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Surface Structural Analysis of the Layered Perovskite $Ca_{1.9}Sr_{0.1}RuO_4$ by Low Energy Electron Diffraction I-V

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Abstract – The atomic structure at surface of the layered perovskite $Ca_{1.9}Sr_{0.1}RuO_4$ has been studied by Low Energy Electron Diffraction (LEED) I-V. The perovskite $Ca_{1.9}Sr_{0.1}RuO_4$ of single crystal was cleaved in ultra-high vacuum chamber (the pressure in the chamber was about $1x10^{-10}$ Torr). The experiments were conducted at room temperature (T=300 K). The sharp LEED pattern was observed which indicates that the surface of $Ca_{1.9}Sr_{0.1}RuO_4$ is flat and it is a well ordered crystal. LEED I-V data, nine equivalent beams of the layered perovskite $Ca_{1.9}Sr_{0.1}RuO_4$ were recorded at room temperature. LEED I-V calculation was performed to fit experimental data to obtain the surface atomic structure. The LEED I-V analysis reveals that in the surface of the layered perovskite $Ca_{1.9}Sr_{0.1}RuO_4$ the RuO_6 octahedral are rotated (in-plane rotation) alternating clockwise and counterclockwise. The in-plane rotation at the surface is 11 degrees which is smaller than that in the bulk (13 degree). The Ru – O(1) bond-length at the surface is found to be 1.936 Å which is about the same as in the bulk (1.939 Å). The Ru – O(2) bond length at the surface is 1.863 Å which is much shorter than that in the bulk (2.040 Å). The volume of octahedral $Ru-O_6$ at the surface is reduced by 9% with respect to the bulk. This finding shows that the atomic structure at surface of the layered perovskite $Ca_{1.9}Sr_{0.1}RuO_4$ is significantly different than that in the bulk. These lattice distortions strongly influence its electronic properties.

Key words: Transition Metal Oxide; Perovskite; Surface Atomic Structure; LEED I-V

Introduction

Worldwide, Nano-scale Science, Nano Engineering, and Nano Technology have become a hot topic for discussing in material sciences or material physics. Most international science agenda has been focused on nano scale science and technology. It seems that a lot of nano center is appearing at universities and national laboratories because nano scale materials are so interesting. Its size constraints often produce qualitatively new behavior. Complex materials can be used in nano technological applications since those materials can be designed to have desired properties. For examples: artificially patterned structures, forever-smaller integrated circuits, magnetic storage devices, composite materials, polymer blends, doped transition-metal oxides, self-assembling nanostructures, molecular electronics, etc.

Conceptually, creating a surface material by truncating a single crystal is a controlled way to disturb a coupled system by breaking the translation symmetry, providing a fresh approach to the study of the charge-lattice orbital-spin coupling in transition metal oxide materials (TMOs). These transition metal oxide materials have been investigated extensively because these materials exhibit a lot of fascinating phenomena. For example $SrRuO_4$, this layered perovskite without copper exhibits superconductivity (Maeno *et al.* 1994) and it shows spin-triplet pairing with a p-wave order parameter (Rice and Sigrist, 1995; Graf and Balatsky, 2000). The bulk of this material has a non-distorted tetragonal K2NiF4 structure (*space-group* I4/mmm) with a nonmagnetic ground state (Braden *et al.*, 1997). However, the surface atomic structure of $SrRuO_4$ is quite different than that in the bulk. At the surface, the bulk soft-phonon mode freezes into a static lattice distortion associated with an in-plane rotation of the RuO_6 octahedron (Matzdorf *et al.*, 2000). First-principle

calculations confirm this surface structure and predict a ferro magnetic ground state at the surface (Matzdorf *et al.*, 2000). They concluded that the physical complexity in these phenomena is the result of the strong coupling between charge, lattice, orbital, and spin degrees of freedom in $SrRuO_4$.

Chemically doping a material has been an effective way to explore new emergent phenomena. Recent study shows that the local density of states at the surface of $Ca_{2-x}Sr_xRuO_4$ ($0.1 \leq x \leq 2.0$) clearly shows a strong doping dependent nano scale electronic in-homogeneity (Jiandi *et al.*, 2006). The surface electronic roughness measured by scanning tunneling microscopy (STM) and the inverse spectral weight of quasi particle states determined by angle resolved photoelectron spectroscopy (ARPES) are found to vary with x, indicating a doping-induced electronic disorder in the surface of $Ca_{2-x}Sr_xRuO_4$ (Jiandi *et al.*, 2006). Without any doping of Ca, the atomic structure in the bulk of $SrRuO_4$ has *I4/mmm* symmetry. However, when it is doped with Ca (for x=0.1), the atomic structure in the bulk of $Ca_{1.9}Sr_{0.1}RuO_4$ becomes *Pbca* symmetry (Friedt *et al.*, 2001). Its electronic property changes significantly where the bulk of the bulk of $Ca_{1.9}Sr_{0.1}RuO_4$ behaves as conductor at room temperature but it is insulator for temperature below 154 K (Nakatsuji and Maeno, 2000). The atomic structure in the bulk of $Ca_{1.9}Sr_{0.1}RuO_4$ at room temperature has been measured where it is found that the RuO_6 octahedra are rotated (in-plane rotation) alternating clockwise and counterclockwise by 12.65 degree; the RuO_6 octahedra are tilted (out of plane) by 6.5 degree; Ru-O(1) bond length is 1.94 Å; Ru-O(2) bond length is 2.04 Å; the volume of RuO_6 octahedron is 10.27 Å³ (Friedt *et al.*, 2001). Therefore, it is very interested to study the surface atomic structure of this material. In this paper we report on a detailed surface-structure analysis of $Ca_{1.9}Sr_{0.1}RuO_4$ by Low Energy Electron Diffraction (LEED) I-V at room temperature.

Materials and Methods

High-quality $Ca_{1.9}Sr_{0.1}RuO_4$ single crystal used in this study was grown by the floating-zone technique in the Oak Ridge National Laboratory, Tennessee, USA. The LEED I-V experiment was conducted at the University of Tennessee, Knoxville, Tennessee, USA. The experiment was conducted in the ultra-high vacuum chamber in order to maintain the surface (sample) free from contamination for the duration of the experiment performed. The ultra-high vacuum chamber system is made from a stainless steel vessel pumped by a regular pump, a turbo pump, an ion pump, and a titanium sublimation pump. All experimental apparatus and pumps mounted onto stainless steel flanges were sealed by standard commercial copper gaskets. To achieve ultra-high vacuum, the main chamber was pumped and baked at temperature 150 °C for 24 hours. The pressure in the main chamber was achieved to be about 1×10^{-10} Torr. The main chamber was also shielded with μ-metal to prevent magnetic field effect from outside chamber. The chamber is equipped with Omicron LEED optics. The sample holder was allowed to rotate and tilt the sample to adjust the sample precisely to the normal incidence condition for the LEED experiments. The sample was glued to a sample holder with silver epoxy and a metal post was glued on top of the sample. After inserting the samples into a load-lock chamber, the load lock was closed, pumped and baked for 8 hours at temperature 150 °C to harden and degas the silver epoxy glue and to achieve ultrahigh-vacuum conditions. The samples were then cleaved at room temperature by breaking off the post in the load-lock chamber. After that the sample was immediately transferred to the main ultra-high vacuum chamber.

A schematic LEED I-V experiment is shown in Figure 1. LEED intensities of diffracted beams as a function of incident electron energy were recorded using a video LEED system with 0.5 eV increments at normal incidence at room temperature (T=300 K). Normal incidence was determined by adjusting the position of the sample until the I-V curves of the equivalent beams were identical, i.e., the Pendry R-factor between the equivalent beams is less than 0.1. All equivalent beams were averaged and normalized to the beam current.

Analysis of the LEED I-V spectra was carried out using multiple scattering algorithms (Pendry, 1974; Van Hove *et al.*, 1986) combined with the symmetrized automated tensor-LEED (SATLEED) programs (Barbieri and Van Hove). Energy-dependent phase shifts of Ca, Sr, Ru, and O were calculated within a relativistic formalism from the muffin-tin potentials by using programs of Barbiere and Van Hove (Barbieri and Van Hove). The same phase shifts were used for surface and bulk layers in the calculations. In the calculations, the initial surface structure was set as the bulk atomic structure of $Ca_{1.9}Sr_{0.1}RuO_4$. Calculated intensities are compared to the experimental spectra to search a minimum Pendry R-factor (Rp factor) (Pendry, 1980) by using the automated search algorithm to obtain the surface structures.
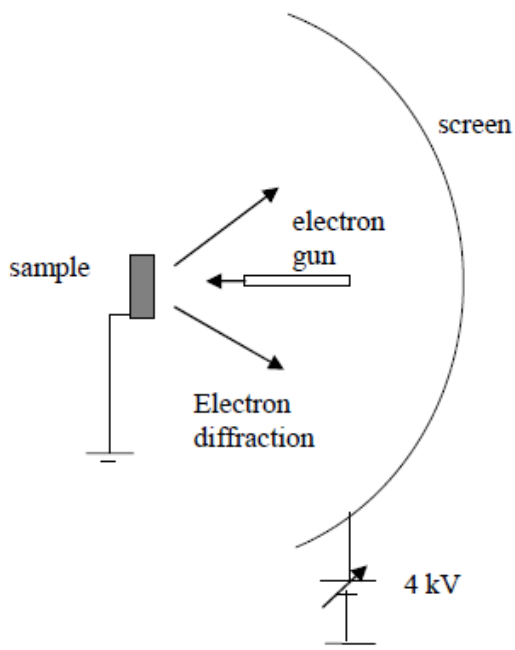
Figure 1. Schematic LEED I-V experiment

Results and Discussion

Sharp LEED patterns have been observed which indicates surface of the layered perovskite $Ca_{1.9}Sr_{0.1}RuO_4$ is well ordered single crystal and the morphology of its surface is flat. An example of LEED pattern of the layered perovskite $Ca_{1.9}Sr_{0.1}RuO_4$ at room temperature is shown in Figure 2.
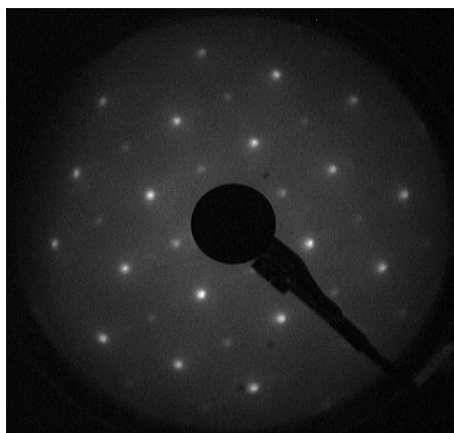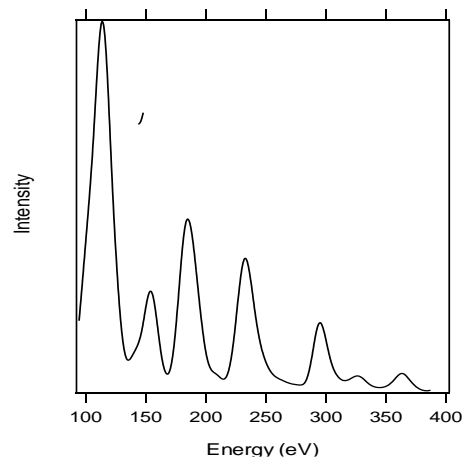

Figure 2. LEED pattern $Ca_{1.9}Sr_{0.1}RuO_4$

Figure 3. I-V spectra (0,2) beam of $Ca_{1.9}Sr_{0.1}RuO_4$

The LEED patterns have been observed at electron energies between 78 and 400 eV. Nine inequivalent beams have been recorded with the total energy of 2296 eV. Those nine inequivalent beams are (0,1); (0,2); (0,3); (1,1); (1,2); (2,2); (1.5,0.5); (1.5,1.5); and (0.5,0.5). One example of beam/data of $Ca_{1.9}Sr_{0.1}RuO_4$ is shown in Figure 3.

We started the structure refinement by using bulk structure of $Ca_{1.9}Sr_{0.1}RuO_4$ where the bulk structure of this material is already known (Friedt *et al.*, 2001). Its lattice parameter is: a=5.3494 Å, b=5.3420 Å, and c=12.3219 Å (Friedt *et al.*, 2001). The ball model of bulk structure is shown in Figures 4 and 5.
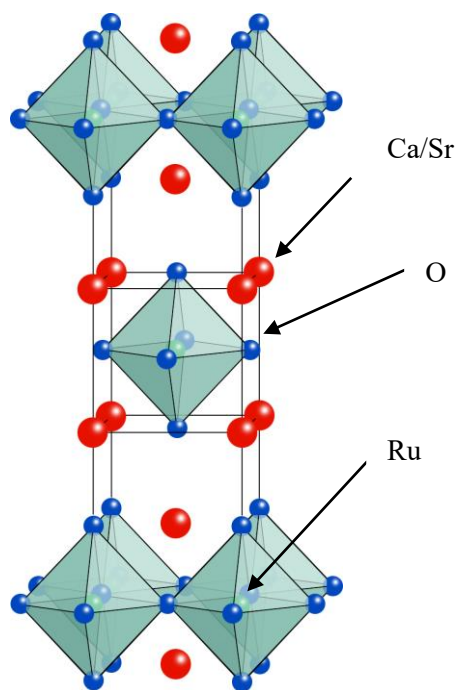
Figure 4. Ball model of the crystal structure of Ca$_{2-x}$Sr$_x$RuO$_4$

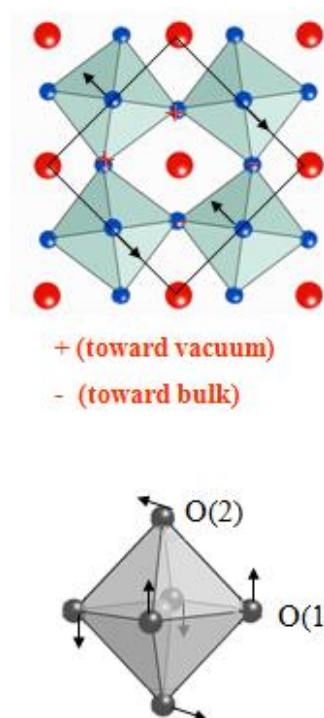Figure 5. Top view and RuO$_6$ of bulk structure Ca$_{1.9}$Sr$_{0.1}$RuO$_4$

The best fit I-V spectra compared to the experimental data of Ca$_{1.9}$Sr$_{0.1}$RuO$_4$ is shown in the Figure 6. The total Pendry R-factor for the best fit is 0.19, which is a very good fit to the experimental data. Our LEED I-V analysis reveals that in the surface of the layered perovskite Ca$_{1.9}$Sr$_{0.1}$RuO$_4$ the RuO$_6$ octahedral are rotated (in-plane rotation) alternating clockwise and counterclockwise. The in-plane rotation of the RuO$_6$ octahedral at the surface is 11 degrees. The RuO$_6$ octahedral are also tilted by 5.67 degree at the surface. The Ru – O(1) bond-length at the surface is found to be 1.936 Å. The Ru – O(2) bond length at the surface is 1.863 Å. The comparison between the surface structure and the bulk of Ca$_{1.9}$Sr$_{0.1}$RuO$_4$ is listed in Table 1.

Table 1. Comparison between the surface and bulk atomic structure of Ca$_{1.9}$Sr$_{0.1}$RuO$_4$

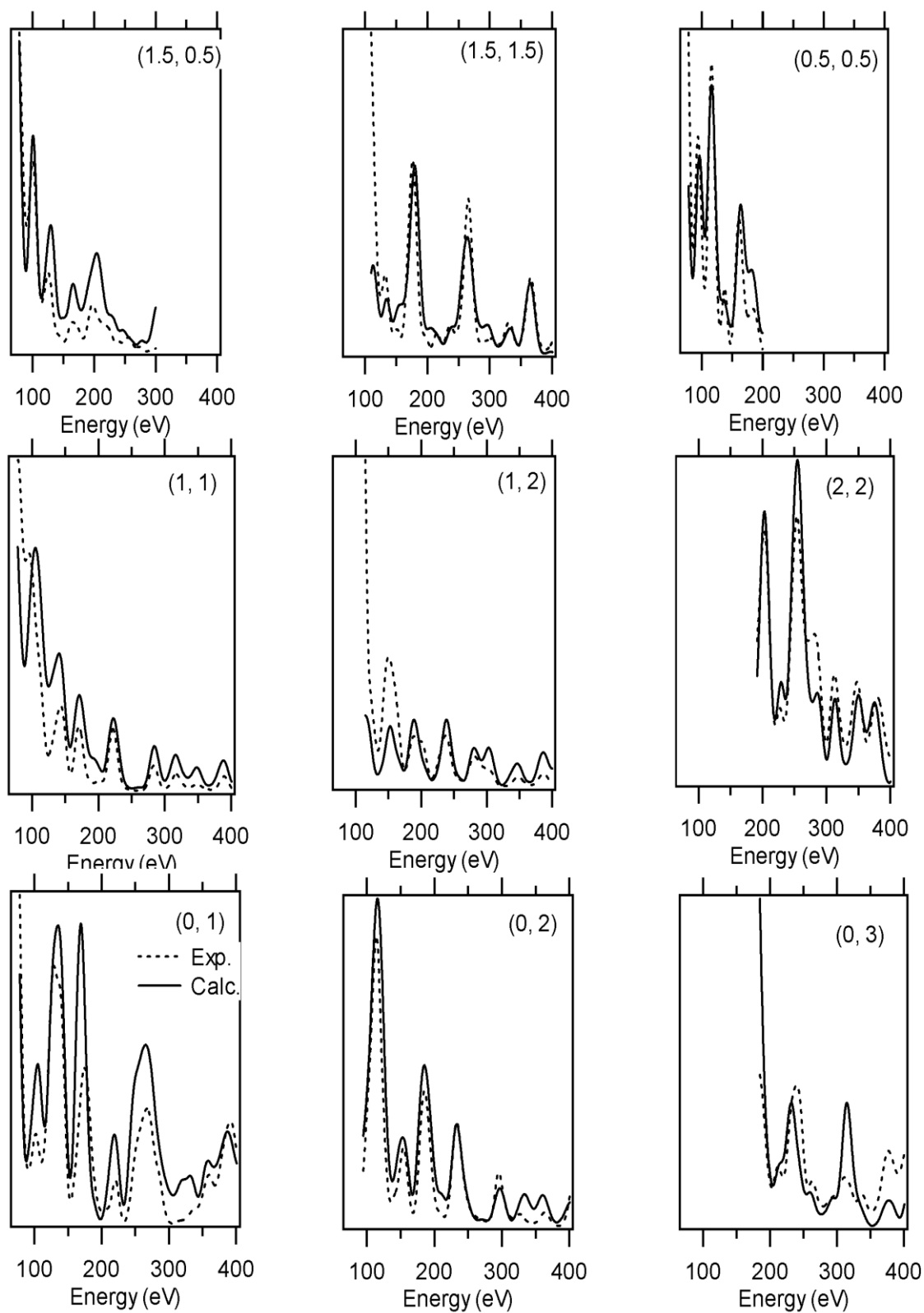| Atomic Structure	Bulk (Friedt *et al.*, 2001).	Surface (this work)
In-Plane Rotation RuO$_6$ (deg)	12.65	11.0
Out-of-Plane Tilt RuO$_6$ (deg)	O(1): 6.52	O(1): 5.2
	O(2): 5.25	O(2): 5.7
Ru-O(1) Bond Length (Å)	1.939	1.936
Ru-O(2) Bond Length (Å)	2.040	1.863
RuO$_6$ Octahedron Volume (Å³)	10.23	9.31

Figure 6. Spot intensity as a function of the electron beam energy. Dashed lines are the experimental data. Solid lines give the best fit corresponding to the atomic structure described in the text.

Table 1 show that the in-plane rotation of RuO_6 at the $Ca_{1.9}Sr_{0.1}RuO_4$ surface is smaller than that in the bulk by 13%. This situation is quite different than that at the $SrRuO_4$ surface. There is no rotation of RuO_6 octahedron in the bulk of $SrRuO4$ [4], but the RuO_6 octahedron at the $SrRuO_4$ surface is rotated (in-plane) by 8.5 degree (Matzdorf *et al.*, 2002). According to the previous study, the rotation of RuO_6 octahedron at the $SrRuO_4$ surface is governed by soft-phonon at the zone boundary (Matzdorf *et al.*, 2000). Thus, the in-plane rotation of RuO_6 at the $Ca_{1.9}Sr_{0.1}RuO_4$ surface is contributed by the surface relaxation. The RuO_6 octahedral at the surface prefer to be at normal position (no rotation) to reduce the stress. The tilt of O(1) is much smaller than in the bulk by 20%. This situation is similar to the RuO_6 case where the creation of surface causes the surface atom to be relaxed. The tilt of O (2) is larger at the surface than in the bulk by 8.6%. The Ru – O (1) bond-length at the surface is found to be the same as in the bulk (0%). However, the Ru – O (2) bond length at the surface is shorter in the bulk by 8.7%. The volume of octahedral Ru-O6 at the surface is reduced by 9% compared to the bulk.

Our LEED I-V analysis above shows that the atomic structure at surface of the layered perovskite $Ca_{1.9}Sr_{0.1}RuO_4$ is significantly different than that in the bulk. Consequently, the electronic property of $Ca_{1.9}Sr_{0.1}RuO_4$ surface could be significantly different than that in the bulk. The previous study found the electronic in-homogeneity at the surface of $Ca_{1.9}Sr_{0.1}RuO_4$ (Jiandi *et al.*, 2006). The temperature of metal insulator transition in the bulk of $Ca_{1.9}Sr_{0.1}RuO_4$ is 154 K (Nakatsuji and Maeno, 2000). While the temperature of metal insulator transition at the surface of $Ca_{1.9}Sr_{0.1}RuO_4$ is 130 K (Ismail *et al.*), which is significantly lower than in the bulk. This behavior is governed by the lattice distortion at the surface.

Conclusions

In summary, we have presented a study of the surface structure of $Ca_{1.9}Sr_{0.1}RuO_4$ by LEED I-V at room temperature. Our finding shows that in the surface of the layered perovskite $Ca_{1.9}Sr_{0.1}RuO_4$ the RuO_6 octahedral are rotated by 11 degrees (in-plane rotation) alternating clockwise and counterclockwise. The in-plane rotation of RuO_6 at the surface is smaller than that in the bulk by 13%. The tilt of O(1) is much smaller than in the bulk by 20%. The tilt of O(2) is larger at the surface than in the bulk by 8.6%. The Ru – O(1) bond-length at the surface is found to be the same as in the bulk (0%). However, the Ru – O(2) bond length at the surface is shorter in the bulk by 8.7%. The volume of octahedral Ru-O6 at the surface is reduced by 9% compared to the bulk. Our finding reveals that the atomic structure at surface of the layered perovskite $Ca_{1.9}Sr_{0.1}RuO_4$ is significantly different than that in the bulk. This finding may explain why the temperature of metal insulator transition at the surface of $Ca_{1.9}Sr_{0.1}RuO_4$ is lower than in the bulk.

Acknowledgments

References

Barbieri A. and Van Hove M. A. private communication.

Braden M., Moudden A.H., Nishizaki S., Maeno Y., Fujita T. 1997. Structural analysis of Sr_2RuO_4. *Journal Physica C* 273(3-4): 248-254.

Friedt O., Barden M., Andree G., Adelmann P., and Maeno Y. 2001. Structural and magnetic aspects of the metal-insulator transition in $Ca_{2-x}Sr_xRuO_4$. *Journal Phys. Rev. B* 63 (17): 174432.

Graf M. J. and Balatsky A. V. 2000. Identifying the pairing symmetry in the Sr_2RuO_4 superconductor. *Journal Phys. Rev. B* 62(14): 9697-9702.

Ismail, Jiandi Zhang, Jin R., Mandrus D., and Plummer E. W., to be published

Jiandi Zhang, Ismail, Moore R. G., Wang S.-C., Ding H., Jin R., Mandrus D., and Plummer E.W. 2006. Dopant-induced nano scale electronic inhomogeneities in $Ca_{2-x}Sr_xRuO_4$. *Journal Phys. Rev. Letter* 96: 66401.

Maeno Y., Hashimoto H., Yoshida K., Nishizaki S., Fujita T., Bednorz J. G., Lichtenberg F. 1994. Superconductivity in a layered perovskite without copper. *Nature* 372: 532-534.

Matzdorf R., Fang Z., Ismail, Jiandi Zhang, Kimura T., Tokura Y., Terakura K., and Plummer E. W. 2000. Ferromagnetism stabilized by lattice distortion at the surface of p-wave superconductor Sr_2RuO_4. *Science* 289: 746-748.

Matzdorf R., Ismail, Kimura T., Tokura Y., and Plummer E. W. 2002. Surface structural analysis of the layered perovskite Sr_2RuO_4 by LEED I-V. *Journal Phys. Rev. B* 65(8): 85404.

Nakatsuji S. and Maeno Y., 2000. Switching of magnetic coupling by a structural symmetry change near the Mott transition in $Ca_{2-x}Sr_xRuO_4$. *Journal Phys. Rev. B* 62(10): 6458-6466.

Pendry J. B. 1974. *Low Energy Electron Diffraction* Academic Press. London.

Pendry J. B. 1980. Reliability Factors for LEED Calculations. *Journal Phys. C*, 13(5): 937-944.

Rice T. M. and Sigrist M. 1995. Sr_2RuO_4: an electronic analogue of ^3He? *Journal Phys.: Condens. Matter* 7 (47): 643-648.

Van Hove M. A., Weinberg W. H., and Chan C.-M. 1986. *Low Energy Electron Diffraction*, Springer, Berlin.