}$ from the list of anomalous Jahn-Teller systems. The orbital correlations were shown to exist even in the cubic phase, while the charge order appears only in the low temperature distorted phase.

DOI: 10.1103/PhysRevB.89.201115

PACS number(s): 71.70.Ej, 61.50.Ah, 75.25.Dk

**Introduction.** The quadruple perovskites based on transition metal (TM) ions with a general formula $A'B'_2B''O_{12}$ and mixed occupation of the $A$ sites of the initial $ABO_3$ perovskite structure by $A'$ (cations with large ionic radii $A' = \text{La, Na, Ca, Bi, etc.},$ $A'' = \text{Jahn-Teller (JT) ions such as Mn}^{3+}, \text{Cu}^{2+}$) ions are known for their unusual physical properties. CaCu$_3$Ti$_4$O$_{12}$ shows a giant dielectric constant [1], LaCu$_3$Fe$_4$O$_{12}$ demonstrates nontrivial charge ordering [2], and CaMn$_7$O$_{12}$ is multiferroic with the largest magnetically induced electric polarization measured to date [3], associated with incommensurate structural modulations coupled with the rotation of the singly occupied $\epsilon_g$ orbital of the Mn$^{3+}$ ion [4]. The ferroelectric properties of another quadruple perovskite, BiMn$_7$O$_{12}$, are also related to the orbital degrees of freedom, which is justified by the study of different doping regimes [5].

The $A$ site ordered quadruple perovskite NaMn$_3$Mn$_4$O$_{12}$ was shown to have intriguing properties. The authors of Ref. [6] argued that this system, which on octahedral $B$ sites contains Mn ions with an average valence of 3.5+, could be similar to half-doped manganites such as La$_{0.5}$Ca$_{0.5}$MnO$_3$, and is better than the latter because it does not show disorder caused in the usual manganites by doping. Thus one could hope to get the “cleanest” signatures of charge and orbital order that are typical for half-doped manganites. And indeed, they discovered such ordering, occurring in NaMn$_3$Mn$_4$O$_{12}$ at 180 K, but of a completely different type. With a further decrease of temperature, the authors of Ref. [6] observed the same magnetic structure of CE type (zigzag chains in the $ac$ plane) as in the usual half-doped manganites.

The occupied orbitals of the JT Mn$^{3+}$ ions in half-doped manganites are of $3x^2-r^2$ and $3y^2-r^2$ type, forming stripes in the basal plane, with locally elongated MnO$_6$ octahedra, long axes alternating in the $x$ and $y$ directions. In contrast, it was argued in Ref. [6] that in NaMn$_3$Mn$_4$O$_{12}$ there exists local compression of these octahedra, with occupied orbitals being $x^2-y^2$. This, however, is very surprising. Local compression around JT ions with $\epsilon_g$ degeneracy in insulators is extremely rare: Among hundreds of such known systems, there are practically none, or at best very few, examples with compressed octahedra. This is mostly due to the anharmonicity of the elastic interaction, and to higher-order Jahn-Teller coupling [7–9].

Thus, compounds with compressed Jahn-Teller octahedra for the case of $\epsilon_g$ degeneracy is a very rare phenomenon, and there must be special reasons for such distortions—for example, the layered structure, as in La$_{0.5}$Sr$_{1.5}$MnO$_3$. But even in this case the occupied orbitals are typically of $3x^2-r^2$ and $3y^2-r^2$ type, not $x^2-y^2$ [10]. Thus this conclusion of Ref. [6] is extremely unusual, and it could be very important to understand the reasons for such behavior. This could have a fundamental importance for a large class of materials and phenomena connected with the behavior of systems with JT ions and with orbital ordering—phenomena which play a more and more important role in modern solid state physics [11].

In the present Rapid Communication, the magnetic, electronic, and structural properties of NaMn$_3$O$_{12}$ were studied using ab initio band structure calculations. We show that the charge ordering indeed occurs in the low temperature phase, but the experimentally claimed [6] magnetic and crystal structures are inconsistent with each other. Performing the optimization of the atomic positions and unit cell vectors with fixed volume, we found a different crystal structure consisting of elongated MnO$_6$ octahedra. The orbital correlations resulting in such a structure are shown to exist even in a nondistorted cubic lattice. Thus, NaMn$_3$O$_{12}$ is not an exception from the general rule of only elongated octahedra for $\epsilon_g$ degenerate Jahn-Teller ions, formulated above.

**Crystal and magnetic structure.** It is worthwhile to rewrite the chemical formula of this compound as $(\text{NaMn}_3^{3+})(\text{Mn}_2^{4+}\text{Mn}_3^{4+})\text{O}_{12}$, which shows the relationship to the perovskite structure $ABO_3$. Thus a part of the Mn$^{3+}$ ($d^5$) ions occupies the $A$ positions (Mn$^{3+}$) in the initial perovskite structure having a square surrounding, while the rest of the Mn ions are situated in the octahedral $B$ sites (Mn$^{4+}$ and Mn$^{4+}$). The checkerboard in the $ac$ plane charge order of Mn$_B$ develops below $\sim 180$ K (see Fig. 1 in Ref. [6]). Mn chains of the same valence are formed along the $b$ axis.

Above the transition to the charge ordered state, NaMn$_3$O$_{12}$ is paramagnetic (PM) and does not show long range magnetic
the calculations were taken from Ref. [6]. We used the linear muffin-tin orbital (LMTO) for the low temperature experimental crystal structure. With a further decrease of the temperature below 90 K, the order down to 89 K, when the spins of the octahedral Mn ions form an antiferromagnetic (AFM)-CE type of structure [6,12].

Details of the calculations. Crystallographic data used in the calculations were taken from Ref. [6]. We used the linear muffin-tin orbital (LMTO) method [13] for the calculation in the experimental structure. The relaxation of this structure was performed using the pseudopotential (PP) Vienna ab initio simulation package (VASP) [14] in the framework of the projector augmented wave method [15].

In spite of the fact that both methods (LMTO and PP) are not full potential, they were successfully used previously for the study of the Jahn-Teller effects [16–19]. The potential in the LMTO is spherical, but the kinetic part retains the symmetry of the lattice, giving rise to an appropriate orbital pattern, as it will be shown below.

The von Barth–Hedin [20] and Perdew-Burke-Ernzerhof (PBE) [21] versions of the exchange-correlation potentials were utilized in the LMTO and PP calculations, respectively. The strong Coulomb correlations were taken into account via the local spin-density approximation (LSDA)+U (for LMTO) and generalized gradient approximation (GGA) + U (for PP) methods [22]. The values of the on-site Coulomb interaction (U) and Hund’s rule coupling (J_H) parameters were taken as U = 4.5 eV, J_H = 0.9 eV [23]. The integration in the course of the self-consistency was performed over a mesh of 144 k points in the irreducible part of the Brillouin zone.

The von Barth–Hedin parameters were taken into account via the von Barth–Hedin [20] and Perdew-Burke-Ernzerhof (PBE) [21] versions of the exchange-correlation potentials. An AFM-CE type of magnetic structure was used. The Fermi energy is in zero.

We utilized Lichtenstein’s exchange interaction parameter (LEIP) calculation procedure [24] for the Heisenberg Hamiltonian, which is written as $H = \sum_{ij} J_{ij} S_i \cdot S_j$. The summation here runs twice over every pair i,j.

Low temperature phase, experimental structure. We start the investigation of NaMn$_2$O$_4$ with the LSDA+U calculations of the low temperature (LT) experimental structure. The total and partial densities of states (DOS) obtained for the AFM-CE type of magnetic order are shown in Fig. 1. It is easy to see that indeed two octahedral Mn ions show different charge states, which agrees with experimental expectations [6].

One class of octahedral Mn$_A$ ions has a $t_{2g}^1e_g^1$ (i.e., Mn$_A^{3+}$) configuration with the half-filled $x^2-y^2$ orbital (middle panel in Fig. 1). The top of the valence band is defined exactly by these states. This in turn agrees with the crystal field theory: The compression of the MnO$_6$ octahedra along the local z axis should result in a crystal field splitting of the $e_g$ shell, such that the $3z^2-r^2$ goes higher in energy and an electron localizes on the $x^2-y^2$ orbital.

The detailed analysis of the occupation matrices shows that the occupied orbital is the same for all octahedral Mn$^{3+}$ ions. The local magnetic moment on this Mn equals $3.4 \mu_B$. It is reduced with respect to ionic value ($4 \mu_B$) due to hybridization with the O 2p states, which is clearly seen in the density of states (DOS) plot in the range from −7 to −5 eV (most pronounced for the $e_g$ states.)

Another class of octahedral Mn ions shows a valence state of 4+ with a basically empty $e_g$ shell (there is, however, some occupation of these states due to hybridization with oxygen—see the lowest panel in Fig. 1). The magnetic moment on this ion equals $2.9 \mu_B$.

The orbital ordering obtained in the distorted LT phase is presented in Fig. 2. One may see that indeed the single electron in the $e_g$ shell of Mn$_B^{3+}$ ions is stabilized on the $x^2-y^2$ orbital. Since the orbital is the same on each Mn$_B^{3+}$ ion, one may expect that the exchange interaction in the ac plane will be ferromagnetic (FM) (exchange between half-filled and empty $e_g$ orbitals of Mn$_B^{3+}$ and Mn$_A^{3+}$, respectively) [25] with all neighboring Mn$^+_B$, not only with those forming a zigzag chain. Thus, this orbital order should stabilize the FM, and not the AFM-CE, type of magnetic ordering in the ac plane.

In order to check this proposal we calculated the exchange constants with the use of the LEIP formalism. This method allows one not only to find all exchange parameters in one magnetic calculation, but also to analyze the stability of a given magnetic configuration (see, e.g., Ref. [26]). The exchange constants between the octahedral Mn$^{3+}_B$-Mn$^{3+}_A$ ions within one zigzag chain was found to be $J_1 \sim -7$ to 10 K, all FM. For the AFM-CE type of magnetic order the coupling between chains, $J_2$, is expected to be AFM, but LEIP calculation shows that...
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$J_2$ could be AFM or FM, depending on the particular pair: $|J_2| \sim 3$–6 K. Thus this magnetic structure is unstable within LEIP [26]. The total energy calculations indeed show that, e.g., the AFM-$A_{ac}$ (ferromagnetic $ac$ planes, coupled AFM in the $b$ direction—see Fig. 1 in the Supplemental Material [27]) solution is lower in energy than AFM-CE (on 22 meV/f.u.).

To sum up, in contrast to naive expectations, the experimental LT crystal structure leads to orbital ordering that is inconsistent with the experimental magnetic order, and the real band structure calculations also show that an AFM-CE type of magnetic structure does not correspond to the lowest total energy.

**Orbital order in a cubic structure.** In order to resolve this inconsistency we performed the calculation for the cubic structure, taken from the high temperature (HT) phase, but with the cell volume corresponding to the LT one. The magnetic structure is experimental, AFM-CE in the $ac$ plane for the Mn$_B$ and antibody-centered AFM for Mn$_A$. The orbital ordering in the $e_g$ shell obtained is shown in Fig. 3. One may see two distinct features that are different from the results for the experimental LT crystal structure (i.e., with Fig. 2).

First of all, there is no clear charge order in this structure, which is seen from the substantial charge density on the corners of the zigzags, the Mn$_B^{4+}$ ions in the LT experimental structure. This is related to equal volumes of all oxygen octahedra surrounding Mn ions sitting in the $B$ sites in this cubic structure.

The second difference is more important. Even in the absence of the corresponding distortions of the MnO$_6$ octahedra, the single half-filled orbital in the $e_g$ shell of the Mn$_B^{3+}$ ions is of $3z^2$-$r^2$ symmetry (actually these are alternating $3x^2$-$r^2$ and $3y^2$-$r^2$ orbitals). Thus the exchange coupling alone (without lattice distortions) stabilizes a certain orbital order. This orbital pattern is fully consistent with the Goodenough-Kanamori-Anderson rules [25]. It explains the ferromagnetic (FM) coupling in the zigzag chains and antiferromagnetic (AFM) between them (due to the half-filled $t_{2g}$ orbitals).

However, stabilization of the $(3z^2$-$r^2$)-type orbital should lead to a certain distortion of the Mn$_B^{3+}$O$_6$ octahedra: elongation in the $ac$ plane. In order to check this hypothesis we performed the optimization of the atomic positions and cell shape, keeping the volume constant and equal to the volume of the unit cell in the LT phase. The calculations were performed using the VASP code within the GGA + $U$ approximation.

**Lattice optimization.** The Mn$_B^{3+}$O$_6$ octahedra in the optimized structure for the AFM-CE type indeed turn out to be elongated, not compressed (the corresponding crystal structure data are given in the Supplemental Material [27]). There are two long (2.08 Å) and four short (two 1.93 Å and two 1.92 Å) Mn$_B^{3+}$-O bonds. The Mn$_B^{3+}$O$_6$ octahedra remain slightly distorted (the Mn-O bond lengths are 1.92 × 2, 1.93, 1.91, 1.88, and 1.87 Å). The total energy of the optimized structure for the AFM-CE type of magnetic order is 81 meV/f.u. lower than the experimental one.

The magnetic moments on the two types of Mn ions sitting in the $B$ sites (in the middle of the bar and in the corner of the zigzags) were found to be 3.6μ$_B$ and 3.0μ$_B$, which certifies the presence of the charge ordered state. The band gap equals $\sim$0.7 eV.

As it was discussed above, for AFM-CE magnetic structure the stabilization of the $3x^2$-$r^2$ and $3y^2$-$r^2$ orbital ordering is favorable. It coexists with the lattice distortion with locally elongated Mn$_B^{3+}$O$_6$ octahedra. The mechanism of such ordering could be the superexchange interaction [28], but it could be also the elastic interaction of locally distorted Jahn-Teller centers [29].

Since the strength of the superexchange interaction depends on the on-site Hubbard repulsion, we repeated lattice relaxation for a much larger value of $U = 8$ eV and found that, even...
TABLE I. Total energies and absolute values of spin moments on the Mn ions for different magnetic configurations in the ac plane. The atomic positions and the unit cell shape were relaxed for each magnetic structure in the GGA + U calculation. Experimental magnetic orders for the Mn$_A$ ions and AFM order of spins for Mn$_B$ in the b direction were used. We checked that for FM coupling along the b axis AFM-CE type also provides the lowest total energy. Different types of magnetic structures are shown in Fig. 1 in the Supplemental Material [27].

| Magnetic structure | Total energy (meV/f.u.) | Magnetic moments ($\mu_B$) | Mn$_A$$^{3+}$ | Mn$_B$$^{3+}$ | Mn$_B$$^{4+}$ |
|--------------------|------------------------|----------------------------|--------------|--------------|--------------|
| AFM-CE             | 0                      | 3.8                        | 3.6          | 3.0          |
| AFM-A$_{ac}$       | 58                     | 3.8                        | 3.7          | 3.1          |
| AFM-C$_{ac}$       | 72                     | 3.8                        | 3.6          | 2.9          |
| AFM-G$_{ac}$       | 123                    | 3.8                        | 3.7          | 2.8          |

for this $U$, octahedra surrounding Mn$_B$$^{3+}$ ions are elongated in the optimized structure.

However, there may exist other types of magnetic ordering in the ac plane for Mn$_B$, which may result in a different orbital pattern and different lattice distortions (this occurs, e.g., for AFM-A$_{ac}$). To check this possibility we carried out the crystal structure optimization for the AFM-A$_{ac}$, AFM-C$_{ac}$ (FM chains in the ac plane), and AFM-G$_{ac}$ (all neighbors in the ac plane are AFM). One may see from Table I that these three types of magnetic structures are higher in energy than the experimental AFM-CE type.

The situation in NaMn$_7$O$_{12}$ reminds one of that in K$_2$CuF$_4$, in which, on the basis of net tetragonal compression with c/a < 1, it was initially concluded that the CuF$_6$ octahedra are compressed in the c direction, so that K$_2$CuF$_4$ was even cited in the textbooks as the only example with Cu$^{2+}$ in compressed octahedra [25,30]. But it was later shown theoretically [31] and confirmed experimentally [32] that actually CuF$_6$ octahedra are elongated, but with long axes oriented in the a and b directions.

Discussion. Our results demonstrate that the situation in the ordered phase of NaMn$_7$O$_{12}$ should be different from that deduced in Ref. [6]: Whereas the observed charge and magnetic ordering of the CE type are reproduced in our calculation, the orbital order obtained theoretically is completely different from the one previously proposed. Instead of the $x^2-y^2$ orbitals, occupied at all Mn$_B$$^{3+}$ ions, we obtained that the $3x^2-r^2$ and $3y^2-r^2$ orbitals should be occupied, forming a stripe pattern of the same type as in the more conventional half-doped manganites such as La$_{0.5}$Ca$_{0.5}$MnO$_3$.

Such an orbital order naturally explains the AFM-CE type of magnetic structure, observed experimentally, whereas the $x^2-y^2$ orbital ordering proposed in Ref. [6] would give ferromagnetic ac planes. The orbital order obtained in the present Rapid Communication is accompanied (or is caused) by corresponding changes of the crystal lattice not with compressed but with elongated MnO$_6$ octahedra, with long axes alternating in the x and y (i.e., a and c) directions. The average distortion in this case is also a contraction of the unit cell in the b direction, as it was found experimentally [6], but with this average contraction not being due to the respective compression of the MnO$_6$ octahedra along b, but rather elongation in the a and c directions. More careful structural studies, as well as, e.g., NMR or x-ray absorption spectroscopy (XAS) measurements are expected to reveal corresponding extra lattice distortions predicted by the present calculations.

In effect, it turns out that the general rule that the local distortions around the Jahn-Teller centers with double degeneracy always correspond to local elongation is also valid in this system, so that it seems to be valid without any known exceptions. This general message should be kept in mind in studying other systems with double $e_g$ orbital degeneracy.

Acknowledgments. S.S. is grateful to M. Korotin, who showed us his earlier results on the study of the charge and spin states of the Mn ions in this material, and to A. Gubkin and E. Sherstobitova for useful discussions about the symmetry of the crystal lattice of NaMn$_7$O$_{12}$. This work is supported by the Russian Foundation for Basic Research via RFFI-13-02-00374, RFFI-13-02-91341, RFFI-13-02-00050, and the Ministry of Education and Science of Russia (MK-3443.2013.2). The work of D.Kh. is supported by the German project FOR 1346 and by the Cologne University via German excellence initiative. Parts of the calculations were performed on the “Uran” cluster of the IMM UB RAS.

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