Geometric Simulation of Perovskite Frameworks with Jahn-Teller Distortions: Applications to the Cubic Manganites

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A new approach is presented for modeling perovskite frameworks with disordered Jahn-Teller (JT) distortions and has been applied to study the elastic response of the $LaMnO_3$ structure to defects in the JT ordering. Surprisingly, antiphase domain boundary defects in the pattern of ordered JT octahedra, along the [110] and [1$\bar{1}$0] bonding directions, are found to produce 1D stripe patterns rotated 45° along $\mathbf{a}^*$ directions, similar to stripe structures observed in these systems. Geometric simulation is shown to be an efficient and powerful approach for finding relaxed atomic structures in the presence of disorder in networks of corner-shared JT-distorted octahedra such as the perovskites. Geometric modeling rapidly relaxes large supercells (thousands of octahedra) while preserving the local coordination chemistry, and shows great promise for studying these complex systems.

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The manganese-based perovskite compounds $La_{1-x}A_xMnO_3$ (A = Ca, Sr, Ba) are of great interest because of the delicate interplay of charge, magnetic, and lattice degrees of freedom that imbue them with a rich phase diagram [1] and novel properties such as colossal magnetoresistance (CMR) [2,3]. Much of the interesting physics comes from the existence of a Jahn-Teller (JT) distortion which deforms the $Mn^{3+}O_6$ octahedra by elongating them and breaking the degeneracy of the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ electronic orbitals. These orbitals play a key role in electronic transport since doped holes move by hopping from an Mn^{4+} site into the filled $d_{3z^2-r^2}$ orbital of a neighboring site. Through the double-exchange mechanism [4] this also results in a ferromagnetic exchange interaction between localized spins on the two manganite sites instead of the antiferromagnetic superexchange that exists when neighboring orbitals are both filled or empty. Clearly, the ordering of these orbitals is a key factor in the interesting features of the doped manganite phase diagram including the different magnetically ordered states [5] and the CMR itself. When the orbitals are long-range ordered, the ordering can be studied directly using resonant methods [6], or crystallographically from atomic displacements [7]. However, in the interesting doped region where CMR is observed, and in the undoped $LaMnO_3$ compound at high temperature [8] virtually no JT distortion is observed crystallographically. Various techniques indicate that the JT distortions persist locally but are not long-range ordered in these parts of the phase diagram [8].

Quantitative modeling of *disordered* JT-distorted octahedra is difficult in a topologically connected network where the MnO_6 octahedra share oxygen ions at the vertices. This is because the structure is geometrically over constrained; that is, the number of constraints involved in linking the framework together (three at every joined vertex, giving nine per octahedron) exceeds the number of degrees of freedom of the octahedral bodies (six per octahedron). This means that it is not, in general, possible to form the framework with geometrically regular JT octahedra; some degree of distortion of the units is inevitable over and above the imposed JT distortion. This will broaden the distribution of bond lengths and angles, independently of thermal broadening. Geometric frustration can lead to interesting variations in the tilting pattern of the octahedra.

Simulations of JT-distorted systems are difficult using conventional empirical interatomic potentials for a combination of reasons. Standard two-body potentials do not capture the nonspherical behavior of the Mn^{3+} ions, even with the use of a shell model to represent ionic polarization [9]. The angular overlap force field [9,10] successfully duplicates some of the structural properties of manganites. However, a very high degree of computational complexity is required to obtain even qualitative agreement with experiment in the behavior of cell parameters and JT distortions of the octahedra. The cases that interest us, where the ordering of JT orbitals is not perfect, require large simulations that certainly are not tractable using standard approaches. Previous studies have highlighted the importance of elasticity to the nanoscale structure and the properties [11,12] of these systems, though these methods do not produce detailed atom positions and geometries for tilted octahedra.

Here we describe a new method for the rapid simulation of perovskite manganites containing JT distortions, based on a geometric analysis that maintains the local chemistry. It is adapted from a method for modeling silicate framework structures such as quartz and zeolites [13–16]. The method of geometric simulation constrains the bond

lengths and angles of a group of bonded atoms by tethering them to the vertices of a nondistortable geometric template used as a device to steer the motion of the atoms. The atoms are connected to the vertices by harmonic spring forces and the templates are superimposed over the group of atoms by least-squares fitting. Previous studies of aluminosilicates used geometrically regular tetrahedral templates. Here we have extended the procedure to allow for axially elongated octahedral templates used to simulate JT distortions. This allows us to study orbital disorder, as well as to study relaxation of octahedral rotations around chemical impurities in JT-distorted systems. Finally, it also allows the study of doping-induced changes in the octahedral shape, such as would be expected in the small polaron picture in the manganites where discrete sites contain undistorted $Mn^{4+}O_6$ octahedra dispersed in a background of JT-distorted $Mn^{3+}O_6$ octahedra. Here we present results from an initial study that is limited to fixed distributions of ordered JT-distorted octahedra broken up into square domains separated by antiphase boundaries; i.e., the case of quenched orbital disorder. Already, this result is interesting and unanticipated extended 1D structures occur with relaxed atomic structures with stripelike patterns of distortions arising purely from the geometric frustration. This empirical approach does not explicitly address the physical driving forces for the distortion and moment ordering which have been studied elsewhere [11,17], but will yield structural relaxations in the presence of orbital disorder such as in the orbital liquid [8] and glass [18] such as in doped manganite systems.

First we describe the geometrical modeling method implemented here, and illustrated in Fig. 1. We start with some initial positions for all atoms in the supercell. We impose templates having an ideal octahedral shape. We then apply a JT distortion to the templates [Fig. 1(a)], specifying a quenched ordering scheme. We define a "moment" direction for each octahedron; the Mn-O bonds in this direction are elongated. During the relaxation process the atoms and the templates are moved so as to minimize the energy in springs connecting the atoms to the vertices of the templates:

$$U = \frac{1}{2} k_{\text{bend}} \sum b_i^2 + \frac{1}{2} k_{\text{stretch}} \sum s_i^2, \qquad (1)$$

where k_{bend} and k_{stretch} are spring constants and b_i and s_i are the bending and stretching components of the displacement vector as defined in Fig. 1(c). The relaxation proceeds by iteratively repositioning and reorienting the template (without flipping the moment direction) and relaxing the atom position with respect to the templates. After multiple cycles of relaxation the structure reaches equilibrium [Fig. 1(b)]. Spectroscopic data on the frequencies of different phonon modes in manganites [19–21] indicate that the spring constants for stretching and bending motions of $Mn^{3+}O_6$ octahedra are in the ratio of approximately 3:1; we use this ratio in our simulations, with values of 12 and 4 eV/Å^2 [20]. Minimizing the mismatch between the atoms and the vertices of the templates is equivalent to satisfying their length and angle constraints, so that a geometrically relaxed structure will have a low energy [15].

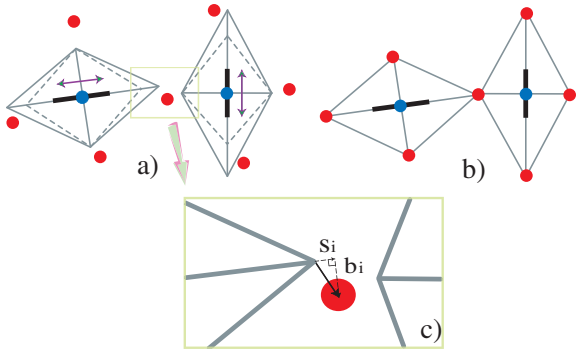


FIG. 1 (color online). (a) Initial atom positions of oxygen (red) and Mn (blue, central atoms) forming regular octahedra. The dashed lines indicate the shape that regular octahedra templates would have. The solid lines represent the axially JT-distorted octahedral templates, with the long axis ("moment" direction) picked out by double-headed arrows. (b) The configuration after iteratively fitting atoms to templates and templates to atoms. Black sticks represent moments. (c) Enlargement of the central area of panel (a) showing how the displacement of an atom from a template vertex is decomposed into stretching and bending components, each of which has a spring of spring constant k and natural length zero associated with it.

As a first case we consider how the tilting pattern of the octahedra in *fully-ordered* $LaMnO_3$ arises from the checkerboard arrangement of moments alternating in the xy plane. In the JT-distorted octahedra about Mn^{3+}, previous studies [22–24] reported a large difference between the long (2.16–2.17 Å) bond and the slightly split short (1.91 Å) and medium (1.96 Å) bonds. Since the splitting is small between the short and medium bonds, for the first approximation we use a long bond of 2.16 Å and a short bond of 1.94 Å, and cell parameters from [8]. We constructed the initial framework by starting with the atomic fractional coordinates of a supercell of cubic perovskite (no JT distortion). The cell parameters and geometric templates of JT-distorted octahedra, in the pattern of moments appropriate for fully ordered $LaMnO_3$, were then superposed on this network. We then perturbed (randomly displaced by up to 0.01 Å) all the atom positions and relaxed the structure geometrically. As a result all the octahedra tilted. The geometrically relaxed model was compared against data and against parameters refined from the data using the program PDFFIT [25]. The data were collected at 300 K on the sample described in Ref. [8], using the NPDF diffractometer at LANSCE at Los Alamos National Laboratory. In both the experimental and simulated structures the average O-Mn-O angles remained at 90° with variations on the order of half a degree. In the initial perovskite structure the Mn-O-Mn angles were all set to 180°, while in the geometrically relaxed

structure those angles had an average value of $162 \pm 6°$ compared with $155 \pm 4°$ from experiment [8]. Full relaxation of this structure with 1728 polyhedra took about 5 CPU minutes on 1 processor. To illustrate the importance of the tilt in the structure we show (Fig. 2) the pair distribution function (PDF) $G(r)$ observed from experiment compared to that calculated for our geometrically relaxed (ordered) structure. Additionally we show the $G(r)$ of the untilted starting model, to demonstrate the changes in the geometrically relaxed structure. There is remarkably good agreement between the experimental and geometrically relaxed PDFs, considering that the model is not being fit to the data. This shows that our model successfully produces the JT distortions and tilting of the octahedra.

As a second case we consider medium-range order in the pattern of moments. We have investigated the effects of introducing antiphase domain boundaries into the ordered pattern of moments to see how the structure relaxes when undesirable short-short and long-long bond contacts appear in the structure. Geometric frustration due to incompatible adjacent moments leads to additional tilting of the octahedra and hence a strong perturbation of the atomic positions. We once again use the cell parameters from [8] and initial atomic fractional coordinates from cubic perovskite. Introducing an antiphase modulation of moments in planes in a single direction (x or y) produces (unsurprisingly) a stripelike domain structure along the direction of moment modulation. Octahedra near the domain walls are frustrated while those further from the walls are tilted as normal.

When we introduce a 2D planar antiphase domain pattern of moments (along the [110] and $[1\bar{1}0]$ orthorhombic directions), as shown schematically in the inset of Fig. 3(a), the results are more interesting and unexpected. After geometric relaxation, the modulation of atomic positions reveals a 1D stripelike pattern running along the $\mathbf{a}^*$ orthorhombic direction [Fig. 3(a)]. The underlying 2D checkerboard pattern of defects in the moment ordering is hidden. The stripes are made up of two distinct behaviors of tilt patterns: A and B. In A-type areas, octahedra are highly tilted relative to cubic perovskite (with an Mn-O-Mn angle of around 140–150°), with octahedra in alternate layers along z tilting in opposite directions. In B-type areas, octahedra are less tilted, with Mn-O-Mn angles close to 180°. The inclusion of steric interactions with La ions does not qualitatively change the result and does not disrupt the stripe.

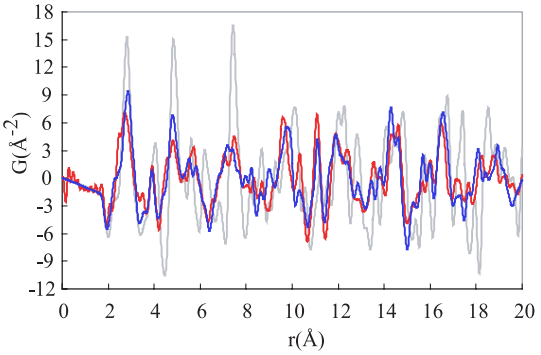


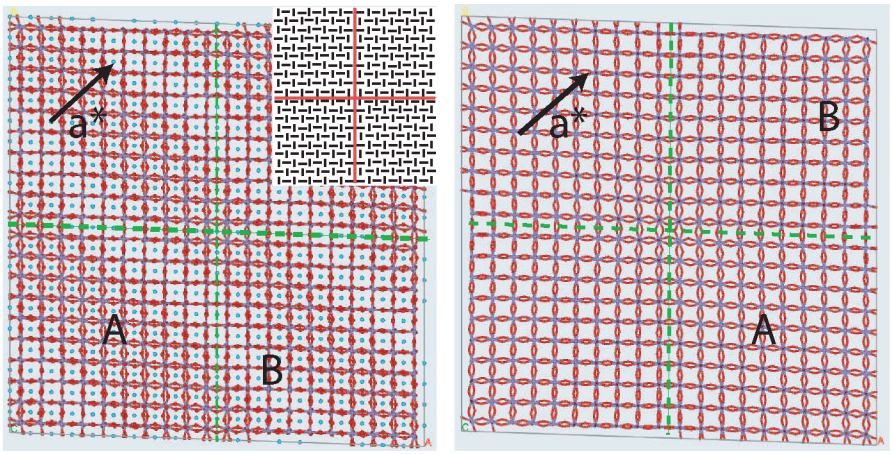
FIG. 2 (color online). The pair distribution functions, $G(r)$, for the experimental data from $LaMnO_3$ collected at 300 K (red), the untilted starting model (gray), and the relaxed simulated structure of fully ordered JT-distorted octahedra (blue). Note, that the relaxed simulated structure has not been fit to the experimental data; the improved match is entirely due to the presence of JT distortion and octahedral tilting.

These simulations were performed on periodic structures with varying sizes of domain in the xy plane and with either two or four layers of octahedra along the z direction. Such regular, periodic, square domain structures are idealizations of the real structures of short-range ordered JT distortions that are thought to exist in the orbitally disordered phase of $LaMnO_3$ at high temperature [8]. However, they do provide interesting insight into the elastic response of the lattice to such defects. These stripes arise purely from the *geometric frustration* introduced by the insertion of the domain walls.

The stability of the stripe depends on the size of the domains of moment ordering. For domains larger than 11×11 octahedra, the stripe is the stable ground state. For domains with sizes between 7×7 to 11×11 octahedra (about 28 to 44 Å), the pattern is metastable, persisting for some thousands of iterations before collapsing into a post-stripe pattern, shown in Fig. 3(b). In the stripe pattern, the width of area B (untilted) does not change with the size of the supercell, being always around 3 to 4 octahedra (12–16 Å) wide. The width of area A does vary with the domain size.

We note that a symmetry lowering orthorhombic distortion exists in the unit cell, consistent with observations of the physical system [22]. We tested for the existence of the stripe structures for the tetragonal case. 1D stripes were again formed, with wave vectors sometimes along $\mathbf{a}^*$ and sometimes along $\mathbf{b}^*$. This suggests that the symmetry breaking from a 2D domain pattern to a 1D relaxed structure of tilts is inherent in the coupling between the defects and the octahedral network. The underlying orthorhombicity then simply selects the preferred orientation of the stripe. We have also made the moment ordering pattern rectangular, with different periodicities along the [110] and $[1\bar{1}0]$ directions. This produces a stripe along the domain diagonal, so that the modulation wave vector lies near but not exactly parallel to $\mathbf{a}^*$, as observed in some manganite systems [26,27].

To sum up the domain studies, a stripe pattern along $\mathbf{a}^*$, which would conventionally be attributed to a charge ordering pattern [28,29] or a charge-orbital ordering pattern [17] along $\mathbf{a}^*$, can in fact be produced by geometric frustration due to defects in a 2D moment ordering pattern, where the antiphase boundaries (the regions of high moment frustration) do not lie along $\mathbf{a}^*$. Thus, a contribution towards the stability of 1D structural modulations comes



(a) (b)

FIG. 3 (color online). (a) The striped pattern of atomic displacements viewed down the c axis. The orthorhombic $\mathbf{a}^*$ direction is labeled. Green dashed lines indicate the positions of antiphase domain walls in the quenched pattern of moments. Regions of distinct tilt patterns that occur in the relaxed structures are indicated as A and B. Oxygens are red, Mn atoms are dark blue, La interstitial atoms are shown in pale blue. Mn-O bonds are shown as lines. The lobelike patterns in area A are due to tilting of the octahedra, making oxygen atoms noncollinear when viewed along the c axis. Inset: Schematic view of the quenched 2D domain pattern of moments imposed on the simulation (moments here are the long bonds of JT octahedra). Red lines indicate the antiphase domain walls. (b) The poststripe structure obtained from smaller domains.

from the elastic response of the octahedral network to 2D defects in JT ordering.

We intend to use this method to study the disorder of moments, e.g., high-temperature structures [8]. We would like also to investigate doped structures with charge ordering. In this case there is a difference in the shape between Mn^{4+} polaronic octahedra and Mn^{3+} JT octahedra, which can be represented by two different shaped templates. This means that for any proposed scheme of charge and moment ordering we can evaluate the geometric consequences.

In summary, we have shown that the method of geometrical simulation allows for the representation of Jahn-Teller distortion of octahedra. This makes possible rapid and simple simulations of large supercells of manganite framework structures for the evaluation of proposed moment ordering schemes. We investigate medium-range ordering of JT octahedra in $LaMnO_3$ using a domain model, obtaining the unexpected result that modulations of atomic positions with wave vectors parallel or close to $\mathbf{a}^*$ can be obtained from two-dimensional moment ordering patterns along diagonal directions.

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[1] J. F. Mitchell *et al.*, Phys. Rev. B **54**, 6172 (1996).
[2] T. Saitoh *et al.*, Phys. Rev. B **62**, 1039 (2000).
[3] *Colossal-Magnetoresistive Oxides*, edited by Y. Tokura (Gordon and Breach, New York, 2000).
[4] C. Zener, Phys. Rev. **81**, 440 (1951).
[5] J. B. Goodenough, Phys. Rev. **100**, 564 (1955).
[6] Y. Okimoto *et al.*, Phys. Rev. B **55**, 4206 (1997).
[7] C. P. Adams *et al.*, Phys. Rev. Lett. **85**, 3954 (2000).
[8] X. Qiu *et al.*, Phys. Rev. Lett. **94**, 177203 (2005).
[9] S. M. Woodley *et al.*, Chem. Mater. **15**, 1669 (2003).
[10] S. M. Woodley *et al.*, J. Chem. Phys. **119**, 9737 (2003).
[11] D. I. Khomskii *et al.*, Phys. Rev. B **67**, 134401 (2003).
[12] A. R. Bishop, J. Phys. Chem. Solids **65**, 1449 (2004).
[13] G. D. Gatta *et al.*, Phys. Chem. Miner. **31**, 1 (2004).
[14] A. Sartbaeva *et al.*, J. Phys. Condens. Matter **16**, 8173 (2004).
[15] A. Sartbaeva *et al.*, J. Phys. Condens. Matter **17**, 1099 (2005).
[16] S. A. Wells *et al.*, J. Appl. Crystallogr. **37**, 536 (2004).
[17] T. Hotta *et al.*, Phys. Rev. Lett. **86**, 4922 (2001).
[18] M. A. Ivanov *et al.*, Sov. Phys. Solid State **20**, 1744 (1978).
[19] K. H. Ahn and A. J. Millis, Phys. Rev. B **58**, 3697 (1998).
[20] A. J. Millis, Phys. Rev. B **53**, 8434 (1996).
[21] M. N. Iliev *et al.*, Phys. Rev. B **57**, 2872 (1998).
[22] J. Rodŕıguez-Carvajal *et al.*, Phys. Rev. B **57**, R3189 (1998).
[23] Q. Huang *et al.*, Phys. Rev. B **55**, 14 987 (1997).
[24] T. Proffen *et al.*, Phys. Rev. B **60**, 9973 (1999).
[25] T. Proffen *et al.*, J. Appl. Crystallogr. **32**, 572 (1999).
[26] R. Wang *et al.*, Phys. Rev. B **61**, 11 946 (2000).
[27] M. Hervieu *et al.*, Eur. Phys. J. B **8**, 31 (1999).
[28] C. H. Chen *et al.*, Phys. Rev. Lett. **76**, 4042 (1996).
[29] S. Mori *et al.*, Nature (London) **392**, 473 (1998).