



Experiment title: Study of the electron-phonon interaction in SrTiO₃ and SrTiO₃ based heterostructures by Resonant Inelastic x-ray scattering	Experiment number: HC-2712	
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Report:

After the discovery of a high mobility two-dimensional electron gas (2DEG) at the interface between SrTiO₃ (STO) and other polar insulating oxides (like LaAlO₃), the research on the bulk and surface electronic properties of SrTiO₃ has received a renewed worldwide interest. Doped SrTiO₃ single crystals show a variety of interesting electronic properties, still not understood, including low T_c superconductivity (SC) and magnetism. Moreover, STO plays a key role in high-T_c SC in heterostructures, like in CaCuO₂/SrTiO₃ and FeSe/SrTiO₃ bilayers where T_c is larger than 100 K [2]. All these properties are linked to the peculiar characteristics of this material, and in particular to the high dielectric permeability and to the coupling between high energy longitudinal optical (LO) phonons and conduction band electrons. Up to now there is no consensus about the mechanism governing the transport properties and, in particular, superconductivity, which has been attributed either to the formation of large (bi)polarons [3], either to the creation of an electron liquid state. Recently, Froehlich polarons with energy as high as 90 meV were reported at the surface of SrTiO₃ [4] and at the LAO/STO interface [5] as observed by angle resolved photoemission spectroscopy (ARPES). However, ARPES is insensitive to the bulk electronic properties, thus it is unclear if large polarons are already formed in STO in the bulk and if and how they differ from 2D Froehlich polarons measured by ARPES, and what is their role in the superconductivity of these materials.

In the experiment HC-2712, we have used high resolution Resonant Inelastic X-ray scattering (RIXS) at the Ti L₃ and O K edges to investigate the electron-phonon coupling of Ti 3d electrons in insulating SrTiO₃ and conducting (vacuum reduced) SrTiO₃ single crystals, and in single and multiple LAO/STO interfaces in a LaAlO₃/SrTiO₃ superlattice and in a LAO/STO bilayer. Commercial SrTiO₃ single crystals have been prepared with a unique TiO₂ surface termination by chemical etching and high temperature annealing. The LaAlO₃/SrTiO₃ superlattice, composed of 8 repetitions of 10 unit cells of each layer, and the LAO/STO bilayer have been deposited on on a TiO₂ terminated SrTiO₃, by pulsed laser deposition at the CNR-SPIN laboratories in Naples. All samples have been carefully studied by in-situ STM, LEED, XPS and ex-situ transport measurements. On all the samples we were able to successfully acquire high resolution spectra, with

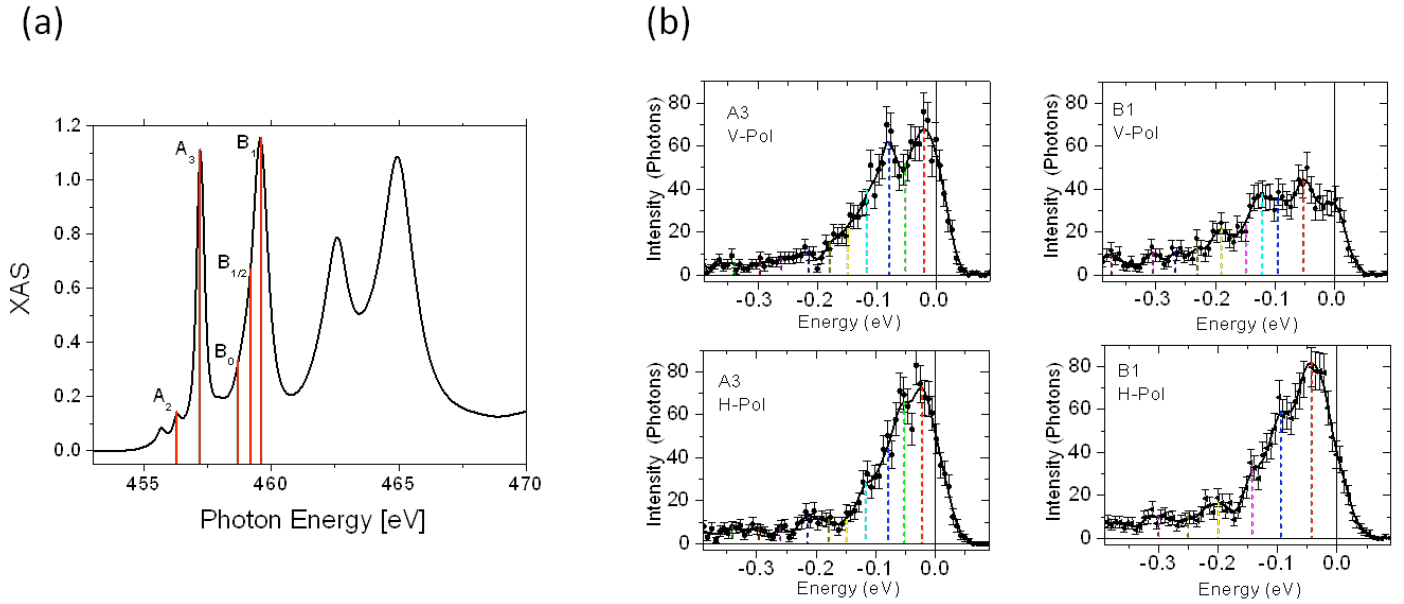


Fig.1: (a) XAS (total electron Yield) spectrum of an SrTiO₃ sample. (b) Low energy RIXS spectra acquired at two selected incident photon energies (A3 and B1). Short dashed lines are features related to the emission of (multi)phonons.

sufficient statistics, at 20 K, as function of the excitation energy, incident polarization and, for some samples, also at different transferred momenta.

In Fig. 1 we show a typical XAS spectrum and some RIXS high resolution data on insulating SrTiO₃ single crystals acquired at two different incident photon energies, with both Horizontal and Vertical polarizations. Each spectrum was obtained by summing a sequence of 8 spectra of 5 minutes each, with a total accumulation time of 45 minutes.

The energy resolution was about 30 meV, estimated on reference sample. The data show a number of low energy features which can be ascribed to phonon excitations of SrTiO₃. Very interestingly, the RIXS spectrum acquired at A3, corresponding to final XAS states (intermediate RIXS state) with mostly *t_{2g}* symmetry (*xy*, *xz*, *yz*), is qualitatively and quantitatively different from the spectrum acquired at B1, which corresponds to final XAS state (intermediate RIXS state) with *eg* (*x²-y²* and *z²*) symmetry. In particular at A3, we observe main features at the following energies (indicated by short dashed lines in Fig. 1b) : 20 meV, 60 meV , 115 meV, 144 meV, 175 meV. Some of these features might be replicas of a single phonon process (i.e. a multiphonon process), which result in an extremely complex and rich spectrum with electron-phonon replicas visible up to 500 meV. At B1, on the other, hand, the lowest energy excitation is at about 45 meV, followed by two other pronounced features a 100 meV and 120 meV, and replicas at 200 meV and at higher energy. Thus some of the electron-phonon features depend on the intermediate state. We see that the RIXS spectrum is also strongly dependent on the incident polarization. Finally, we have performed some measurements as function of the transferred momentum, demonstrating that, at least technically, it is possible to study the momentum dispersion of the electron-phonon interaction.

The HC 2712 experiment has demonstrated that it is possible to study the electron-phonon interaction with RIXS also at the unfavorable Ti *L*3 edge, where intensity is very small, and that the resolution is high enough to study low energy phonons and their dispersion even in the case of a LAO/STO superlattices and single bilayers. It must be noted that the data presented here are almost 10 times better in resolution than what was published in the last 2 years on TiO₂ and BaTiO₃ based on measurements done at other RIXS facilities [6, 7]. For the first time a real detailed analysis of the phonon spectra in the RIXS of cuprates has become possible, a huge step forward with respect to the rough models utilized in the recent literature.

Therefore we are now working on the complex analysis of the data using both phenomenological models and complex model-Hamiltonian + ab-initio approaches in collaboration with the K. Gilmore and A. Geondzhian (theory group of the ESRF), to extract from the data the effective electron phonon coupling of all the electron-phonon excitation features observed, and their evolution from insulating to conducting STO and to the LAO/STO heterostructures which host a 2DEG.

REFERENCES

- [1] Ohtomo, A. & Hwang, H. Y. A high-mobility electron gas at the LaAlO₃/SrTiO₃ heterointerface. *Nature* **427**, 423–426 (2004).
- [2] Ge, J. F. *et al.* Superconductivity above 100 K in single-layer FeSe films on doped SrTiO₃. *Nature Materials* **14**, 285–289 (2015).
- [3] Devreese, J. T., Klimin, S. N., van Mechelen, J. L. M. & van der Marel, D. Many-body large polaron optical conductivity in SrTi_{1-x}Nb_xO₃. *Phys. Rev. B* **81**, 125119 (2010).
- [4] Chen, C., Avila, J., Frantzeskakis, E. & Levy, A. Observation of a two-dimensional liquid of Frohlich polarons at the bare SrTiO₃ surface. *Nature Communications* (2015). doi:10.1038/ncomms9585
- [5] Cancellieri, C. *et al.* Polaronic metal state at the LaAlO₃/SrTiO₃ interface. *Nature Communications* **7**, 10386 (2016).
- [6] [1] S. Moser, S. Fatale, P. Krüger, H. Berger, P. Bugnon, A. Magrez, H. Niwa, J. Miyawaki, Y. Harada, and M. Grioni, *Phys. Rev. Lett.* **115**, 096404 (2015).
- [7] [1] S. Fatale, S. Moser, J. Miyawaki, Y. Harada, and M. Grioni, *Phys. Rev. B* **94**, 195131 (2016).