TMS2015 Annual Meeting Supplemental Proceedings
TMS (The Minerals, Metals & Materials Society), 2015

TMS2015

144th Annual Meeting & Exhibition

SUPPLEMENTAL PROCEEDINGS

Advances in Thin Films for Electronics and Photonics

Role of Complex Energy Landscapes and Strains in Multiscale Inhomogeneities in Perovskite Manganites

Keun Hyuk Ahn[1], Tsezar F. Seman[2,3], Turab Lookman[4], A. R. Bishop[4]

[1] Department of Physics, New Jersey Institute of Technology; Newark, NJ 07102, USA
[2] Department of Physics, Northern Illinois University; De Kalb, IL 60115, USA
[3] Advanced Photon Source, Argonne National Laboratory; Argonne, IL 60439, USA
[4] Theoretical Division, Los Alamos National Laboratory; Los Alamos, NM 87545, USA

Keywords: Inhomogeneity, Manganite, Strain, Energy landscape

Abstract

Perovskite manganites have attracted considerable attention recently due to inhomogeneities in multi-functional properties, observed by various high resolution probes. We present an analysis of the essential role played by complex energy landscapes in the nanometer to micron-scale inhomogeneities observed in perovskite manganites using a model expressed in terms of symmetrized atomic-scale lattice distortion modes. We also discuss the origin for the stability of large metal and insulator domains in the absence of defects. We demonstrate that an intrinsic mechanism, which specifically involves long-range interactions between strain fields, the Peierls-Nabarro energy barrier, and complex energy landscapes with multiple metastable states is responsible for the inhomogeneities in perovskite manganites. This is in contrast to an extrinsic mechanism such as chemical randomness. We highlight experimental results which support our intrinsic, rather than extrinsic, mechanism.

Introduction

One of the most important research topics on minerals, metals, and materials has been phase transition. Therefore, understanding unusually stable metal-insulator phase coexistence observed in perovskite manganites [1, 2, 3, 4, 5] would have broad implications on applications of materials, particularly in the form of thin films, for which different phases can be imaged, accessed, and manipulated from the perpendicular direction. In this proceeding, we first summarize basic properties of manganites, particularly the properties that we believe important for unusually stable phase coexistence. Next, we briefly describe our model, originally proposed in Ref. [6] and explained in detail in Ref. [7], where details of the work presented here can be found We also discuss the origin of unusual stability of phase coexistence. Conclusions are provided at the end.

Basic properties of perovskite manganites

Perovskite manganites typically have the chemical formula of $RE_{1-x}AK_x\mathrm{MnO}_3$, where RE represents rare earth elements, such as La, Nd, and Pr, and AK represents alkaline earth metal elements such as Ca and Sr [5, 8, 9]. One of the key pieces of physics in manganites is the strong coupling between the lattice distortions and the state of the

outermost shell e_g electrons on Mn ions [9]. If an e_g electron is localized at a Mn site in the insulating phase, the symmetry of the surrounding oxygen octahedron is lowered from cubic to tetragonal through a Jahn-Teller coupling. At low temperatures, the distorted octahedra order in particular patterns, often referred to as charge and orbital ordered state. For example, in $La_{0.5}Ca_{0.5}MnO_3$, the long Mn-O bonds of the elongated octahedra form a zigzag pattern in the xy plane [10], responsible for short-wavelength lattice distortions. The repetition of the short Mn-O bonds along the z-direction gives rise to the uniform tetragonal (more accurately orthorhombic) distortion. Such lattice distortions are absent in the metallic phase due to the delocalized nature of the e_g electrons.

We propose that the characteristics of manganites that are important for stable metal-insulator phase coexistence are that the phase with short wavelength and uniform distortions is an insulator, whereas the phase without distortion is a metal, and that these two phases are separated by an energy barrier, forming a first-order-like energy landscape. It is the structural aspect that is essential for the multiphase coexistence, which is common to purely elasticity-based materials, such as martensites [11]. Manganites are special because of the strong coupling between their structural templates and other novel properties, such as electronic, magnetic, and optical properties. Therefore, external perturbations, such as magnetic field, electric field, or X-rays can induce changes in structures and, therefore, inhomogeneity.

Model for strain-induced metal-insulator phase coexistence

To capture the essential properties of manganites in a simple model, we proposed an approach that uses atomic-scale modes to describe lattice distortions [12]: general lattice distortions are separated into short-wavelength modes (s_x, s_y) and long-wavelength strain modes (e_1, e_2, e_3), as shown in Fig. 1(a) for the case of a monatomic square lattice in 2-dimensional space. This approach is ideal for the problem at hand. In particular, the distorted lattice with s_x and negative e_3, or equivalently that with s_y and positive e_3 [see Fig. 1(a)], leads to a gap in the electronic density of states (DOS) near electronic energy $\varepsilon = 0$. Thus, if the Fermi energy ε_F lies in the gap, the distorted lattice behaves as an insulator. Such short-wavelength and uniform-mode lattice distortions can be simultaneously generated through the minimal symmetry-allowed coupling $C_3(s_x^2 - s_y^2)e_3$ at each site, where C_3 is the strength of this coupling. In the structure without distortions, the DOS has no gap, and the electrons are in a metallic state. Therefore, these undistorted and distorted states capture the essential structural and electronic features of manganites mentioned above. The energy landscape shown in Fig. 1 has been considered in simulations. Using the Euler model, we obtain stable coexistence of a metallic undistorted phase and an insulating distorted phase, as shown in Fig. 2. Details of our model are described in Refs. [6] and [7].

Stability of phase coexistence

We examine the stability of phase coexistence against various perturbations. We first study the stability against a uniform shift of the domain wall, as shown in Figs. 3 and

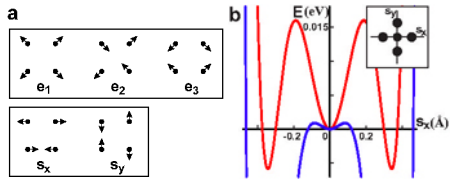

Figure 1: (Color online) Modes and energy landscape [6]. (a) Atomic scale lattice distortion modes for a monatomic square lattice in 2-D. All modes are illustrated for positive values of the variables. (b) Energy landscapes along $s_y = 0$ in $s_x - s_y$ plane for two sets of parameter values (the global minimum of the blue curve has E = - 0.11 eV.). The solid circles in the inset schematically represent the locations of local minima in the $s_x - s_y$ plane. In this proceeding, only the results for the upper red curve are presented. See Refs. [6] and [7] for the results for the lower blue curve, which gives rise to a nanoscale inhomogeneity.

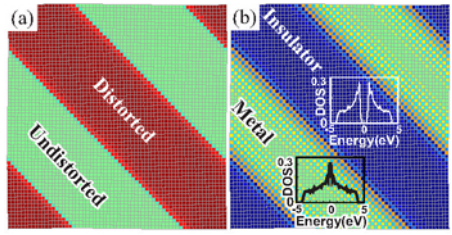

Figure 2: (Color online) (a) Stable configuration of distorted and undistorted domains for a 64×64 lattice for the energy landscape with a deep local minimum, shown by the upper red curve in Fig. 1. The color represents p_3 with red and green for s_0^2 and 0, respectively [6, 7]. (b) Map of the local electron DOS calculated at $E = 0$ for the distortions in (a). Red, green, and blue correspond to 0.6, 0.3, and 0 state per site per eV, respectively. Local electron DOS per site per eV calculated at the center of the undistorted and the distorted regions are shown over the corresponding domains.

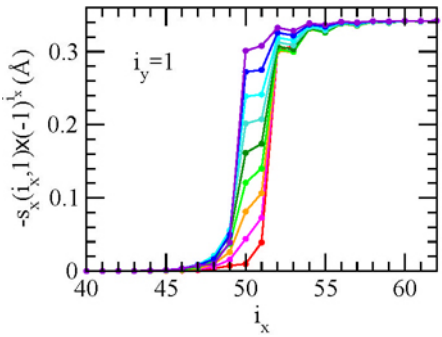

Figure 3: (Color online) The red dots represent the profiles of $s_x(i_x, i_y) \times (-1)^{i_x+i_y}$ with $i_y = 1$ near the domain boundary in Fig. 2(a). Dots of other colors show how this profile changes as the domain boundary shifts uniformly by two interatomic distances.

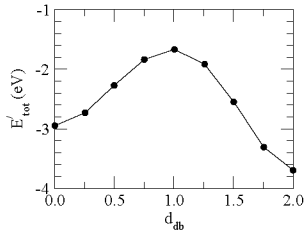

Figure 4: Total energy $E'_{\rm tot}$ for the 64×64 system versus the location of the domain boundary, as the boundary moves by two interatomic distances. Each point is found from the corresponding curve in Fig. 3.

4. Figure 3 shows how the profile near the boundary between an undistorted metallic domain on the left and a distorted insulating domain on the right evolves as the domain wall moves by two interatomic distances. Due to the discreteness of the lattice, the profile cannot be simply shifted parallel but changes its discrete functional form, which gives rise to an energy barrier as shown in Fig. 4, an example of a Peierls-Nabarro barrier [13]. Such an energy barrier inherent to atomic scale discreteness of materials prevents a simple expansion of the lower energy insulating phase through the uniform shift of the domain wall, which demonstrates the inadequateness of continuum models, such as a phase field model, for the coexistence of two phases with *different* energies.

Next, we study the stability against nonuniform domain wall modification, as shown in Figs. 5 and 6. For the simulations shown in Fig. 5, we convert a patch of region near the interface from undistorted high energy phase into a distorted low energy phase, and relax according to the Euler method. The results show that the system relaxes back to the original configuration, indicating the stability of the phase coexistence. We plot the distortion components and energy distribution in Fig. 6 for the intermediate state shown in Fig. 5(b). We find that the distortion components in the converted patch are

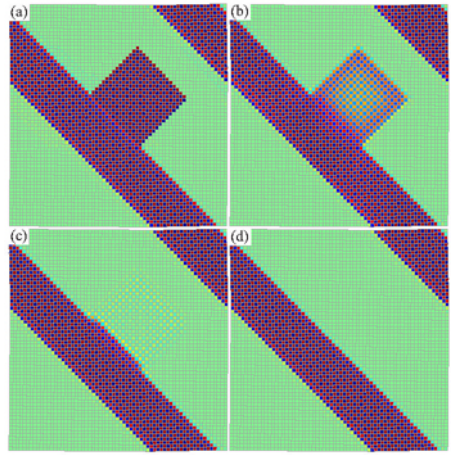

Figure 5: (Color online) Simulation of the domain wall stability against a small nonuniform modification of the domain boundary for the configuration similar to Fig. 2(a). Color represents s_x distortions with red and blue for distorted plaquettes and green for undistorted plaquettes, (a) represents the initial perturbed configuration, (b) and (c) show intermediate configurations, (d) represents the final stable configuration, which is identical to the original configuration before the perturbation, similar to Fig. 2.

not identical to the low energy phase deep inside the domain, as can be seen in Fig. 6(c). This is due to the constraint of lattice distortions, or, long range interactions between strain fields. Therefore, the energy cost for creating such a patch is not confined within the domain wall, but is distributed over the whole patch as shown in Fig. 6(d), which is responsible for unusual stability of the phase coexistence in manganites.

Results of further simulations, such as relaxation after converting a larger patch into a distorted state or relaxation after converting a patch from distorted state into undistorted state, are described in Ref. [7].

Conclusions

The results demonstrate that the long range interaction between stain fields, complex energy landscapes, and the Peierls-Nabarro energy barrier play an important role in metal-insulator coexistence in perovskite manganites. Our theory emphasizes the important role played by the lattice degrees of freedom for complex phenomena in minerals, metals, and materials, which has been further supported by recent experiments [14].

References

[1] M. Uehara, S. Mori, C. H. Chen, and S.-W. Cheong, "Percolative phase separation underlies colossal magnetoresistance in mixed-valent manganites," *Nature (London)*,

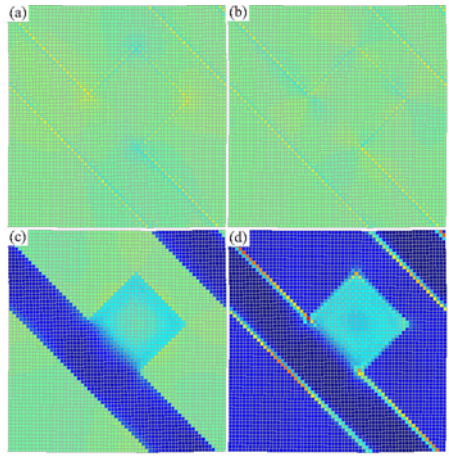

Figure 6: (Color online) Modes and energy distribution for the configuration shown in Fig. 5(b). Colors in (a), (b) and (c) show $e_1(\vec{i})$, $e_2(\vec{i})$, and $e_3(\vec{i})$ with red and blue corresponding to ± 0.45 Å and green to zero. Colors in (d) show energy distributions, with red and blue corresponding to 0.06 eV and -0.006 eV, respectively. Typical values of $e_3(\vec{i})$ and $E_{\rm tot}(\vec{i})$ inside the converted patch are -0.08 Å and 0.02 eV, respectively.

399 (1999), 560-563.

[2] M. Fäth, S. Freisem, A. A. Menovsky, Y. Tomioka, J. Aarts, and J. A. Mydosh, "Spatially Inhomogeneous Metal-Insulator Transition in Doped Manganites," *Science*, 285 (1999), 1540-1542.

[3] Ch. Renner, G. Aeppli, B.-G. Kim, Y.-A. Soh, and S.-W. Cheong, "Atomic-scale images of charge ordering in a mixed-valence manganite," *Nature (London)*, 416 (2002), 518-521.

[4] L. Zhang, C. Israel, A. Biswas, R. L. Greene, and A. de Lozanne, "Direct Observation of Percolation in a Manganite Thin Film," *Science*, 298 (2002), 805-807.

[5] N. Mathur and P. Littlewood, "Mesoscopic texture in manganites," *Phys. Today*, 56 (2003), 25-30.

[6] K. H. Ahn, T. Lookman, and A. R. Bishop, "Strain-induced metalinsulator phase coexistence in perovskite manganites," *Nature (London)*, 428 (2004), 401-404.

[7] K. H. Ahn, T. F. Seman, T. Lookman, and A. R. Bishop, "Role of complex energy landscapes and strains in multiscale inhomogeneities in perovskite manganites," *Phys. Rev. B*, 88 (2013), 144415.

[8] M. B. Salamon and M. Jaime, "The physics of manganites: Structure and transport," *Rev. Mod. Phys.*, 73 (2001), 583-628.

[9] A. J. Millis, P. B. Littlewood, and B. I. Shraiman, "Double Exchange Alone Does Not Explain the Resistivity of $La_{1x}Sr_xMnO_3$," *Phys. Rev. Lett.*, 74 (1995), 5144-5147; H. Röder, J. Zang, and A. R. Bishop, "Lattice Effects in the Colossal-Magnetoresistance Manganites," *ibid.*, 76 (1996), 1356-1359; A. J. Millis, B. I. Shraiman, and R. Mueller, "Dynamic Jahn-Teller Effect and Colossal Magnetoresistance in $La_{1x}Sr_xMnO_3$," *ibid.*, 77 (1996), 175-178; A. J. Millis, "Lattice effects in magnetoresistive manganese," *Nature (London)*, 392 (1998), 147-150.

[10] C. H. Chen and S.-W. Cheong, "Commensurate to Incommensurate Charge Ordering and Its Real-Space Images in $La_{0.5}Ca_{0.5}MnO_3$," *Phys. Rev. Lett.*, 76 (1996), 4042-4045.

[11] V. Podzorov, B. G. Kim, V. Kiryukhin, M. E. Gershenson, and S.-W. Cheong, "Martensitic accommodation strain and the metal-insulator transition in manganites," *Phys. Rev. B*, 64 (2001), 140406(R).

[12] K. H. Ahn, T. Lookman, A. Saxena, and A. R. Bishop, "Atomic scale lattice distortions and domain wall profiles," *Phys. Rev. B*, 68 (2003), 092101.

[13] F. Nabarro, *Theory of Crystal Dislocations* (Clarendon, Oxford, U.K., 1967).

[14] A.C. Mclaughlin, F. Sher, and J.P. Attfield, "Negative lattice expansion from the superconductivityantiferromagnetism crossover in ruthenium copper oxides," *Nature*, 436 (2005), 829-832; R.P. Rairigh, G. Singh-Bhalla, S. Tongay, T. Dhakal, A. Biswas, and A.F. Hebard, "Colossal magnetocapacitance and scale-invariant dielectric response in phase-separated manganites," *Nature Phys.*, 3 (2007), 551-555; J. Cao, E. Ertekin, V. Srinivasan, W. Fan, S. Huang, H. Zheng, J.W.L. Yim, D.R. Khanal, D. F. Ogletree, J.C. Grossman, and J. Wu, "Strain engineering and one-dimensional organization of metalinsulator domains in single-crystal vanadium dioxide beams," *Nature Nanotech.*, 4 (2009), 732-737; Y. Murakami, H. Kasai, J.J. Kim, S. Mamishin, D. Shindo, S. Mori, and A. Tonomura, "Ferromagnetic domain nucleation and growth in colossal magnetoresistive manganite," *ibid.*, 5 (2010), 37-41; T.-H. Kim, M. Angst, B. Hu, R. Jin, X.-G. Zhang, J.F. Wendelken, E.W. Plummer, and A.-P. Li, "Imaging and manipulation of the competing electronic phases near the Mott metal-insulator transition," *Proc. Natl. Acad. Sci. U.S.A.*, 107 (2010), 5272-5275; K. Lai, M. Nakamura, W. Kundhikanjana, M. Kawasaki, Y. Tokura, M.A. Kelly, and Z.-X. Shen, "Mesoscopic Percolating Resistance Network in a Strained Manganite Thin Film," *Science*, 329 (2010), 190-193; G.E. Ice, J.D. Budai, and J.W.L. Pang, "The Race to X-ray Microbeam and Nanobeam Science," *ibid.*, 334 (2011), 1234-1239; A. Y. Borisevich, E. A. Eliseev, A. N. Morozovska, C.-J. Cheng, J.-Y. Lin, Y. H. Chu, D. Kan, I. Takeuchi, V. Nagarajan, and S. V. Kalinin, "Atomic-scale evolution of modulated phases at the ferroelectricantiferroelectric morphotropic phase boundary controlled by flexoelectric interaction," *Nat. Commun.*, 3 (2012), 3:775 doi: 10.1038/ncomms1778; D. D. Sarma, D. Topwal, U. Manju, S. R. Krishnakumar, M. Bertolo, S. La Rosa, G. Cautero, T. Y. Koo, P. A. Sharma, S.-W. Cheong, and A. Fujimori, "Direct Observation of Large Electronic Domains with Memory Effect in Doped Manganites," *Phys. Rev. Lett.* 93 (2004),

097202; J. Tao, D. Niebieskikwiat, M. B. Salamon, and J. M. Zuo, "Lamellar Phase Separation and Dynamic Competition in $La_{0.23}Ca_{0.77}MnO_3$" *ibid.* 94 (2005), 147206; T. Z. Ward, J. D. Budai, Z. Gai, J. Z. Tischler, L. Yin, and J. Shen, "Elastically driven anisotropic percolation in electronic phase-separated manganites," *Nature Phys.*, 5 (2009), 885-888.