The Surface Phases of the *p*-wave Superconductor Sr_2RuO_4

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We have investigated the surface electronic, vibrational and structural properties properties of Sr_2RuO_4 [1-3], an unconventional superconductor [4,5]. The strong mutual coupling between charge and spin of the electrons and the lattice degrees of freedom in transition-metal oxides (TMOs) results in effects such as charge-, orbital-, and spin ordering; colossal magnetoresistance; and unconventional superconductivity. Conceptually, creating a surface by cleaving a single crystal is a controlled way to disturb the coupled system by breaking the symmetry without changing the stoichiometry. This unique environment at the surface could produce new phenomena, while providing a fresh approach to the study of the spin-charge-lattice coupling in these complex materials. Here we show, using the unconventional superconductor Sr_2RuO_4, that all of these expectations can be realized. Even for this layered material, where the bonding between layers is weak and the electrons are strongly localized to the layers, the surface has a surprising new phase, which clearly elucidates the close coupling in the bulk between lattice distortions and magnetism. Furthermore, the influence of surfaces and interfaces on thin-film properties is of technological interest for the design of TMO devices.

Sr_2RuO_4, the only known layered perovskite without copper that exhibits superconductivity, has attracted much attention, because it shows spin-triplet pairing with a *p*-wave order parameter [5]. The bulk has a non-distorted tetragonal K_2NiF_4 structure with a nonmagnetic ground state. However, this ground state is close to structural and magnetic instabilities, characterizing a common feature in this class of materials that the energy difference between different structural/magnetic phases is very small. Inelastic neutron scattering experiments show that the phonon mode corresponding to the in-plane octahedron rotation with Σ_3 symmetry exhibits a significant drop in energy near the zone boundary [6]. The phonon dispersion of in the [110] direction (parallel to the surface) is shown in Fig. 1a and the corresponding zone boundary rotational mode of the octahedra is displayed in Fig. 1b. The existence of spin fluctuations has been documented by nuclear magnetic resonance experiments. This is important, because theory suggests that the spin-triplet pairing for the unconventional superconductivity in Sr_2RuO_4 is mediated by exchange of FM spin fluctuations [7].

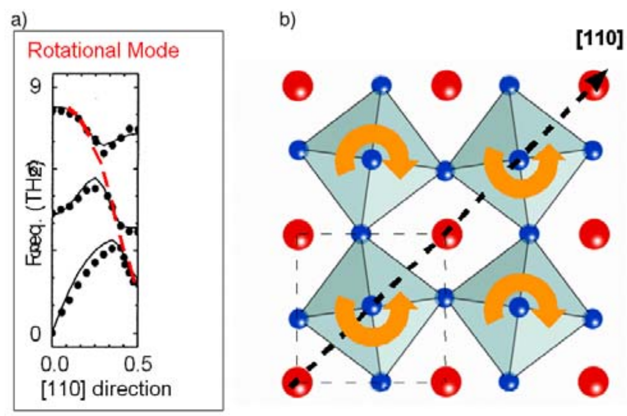

Fig. 1. (a) bulk phonon dispersion showing soft phonon mode [6]. (b) Structural model of zone boundary phonon and surface structure.

Fig. 2 shows a large scale STM image of a surface cleaved inside the vacuum system and transferred to the STM stage. It shows very large flat terraces with an extension up to 10 μm. All step heights are integral multiples of half the unit cell (6.4Å) shown on the left. Both LEED *I-V* measurements and calculations prove that the surface is the SrO plane, as expected. High resolution STM images and LEED diffraction shown in Fig. 3 indicate that the surface is not bulk truncated but reconstructed into a $(\sqrt{2}x\sqrt{2})R45^0$ structure. There are missing fractional order spots in the LEED pattern indicating the presence of glide planes and a *p4gm* plane group symmetry. Given the restrictions of *p4gm* symmetry, and the fact that there is a soft-bulk zone boundary phonon (Fig. 1) corresponding to rotation of the octahedron, the surface structure could have been deduced. But the structure was determined using LEED *I-V* analysis. The intensity vs. energy of five nonequivalent integer beams and three nonequivalent fractional beams has been measured and compared with calculated intensities for surface model structures compatible with the *p4gm* symmetry. The best fit to experimental spectra was obtained for a surface structure with the octahedra rotated by 9 ± 3°. First-principles calculations of the ground state surface structure have been conducted within the generalized gradient approximation (GGA). Our calculations confirm that octahedra rotation indeed happens on the surface but not in the bulk [1]. The optimized structure for a nonmagnetic surface is a surface layer with octahedra rotated by 6.5°. This reconstruction, driven by compressive strain in the RuO_2 layers, lowers the energy by 14 meV per formula unit (f.u.). The reconstruction enhances FM ordering, which in turn further stabilizes the distortion further and increases the rotation angle to 9° to gain additional energy of 51 meV/f.u.

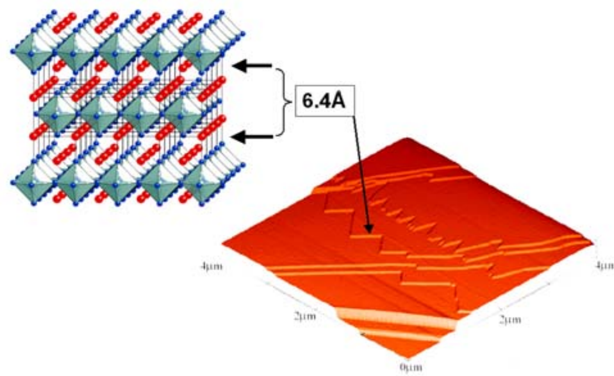

Fig. 2. Structural Model of Sr_2RuO_4 and large scale STM image (4 x 4 μm^2) showing the origin of the step height.

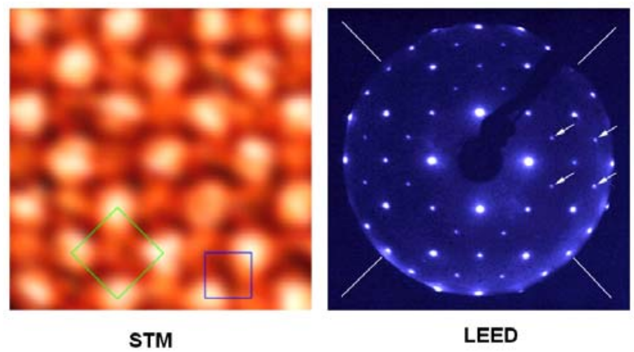

Fig. 3. Left: High resolution STM image showing new surface unit cell. Right: Electron diffraction pattern (LEED) showing fractional spots (marked by arrows) created by the surface reconstruction.

We have been able to analyze the different *d*-orbital character of each band at the Fermi surface and address the coupling of these states to phonons and spin fluctuations giving a clear picture of what occurs at the surface [1]. The key orbital is the d_{xy}, since the Σ_3 bulk phonon mode couples strongly with this orbital which is primarily responsible for the *van Hove singularity* (VHS) slightly above E_F at the Brillouin zone boundary. Most importantly it is the d_{xy} orbital that is primarily responsible to FM spin-fluctuation. This observation at the surface of Sr_2RuO_4 opens up many exciting prospects, relevant to the bulk and surface properties of these layered TMOs.

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