EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal: *https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do*

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report"),*
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title: Resonant inelastic x-ray scattering study of the two-dimensional superconductivity in LaAlO3/KTaO3 heterostructures**	**Experiment number**: HC-4702
Beamline: ID20	**Date of experiment**: from: 17 November 2021 to: 23 November 2021	**Date of report**: 12 February 2022
Shifts: 17	**Local contact(s)**: Faure Quentin	*Received at ESRF:*

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Report:

Oxide interfaces has attracted a lot attention since the discovery of conducting $LaAlO_3/SrTiO_3$(LAO/STO) interfaces. Recently, thediscovery of superconducting two dimensional electronsystem (2DES) in $LaAlO_3$ (or EuO)/$KTaO_3$ (LAO/KTO or EuO/KTO) interfaces triggers a revival in this field. These KTO based interfaces are very appealing. The superconducting critical temperature T_C can be higher and the superconductivity depends on crystallineorientations (∼2.2 K and∼0.9 K for KTO(111) andKTO(110) interfaces) compared with LAO/KTO(∼0.2 K). Analogous to the LAO/STO interfaces where 3d electrons are responsible to the interfacialproperties, the 5d electrons in KTO based in-terfaces are supposed to the key ingredient. In LAO/STO interfaces, the Ti 3d electrons are believed to be composed of localized and itinerant types, which is the key issue to understand the origin of the interfacial 2DES and their tranport and magnetic properties. However, the types of Ta 5d electrons in KTO-based interfaces remain veiled and the answer will help to understand the origin and superconductivity of the interfacial 2DES.

To disclose the interfacial electrons, resonant inelastic x-ray spectroscopy (RIXS) has been proved successful in LAO/STO systems and should have similar power in KTO based interfaces. In LAO/STO systems, the interfaces have Ti^{3+}($3d^1$ configuration) stateswhich will generate dd excitations using RIXS at the Ti L_3 edge. In contrast, the

bulk STO with Ti^{4+}(3d^0 configuration) will not. And the carrier densities of 2DES based on RIXS data were found to be much higher than the value measured by Hall effect, suggesting the simultaneous existence of localized and itinerant chargecarrier in LAO/KTO interfaces. Similarly, the bulk KTO has Ta^{5+} valence (5d^0 configuration) while the EuO/KTO interface show slightly reduced Ta valence by x-ray absorption spectroscopy (XAS). Nevertheless,the electrons can be either itinerant in the hybridized spd conduction bands or localized in the 5d shell, that is, 5d^1 due to possible localization. And the dd excitation by RIXS, which is sensitive to the existence of carriers (no matter localized or itinerant) at the interface, can help to analyze the interfacial 2DES.

The LAO/KTO interfaces with (100), (110) and (111)orientations were prepared by pulsed laser deposition. The resistance and Hall effect of all samples were measured through a vander Pauw method. The KTO(111) and KTO(110) interfaces are superconducting while KTO(100) samples are just metal, illustrated in Fig. 1(a). The itinerant carrierdensities can be estimated by Hall effect, and are roughly $0.7-1.4\times10^{14}$/cm^2 for all interfaces. The electron doped bulk KTO sample (ED KTO) was prepared in our lab. The chemical formula of produced KTO samples should be $(K_{1-x},Ba_x)TaO_{3-y}$, with electron doped by Ba^{2+} and oxygen vacancy. The produced doped KTO samples are black and by measuring resistance versus temperature ,we found metallic behaviour. From Hall measurement, the doped level was estimated to be about 0.001e per Ta site.

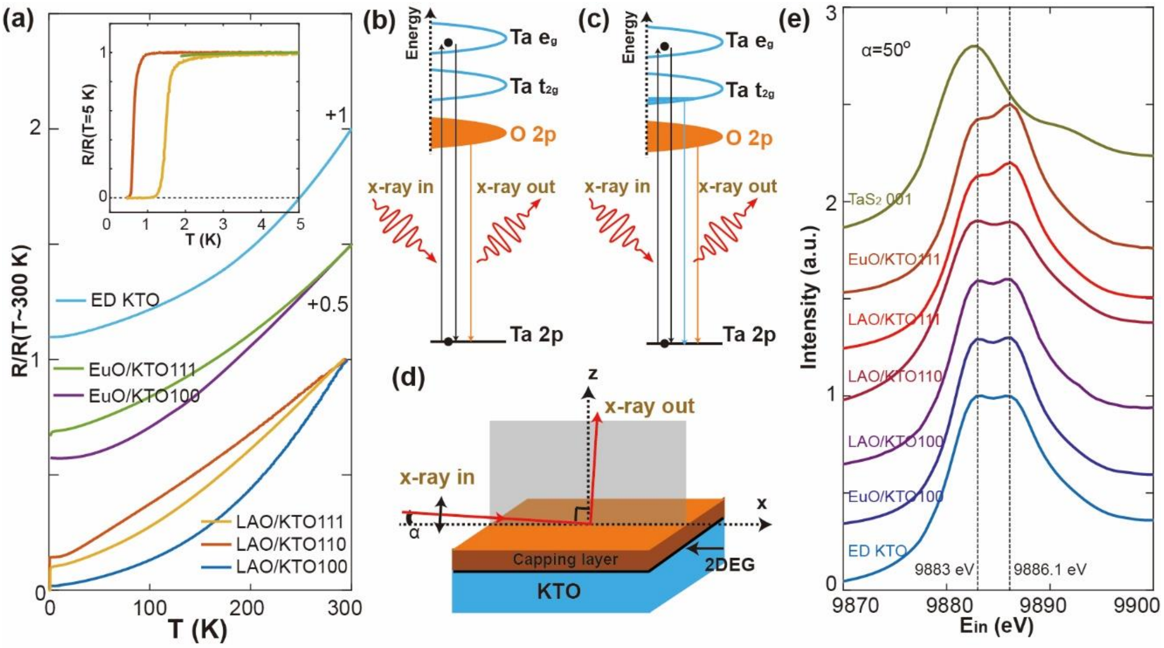

FIG. 1. (a) The resistance of samples versus temperature. The inset shows the resistance of superconducting samplesbelow 5 K. (b) The CT excitation in insulating KTO. (c) The CT and dd excitations in electron doped KTO. (d) Geometry used in ESRF. (e) The TFY XAS of all samples.

The RIXS and XAS measurements were performed at the beamline ID20 of the European Synchrotron Radi-ation Facility (ESRF). The energy resolutions (full width half maximum) were 0.3 eV at ESRF. The KTO interfaces and bulk sample are investigated at Ta L$_3$ edge. XAS was obtained at room temperature (RT) while RIXS measurements were carried out at RT and 20 K. The experimental geometries are illustrated in Fig. 1(d). Grazing incident angle can be used to minimize the x-ray penetration depth and enhance the interfacial signals. The estimated detecting depth is afew nanometer when the incident angle (α) is less than0.2° and~100 nm when α= 1°. The scattering plane (indicated by a shadow plane) is perpendicular to the sample surface.

The TFY of all samples are showed in Fig.1 (e). For TFY XAS, the data were obtained with incident angle α= 50° and RT. The large incident anglemeans that the bulk information are recorded. All KTO samples, no matter interfaces or electron doped bulk, show similar double-peak feature. The double peaks locate at 9883.0 eV and 9886.1 eV respectively. Such feature is typical of Ta^{5+} oxide state. In contrast, the XAS of TaS_2 sample (see Fig. 1(c)) show single peak with peak position slightly lower than 9883.0 eV. The single peak feature in XAS has also been reported in another Ta compound with $5d^1$ electron configuration. By comparison, the XAS of ED KTO is not close toTaS_2 but the KTO interfaces where the bulk is insulatingKTO. This is an weak indication of the absence of $5d^1$ electrons in ED KTO.

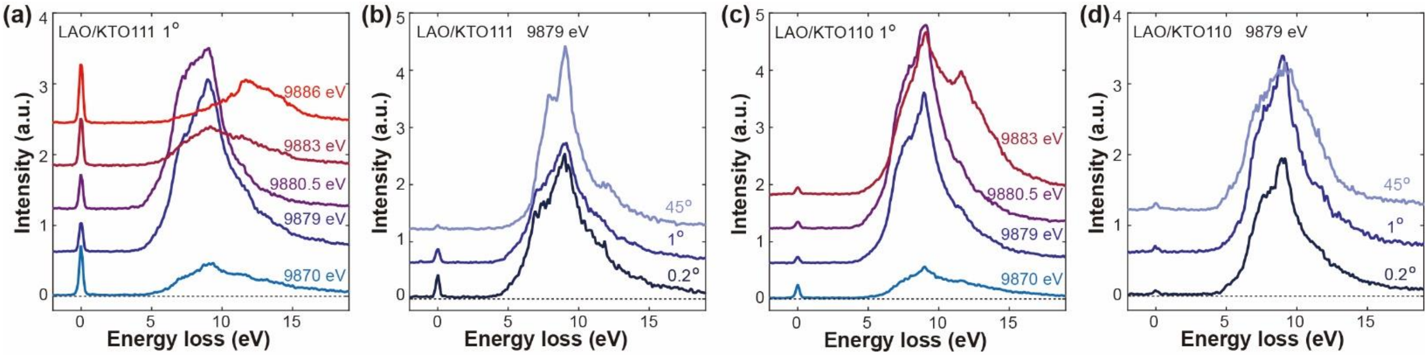

FIG. 2. The RIXS spectra of (a,c) LAOKTO(111), (b,d)LAOKTO(110) interfaces. Parameters for the spectra: (a,c) α= 1°, energy resolution 0.3 eV,vaied incident energy, (b,d) Ein= 9879 eV, energy resolution 0.3 eV, varied α.

To reveal the interfacial electronic structures, RIXS was performed on the superconducting KTO interfaces. We first focus on the LAO/KTO(111) interface. The RIXS spectra were obtained at RT with geometry showed in Fig. 1(d). As illustrated in Fig. 2(a), by increasing the incident photon energy from the t_{2g} to the e_g peak, we observe clear CT signal. The CT signal starts at around the energy loss ~4.0 eV, close to the bandgap of KTO by optical method. And the energy loss for the CT process depends on the incident energy.When incident x-ray is resonant at t_{2g}(or e_g) peak, the energy loss of CT mainly located around 8 eV (or 12 eV),corresponding to the charge transfer from O 2p band toTa t_{2g} (or e_g) band. Considering that all spectra contain 220 points with 20s per point, the dd excitations within the t_{2g} band or between the t_{2g} and e_g bands should be observed if sufficient interfacial Ta 5d carriers exist. However, such signal is absent. To exclude the influence of penetration depth of x-ray, we changed theincident angle by fixing the incident energy at 9879 eV. Still, only CT signal exist (see Fig. 2(b)). The lineshape of CT signal with α= 45° is different from those with the grazing-in angle. Such difference should be attributed tothe momentum-dependent RIXS spectra. We then turned to studying the superconsucting LAO/KTO(110) interface. Similar results were obtained,as showed in

Fig. 2(b) and (d). We observed obvious CT but not dd excitations. The different lineshape herefrom LAO/KTO(111) interface again should be due to the different momentum.

Since the KTO interfaces are actually ED KTO, we did RIXS measurement on the ED KTO bulk materials. As showed in Fig. 3, the dd excitation is still absent in ED KTO samples, no matter with incident angle α= 1°,45° or photon energy E_{in}=9879 eV, 9883 eV. Furthermore, by comparing with the RIXS spectra of the insulating KTO, the spetra of two samples can be scaled well together. These results show that even in the ED KTO bulk materials, the density of Ta 5d characteristic electrons is too low to be detected.

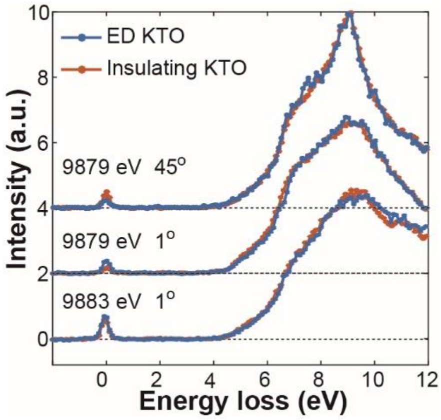

FIG. 3. The RIXS spectra of ED KTO (blue curves) andinsulating KTO (orange curves). The spectra are scaled andshifted.

To understand the type of electrons in KTO based in-terfaces and KTO bulk materials. We compare our resultwith the previous results on STO. Our KTO interfaces has higher itinerant electrons than STO interfaces measured by Hall effect. However, the dd excitations appear in the RIXS spectra of STO interfaces, which should be attributed to the existence of high density of localized Ti $3d^1$ electrons. The absence of dd excitations in KTO interfaces means that the localized Ta $5d^1$ electrons should be absent or at least with very low density. Based on our simulation, the density of the itinerant Ta 5d characteristic electrons is at the edge of the observable dd exitations. The existence of localized Ta $5d^1$ electrons will further contribute to the dd exitations and make such exitations observable. As the dd exitations are absent in our experiments, these localized Ta $5d^1$ electrons should be absent. The absence should be related to the properties of KTO. In ED KTO which has slightly lower electron density than ED STO, the dd exitations again disappear. This indicates the localized Ta 5d1electrons will not form in ED KTO. As the spacial extension of 5delectrons is much larger compared with 3d electrons. The subsequent larger hopping terms for 5d electrons guarantee their delocalization.