

Surface Atomic Structure of $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$ at Low Temperature

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Abstract: *The surface atomic structure of $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$ at low temperature has been investigated by using Low Energy Electron Diffraction (LEED) I-V. The observed LEED pattern indicates that the sample of $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$ surface is flat and single crystal. LEED I-V data, six in-equivalent beams of the layered perovskite $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$ were recorded at the temperature of 90 K. LEED I-V calculations was performed to fit experimental data to obtain the surface atomic structure. Our results show that the RuO_6 in the $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$ surface at low temperature are rotated in-plane alternately. The in-plane rotation of the RuO_6 octahedra at the surface is reduced by 10.8% from the bulk value. The RuO_6 octahedra in the surface are tilted but it is reduced by 52.5% for O(1) and 33.0 % for O(2) from the bulk value. The bond-length of Ru – O(1) at the surface is about the same as in the bulk. However, the bond length of Ru – O(2) at the surface is shorter by 9.1% than its bulk value. The volume of RuO_6 octahedron at the surface is smaller by 8.8% than its bulk value. Obviously, the atomic structure at the $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$ is different than that in the bulk. By comparing to the previous study, it is found that the surface structure of $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$ at low temperature is different than that at room temperature. This finding would explain why the metal insulator transition temperature in the surface of $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$ is different than that in the bulk. It shows that the lattice distortions at $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$ strongly influence its electronic properties.*

Keywords: Surface Atomic Structure, LEED I-V, Transition Metal Oxide, Perovskite

1. Introduction

Transition metal oxide materials have been investigated extensively because these materials exhibit a lot of fascinating phenomena. One of them is $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ ($0.1 \leq x \leq 2.0$). For $x=2$ (SrRuO_4), this layered perovskite material exhibits superconductivity without cooper [1] and it has a spin-triplet pairing of p-wave [2, 3]. The bulk of this material is nonmagnetic [4], but its surface has a ferro magnetic ground state [5]. The atomic structure of bulk SrRuO_4 has K_2NiF_4 symmetry (*space-group* $I4/mmm$) [4]. The surface atomic structure of SrRuO_4 is quite different than that in the bulk. The RuO_6 octahedra at the surface of SrRuO_4 are rotated alternately in plane by 8.5 degree [5]. Matzdorf et al suggested that the lattice distortion at the surface is driven by soft phonon [5]. Obviously, the lattice distortion at the surface of SrRuO_4 affects its electronic and magnetic properties significantly.

Without any doping of Ca, the atomic structure in the bulk of SrRuO_4 has $I4/mmm$ symmetry. However, when it is doping with Ca (for $x=0.1$), the atomic structure in the bulk of $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$ becomes $Pbca$ symmetry [6]. Its electronic property changes significantly from superconductor to insulator where the bulk of $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$ behaves as conductor at room temperature but it is insulator for temperature below 154 K [7]. The atomic structure in the bulk of $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$ has been studied at temperatures of 10 K and 300 K [6]. It is found that the degree of RuO_6 rotation is 12.65 degree at room temperature and it is decreased to 11.77 degree at low temperature. The different degree rotation of RuO_6 at 10 K with respect to structure at 300 K is -6.69%. The out-of-plane tilt RuO_6 at room temperature is 6.52 degree for O(1) and 5.25 degree for O(2). However, the

out-of-plane tilt RuO_6 at low temperature is 11.16 degree for O(1) and 9.40 degree for O(2). The different degree tilt of RuO_6 at 10 K with respect to structure at 300 K is +71.17% for O(1) and +79.05% for O(2) which are very big different. The bond length of Ru – O(1) is 1.929 (1.948) Å at room temperature and increased to 1.987 (1.988) Å at low temperature. Its different is about +2%. Meanwhile the bond length of Ru – O(2) is reduced by about -2% as the temperature is decreased from room temperature to low temperature. However, the RuO_6 octahedron volume becomes larger as the temperature is decreased, which is unusual. Clearly the atomic structure at low temperature is different than that at room temperature which is related to metal insulator transition.

Recent study by Jiandi Zhang *et al.* found nanoscale electronic inhomogeneities at the surface of $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ while the surface atomic structure is well ordered [8]. The surface electronic roughness was doping dependent [8]. Recent study shows that the atomic structure of $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$ surface at room temperature ($T = 300$ K) is significantly different than that in the bulk [9]. The RuO_6 octahedra at the surface of $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$ are rotated by 11 degree which is smaller than that in the bulk. The bond-length of Ru – O(1) at the surface is 1.936 Å which is about the same as in the bulk (1.939 Å). The bond length of Ru – O(2) at the surface is 1.863 Å which is much shorter than that in the bulk (2.040 Å). The volume of RuO_6 octahedral at the surface is 9% smaller than that in the bulk [9]. Furthermore, the temperature of metal insulator transition in the surface of $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$ is found to be 130 K [10], which is significantly different than that in the bulk. Consequently, it is very interested to study the surface atomic structure of $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$ at low temperature in order to compare it with

the surface structure at room temperature and atomic structure in the bulk. In this paper we report on the surface atomic structure of $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$ by using Low Energy Electron Diffraction (LEED) I-V at low temperature ($T = 90$ K).

2. Materials and Methods

The sample of $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$ for this study was a single crystal which was grown by using the floating-zone technique in the Oak Ridge National Laboratory USA. By using silver epoxy, the sample was glued to a sample holder. A metal post was glued on top of the sample. Then, the glue was dried by using heating gun. After that the sample which was already attached to the sample holder was inserted into a load-lock chamber, pumped and baked for 8 – 10 hours at temperature about 150°C to achieve ultrahigh-vacuum. The sample was then cleaved at room temperature by breaking off the metal post in the load-lock chamber. After that the sample was transferred to the main ultra high vacuum chamber with the pressure of 1×10^{-10} Torr. The sample was cooled to 90 K by using liquid nitrogen.

Schematic LEED I-V experiment is shown in Figure 1.

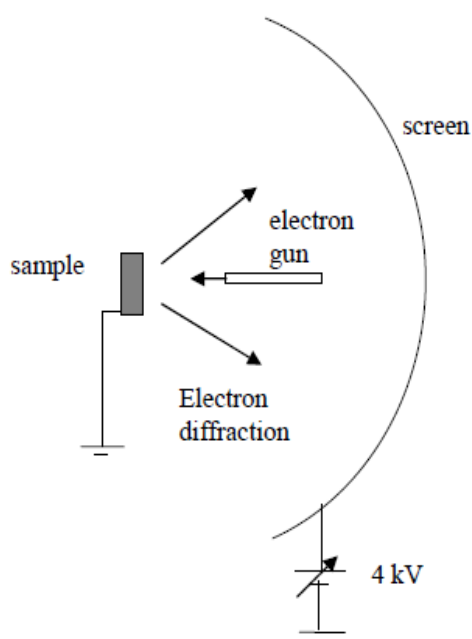


Figure 1: Schematic LEED I-V experiment

LEED experiment was conducted at normal incident. LEED intensities as a function of electron energy were recorded by using a video LEED system. LEED I-V analysis was conducted by using multiple scattering approach [11, 12]. The symmetrized automated tensor-LEED (SATLEED) computer codes developed by Barbieri and Van Hove [13] was used to analyze LEED I-V data. Phase shifts of Ca, Sr, Ru, and O were calculated by using computer codes of Barbieri and Van Hove [13]. In the LEED I-V calculations, the phase shift for surface layers was assumed the same as in the bulk layer. In the calculations, the initial surface structure was set as the bulk atomic structure of $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$. We have used

Pendry R-factor (R_p factor) [14] to determine the agreement (best fitting) between experimental and calculated LEED I-V spectra in order to obtain the surface structures.

3. Results and Discussions

Sharp LEED pattern of the layered perovskite $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$ at low temperature ($T = 90$ K) is observed as shown in Figure 2. This indicates that surface of the layered perovskite $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$ is well ordered single crystal and the morphology of its surface is flat.

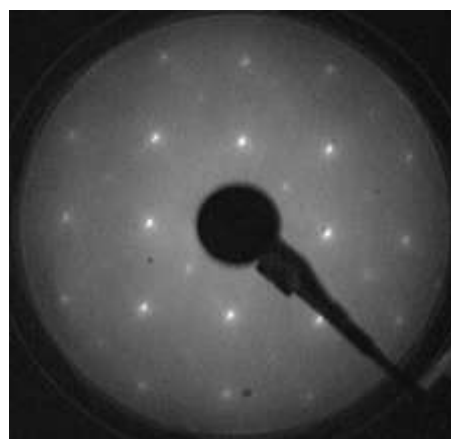


Figure 2: LEED pattern of $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$

Six in-equivalent LEED I-V spectra have been obtained. Those six in-equivalent LEED I-V spectra are (0,1); (0,2); (0,3); (1,1); (1,2); and (2,2). The total energy of LEED I-V data is 1891 eV.

We started the LEED I-V calculation by using bulk structure of $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$ where the bulk structure of this material is already known [7]. All six in-equivalent LEED I-V data mentioned above were fitted by LEED I-V calculations to obtain the best fit surface structure by searching minimum Pendry R-factor. The best fit LEED I-V spectra are shown in the Figure 3. The total Pendry R-factor for our best fit is 0.18, which is a very good agreement to the experimental data. The atomic structure of $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$ surface at low temperature ($T=90$ K) corresponding to the best fit is found to be the following. The RuO_6 octahedra at the surface layer is rotated by 10.5° alternately (clockwise and counterclockwise). Besides rotation, the RuO_6 octahedra at the surface is also tilted by 5.3° for O(1) and 6.3° for O(2). The bond lengths of Ru-O(1) and Ru-O(2) at the surface are found to be 1.990° and 1.810° degree, respectively. The volume of RuO_6 octahedron at the surface is found to be 9.56 \AA^3 . The ball model of surface structure of $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$ is shown in Figure 4.

The comparison between the surface structure and the bulk of $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$ is listed in Table 1. As shown in the Table 1, the in-plane rotation of the RuO_6 octahedra at the surface layer is 10.8% smaller than the value in the bulk. The RuO_6 octahedra in the surface are tilted but it is 52.5% smaller than the bulk values for O(1) and 33.0 % for O(2). The Ru – O(1) bond-length at the surface is about the same as in the bulk.

But the bond length of Ru – O(2) at the surface is 9.1% smaller than that in the bulk. The volume of RuO₆ octahedron at the surface is 8.8% smaller than the value in the bulk. Clearly, the atomic structure at the Ca_{1.9}Sr_{0.1}RuO₄ is quite different than that in the bulk.

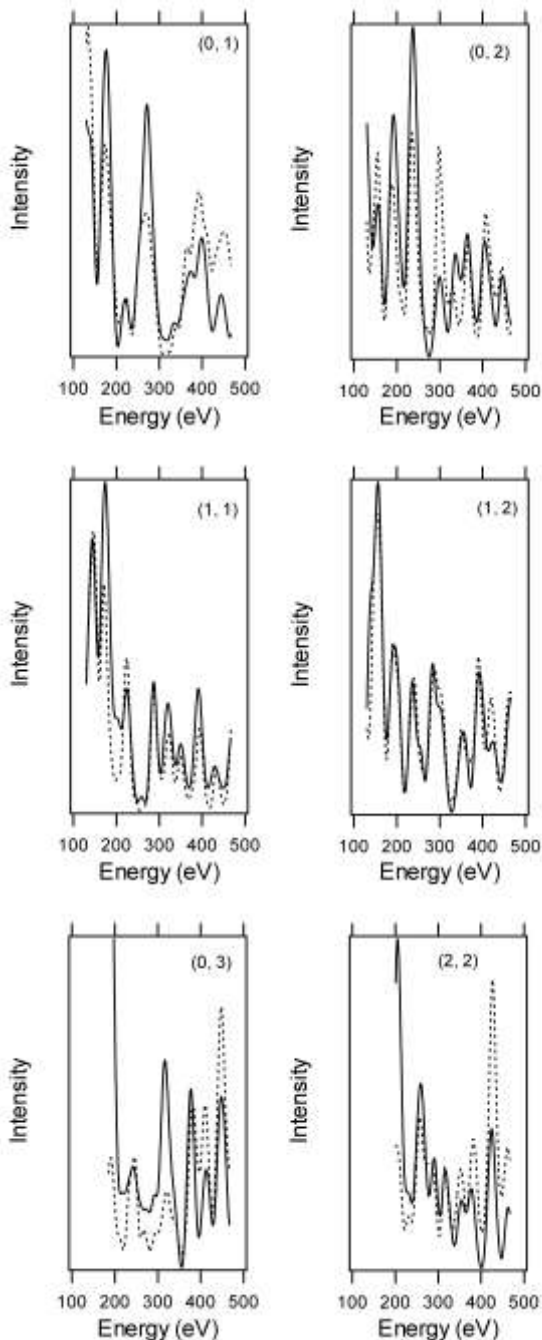


Figure 3: Plot of LEED I-V spectra as a function of the electron energy. Dashed lines are the experimental data and solid lines are the calculation spectra for the best fit surface structure

Table 1: Comparison between the surface and bulk atomic structure of Ca_{1.9}Sr_{0.1}RuO₄

Atomic Structure	Bulk (T=10 K) [6]	Surface (T=90 K) [this study]	Surface atomic structure with respect to bulk (%)
Rotation of RuO ₆ (deg)	11.77	10.5	-10.8
Tilt of RuO ₆ (deg)	O(1): 11.2	O(1): 5.3	-52.5
	O(2): 9.4	O(2): 6.3	-33.0
Bond Length of Ru-O(1) (Å)	1.988	1.990	+0.1
Bond Length of Ru-O(2) (Å)	1.991	1.810	-9.1
Volume of RuO ₆ Octahedron (Å ³)	10.48	9.56	-8.8

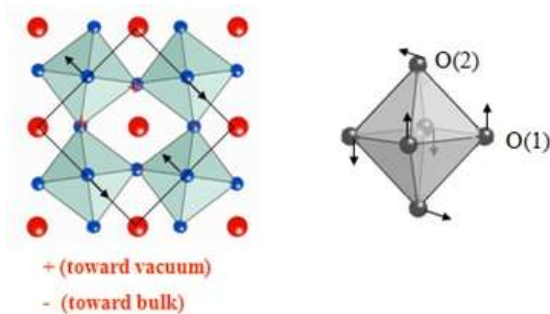


Figure 4: Ball model of the atomic structure at the Ca_{1.9}Sr_{0.1}RuO₄ surface

Now, let's compare the surface structure of Ca_{1.9}Sr_{0.1}RuO₄ at low temperature (T=90 K) to the surface structure of Ca_{1.9}Sr_{0.1}RuO₄ at room temperature (T=300 K) [9] as listed in Table 2. As the temperature is reduced, the in-plane rotation of the RuO₆ octahedra at the surface is decreased by 4.5% compared to the structure at room temperature. The RuO₆ octahedra in the surface are tilted but it is reduced by 1.9% for O(1) and 10.5 % for O(2) at low temperature. The bond-length of Ru – O(1) at the surface is increased by 2.8% as the temperature is reduced. But the bond length of Ru – O(2) at the surface is reduced by 2.9% at low temperature. The volume of RuO₆ octahedron at the surface is increased by 2.7% as the temperature is decreased. Thus, the surface structure at low temperature (T=90 K) is significantly different than that at room temperature (T=300 K). It is unusual that the bond length of Ru – O(1) and the volume of RuO₆ octahedron are increased by lowering the temperature.

As described above, the surface atomic structure of Ca_{1.9}Sr_{0.1}RuO₄ at low temperature is found to be significantly different than that in the bulk. Similarly, the surface atomic structure of Ca_{1.9}Sr_{0.1}RuO₄ at low temperature is also significantly different than that at room temperature. Consequently, the electronic property of Ca_{1.9}Sr_{0.1}RuO₄ surface at low temperature must be significantly different than that in the bulk. This finding would explain why the temperature of metal insulator transition in the surface of Ca_{1.9}Sr_{0.1}RuO₄ is 130 K [10] while it is 154 K in the bulk [7].

Table 2: Comparison between the surface atomic structure of $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$ at room and low temperatures

Atomic Structure	Surface (T=300 K) [9]	Surface (T=90 K) [this study]	Surface structure at T=90 K with respect to structure at T=300 K (%)
Rotation of RuO_6 (deg)	11.0	10.5	-4.5
Tilt of RuO_6 (deg)	O(1): 5.2	O(1): 5.3	+1.9
	O(2): 5.7	O(2): 6.3	+10.5
Bond Length of Ru-O(1) (Å)	1.936	1.990	+2.8
Bond Length of Ru-O(2) (Å)	1.863	1.810	-2.9
Volume of RuO_6 Octahedron (Å ³)	9.31	9.56	+2.7

4. Conclusions

Our LEED I-V analysis shows that the RuO_6 octahedra in the $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$ surface at T=90 K is rotated by 10.5 degree alternatingly (clockwise and counterclockwise) which is 10.8% smaller than that in the bulk. The RuO_6 octahedra in the surface layer are tilted as in the bulk but it is 52.5% smaller for O(1) and 33.0% for O(2) than those bulk values. The bond length of Ru – O(1) at the surface is about the same as in the bulk. However, the bond length of Ru – O(2) at the surface (1.810 Å) is 9.1% smaller than the bulk value. The volume of RuO_6 octahedron at the surface is 8.8% smaller than that in the bulk. In conclusion, the surface atomic structure of $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$ at low temperature is significantly different than that in the bulk. The surface structure at low temperature is also considerably different than that at room temperature. These lattice distortions at the surface of $\text{Ca}_{1.9}\text{Sr}_{0.1}\text{RuO}_4$ would influence its electronic properties.

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