Electronic structure calculations on two-dimensionally localized medium-sized polaron states in doped wide band gap oxides

Creating a two-dimensional electron gas in a bulk crystal

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In Short

- Investigate the possibility of creating a two-dimensional electron gas (2DEG) by aggregation of the dopants in tetragonal oxides with highly anisotropic Bohr-radii.
- Calculate the transport properties of such a 2DEG, for comparison with experiment.
- Simulate the STM image of the 2D polarons for comparison with experiment.

While graphene and other monolayer structures, like hexagonal BN and transition metal dichalcogenides, as well as two-dimensional topological insulators have called renewed attention to a possible practical utilization of two-dimensional (2D) physics, upscaling for mass production, especially in electronics, seems yet far away. In contrast, high electron mobility transistors (HEMT), based on a 2D electron gas (2DEG), are by now commercially utilized in high-power and high-frequency electronic applications. These devices are based on the very high conductivity of a 2DEG at the interface of semiconductors. A 2DEG can also be formed on the surface of wide band gap oxides giving rise to further possibilities for optoelectronic devices. In any practical realization of 2DEG-based devices, an interface has to be constructed, which limits the volatility of device design (horizontal vs. vertical). TiO_2 is probably the most studied transition metal oxide, and it has been shown that a high mobility 2DEG can be formed at the (001) surface of its anatase modification, if interfaced with $LaAlO_3$ [1]. Interestingly, STM studies on the (101) surface of Nb-doped anatase have found a 2D electron state extending along the (001) plane, and it has been speculated, whether that is a shallow donor state of Nb, or a large polaron bound to it [2]. The limited spatial extent of the state observed in STM is indicative of either a hydrogen-like state or of a medium-size polaron (a transition between a strongly localized small polaron and a delocalized large Frölich-polaron). The 2D nature would probably follow in both cases from the large anisotropy of the effective mass in anatase, which leads to Bohr radii of $a_{\perp}$ = 5.45 Å and $a_{||}$ 1.28 Å. It is appealing to assume and investigate, whether these 2D states are the basis of the observed highly conductive 2DEG on the (001) surface of anatase (and also of $SrTiO_3$) [1]. In STM, only their edge is seen on the (101) surface [2], which indicates that they extend into and, in principle, could be produced in the bulk. Since these states are apparently connected to the dopant, it seems plausible that they can be created anywhere in the bulk by well controlled implantation, or – maybe – by 2D aggregation of the dopant. If that is the case, a high mobility 2DEG could be produced anywhere in the bulk of anatase, or in some similarly anisotropic material, opening up new possibilities for designing devices. The present proposal aims at investigating this possibility by electronic structure calculations.

It is based on our experience over the past decade with calculating the electronic structure of TiO_2 , thanks also to earlier HLRN projects (hbc0001, hbc00017). Our group was the first to point out the reason for the very different behavior of rutile and anatase upon doping, in terms of the essentially different polaronic behavior of these two modifications. We have shown that only electrons can form small polaron states in the bulk of rutile, and holes in the bulk of anatase, while the anatase (101) surface allows for both [3–5]. We have also developed the electronic structure methods, beyond the (semi)local density functional approximation, which are suitable to make such delicate predictions [6,7].

In preparation to this project, we have calculated the electronic structure of Nb-, or Ta-doped anatase, both in the 3D bulk and in 2D slabs, using the hybrid functional HSE in smaller, and the PBE+U functional in larger systems. All calculations show a 2D-state in the (001) plane. Figure 1 shows that in the case of a 960-atom (101) anatase slab. As can be seen, this state is limited in extent and is not centered on the dopant, proving that it is a medium-sized polaron, similar to the one observed in STM.

The project seeks answers to the following questions.

- What is the spatial extent of these polaron states?
- Is there an energy gain on having two dopants in the same over having them in different planes?
- In what other crystals can we find similar 2D polaron states?
- Is there a significant conductivity enhancement along the (001) plane, as observed in experiment [1]?

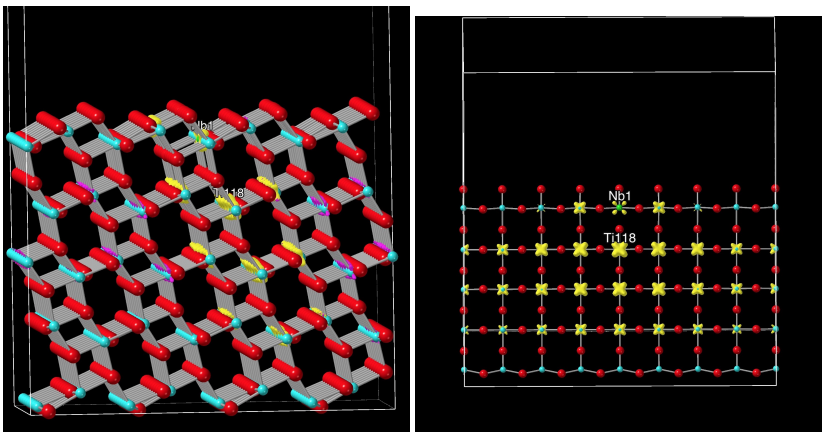

Figure 1: *Two-dimensionally localized electron state in a Nb-doped (101) anatase-TiO_2 slab (left), and its spatial extent along a single (001) plane (right). Blue and red spheres represent Ti and O atoms, the state is represented by yellow lobes.*

- Are 2D polarons we find in anatase identical with the states seen in STM [2]?

To answer these questions, electronic structure calculations on systems with ten thousands of electrons is needed, with sophisticated (beyond semi-local) functionals in density functional theory.

Success of our research may lead to new type of real-life optoelectronic devices.

WWW

`http://www.bccms.uni-bremen.de`

More Information

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