

SLS Symposium on Surface and Interface

Tuesday, October 2, 2012

10:00 to 11:45, WBGB/019

10:00 Disentanglement of Surface and Bulk Rashba Splittings In Non-Centrosymmetric BiTeI

G. Landolt, S.V. Ereemeev, Y.M. Koroteev, B. Slomski, S. Muff, M. Kobayashi, V.N. Strocov, T. Schmitt, Z.S. Aliev, M.B. Babanly, I.R. Amiraslanov, E.V. Chulkov, J. Osterwalder, and H. Dil

10:30 Structure of formic acid in the liquid phase

Matthew A. Brown

11:00 Coffee

11:15 Structural studies of the metal-insulator transition in LaNiO_3 thin films

S. J. Leake, S. A. Pauli, M. Schmitt, I. Kalichava, C. Cancellieri, R. Scherwitzl, M. Gibert, J-M. Triscone, and P. R. Willmott

Disentanglement of Surface and Bulk Rashba Splittings In Non-Centrosymmetric BiTel

G. Landolt^{1,2}, *S.V. Ereemeev*^{3,4}, *Y.M. Koroteev*^{3,4}, *B. Slomski*^{1,2}, *S. Muff*^{1,2},
*M. Kobayashi*², *V.N. Strocov*², *T. Schmitt*², *Z.S. Aliev*⁵, *M.B. Babanly*⁵,
*I.R. Amiraslanov*⁶, *E.V. Chulkov*⁷, *J. Osterwalder*¹, and *H. Dil*^{1,2}

¹Physik-Institut, Universität Zürich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

²Swiss Light Source, Paul Scherrer Institut, CH-5232 Villigen, Switzerland

³Institute of Strength Physics and Materials Science, Siberian Branch, Russian Academy of Sciences, Akademicheskii pr. 2/1, Tomsk, 634021 Russia

⁴Tomsk State University, Tomsk, 634050 Russia

⁵Baku State University, General and Inorganic Chemistry Department, Baku, Azerbaijan

⁶Institute of Physics, Azerbaijan National Academy of Science, Baku, Azerbaijan

⁷Donostia International Physics Center (DIPS) and CFM, Centro Mixto CSIC-UPV/EHU, Departamento de Física de Materiales, UPV/EHU, 20080 San Sebastian, Spain

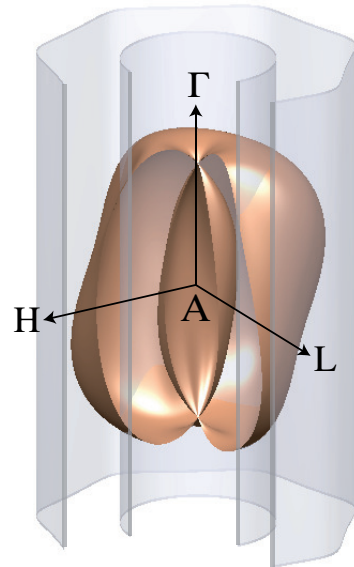
ABSTRACT

BiTel has a layered and non-centrosymmetric structure where strong spin-orbit interaction leads to a giant spin splitting in all bands of the bulk band structure, as was predicted by ab-initio calculations [1].

Even though BiTel has a non-centrosymmetric crystal structure, time-reversal symmetry ensures the *bulk* band structure to be inversion symmetric around the time-reversal invariant momenta, when neglecting spin. However due to the missing inversion symmetry of the crystal, there are two opposite, non-equivalent *surface* terminations.

Here we show that the recently reported two-dimensional state at Fermi level [1] is not a quantum well state but a surface state. In fact, both surfaces host an electron- and a hole-like surface state, respectively. The surface state character is proven by spin-resolved UV-ARPES measurements and is supported by ab-initio calculations. More recent publication corroborate this interpretation [2].

Due to photoemission matrix element effects in the UV regime the hole-like surface state overshadows the bulk conduction band. Here we present the first ARPES data on BiTel in the soft x-ray regime where the spectral intensity of the surface state is very low. The data clearly show the three-dimensional dispersion of the Rashba-type spin-split bulk conduction band, revealing the complex shape of the bulk Fermi surface induced by spin-orbit interaction. It takes the shape of a torus or a spindle-torus, depending on the position of the Fermi level. Comparison of these soft x-ray data with our UV-ARPES measurements allows to disentangle the surface from the bulk electronic structure.



References:

1. K. Ishizaka et al, Nature Materials **10**, 521-526 (2011)
2. A. Crepaldi et al., Phys. Rev. Lett. **109**, 096803 (2012)
3. G. Landolt et al., Phys. Rev. Lett. **109**, 116403 (2012)

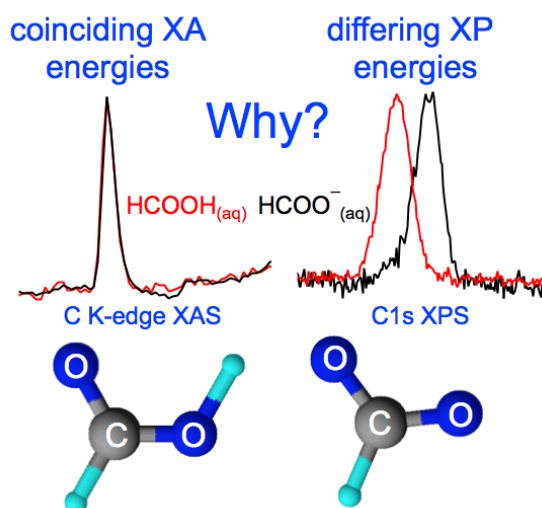
Structure of formic acid in the liquid phase

Matthew A. Brown

Institute for Chemical and Bioengineering, ETH Zürich, CH-8093 Zürich, Switzerland

matthew.brown@chem.ethz.ch

The electronic structure of formic acid (HCOOH) and of the formate ion (HCOO⁻) has been investigated in aqueous solutions over a pH range of 1.88–8.87 using a combination of in situ X-ray photoelectron spectroscopy (XPS), in situ partial electron-yield X-ray absorption spectroscopy (PEY XAS), and density functional theory (DFT). The carbon 1s XPS measurements reveal a chemical binding energy shift of -1.3 eV for deprotonated HCOO⁻ compared with neutral HCOOH in aqueous solutions due to increased electron density on the carbon atom that results from a shortening of the C—O bonds and the delocalization of the negative charge across the O—C—O bonds, and allows for the protonation state of formic acid in aqueous solutions to be easily identified using XPS. Such distinction between neutral HCOOH and deprotonated HCOO⁻ in aqueous solutions cannot be made based solely on the respective carbon K-edge PEY XA spectra. Independent of pH the C1s → π* state excitations occur at 288.0 eV photon energy and may lead to the incorrect conclusion that the energy levels of the π* state are the same for both species in aqueous solutions. The DFT calculations are consistent with the experimental observations only when a dielectric solvation field and explicit solvation are both included in the model, and show a shift to higher energy for both the occupied C1s and unoccupied π* orbitals of deprotonated HCOO⁻ compared to neutral HCOOH in aqueous solutions.



M.A. Brown, F. Vila, M. Sterrer, S. Thürmer, B. Winter, M. Ammann, J.J. Rehr, J.A. van Bokhoven
Electronic structures of formic acid (HCOOH) and formate (HCOO⁻) in aqueous solutions
Journal of Physical Chemistry Letters **3**, 1754 (2012).

Structural studies of the metal-insulator transition in LaNiO₃ thin films

**S. J. Leake¹, S. A. Pauli¹, M. Schmitt¹, I. Kalichava¹,
C. Cancellieri¹, R. Scherwitzl², M. Gibert², J-M. Triscone², and
P. R. Willmott¹**

¹ Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland

² DPMC, University of Geneva, CH-1211, Geneva, Switzerland

steven.leake@psi.ch

LaNiO₃ has proved to be an exception in its class, it is the only rare earth nickelate not to exhibit a metal-insulator (MI) transition in its bulk form remaining a metal at all temperatures[1]. However, Scherwitzl *et al.* recently observed a MI transition (20-40K) when grown as a strained heterostructure on SrTiO₃ below a critical thickness t_c of 8u.c (unit cells) and insulating behaviour at room temperature below 5u.c[2]. Given the lattice mismatch between film and substrate (~1.7%) compared to the bulk the structure is considerable, hence a detailed structural understanding is required to deduce the nature of the MI transition.

Surface X-Ray Diffraction (SXRD) can resolve the entire atomic structure of the film under investigation with the required sub-Angstrom resolution. The SXRD technique will be introduced, its sensitivity to octahedral rotations described and our results on the structure of LaNiO₃ presented as a function of thickness at room temperature. The presence of superstructure signal due to the tilting of oxygen octahedra was seen above t_c [3]. Films of thickness below t_c demonstrated a complete octahedral reconstruction with differing domain populations and registry, see fig.1. No octahedral rotations for films below a thickness of 5u.c.

[1] J. L. Garcia-Munoz et al., Phys. Rev. B. 46, 4414 (1992)

[2] R. Scherwitzl et al., Applied Physics Letters, 95, 222114 (2009)

[3] S. J. May et al., Phys. Rev. B, 82, 014110 (2010)

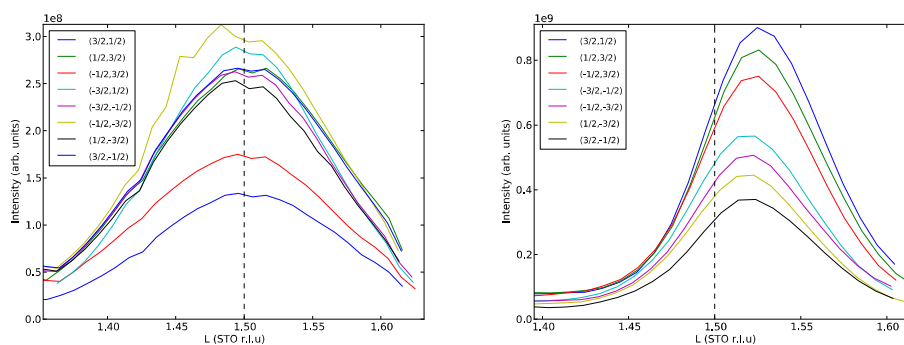


Figure 1: Observed superstructure signal for a set of equivalent positions in a 6u.c and 10u.c thin film.