O 11 Elektronische Struktur I

Zeit: Freitag 15:45–17:00 Raum: TU EB420

O 11.1 Fr 15:45 TU EB420

Oxygen 1s NEXAFS spectra of differently terminated V_2O_3(0001) surfaces: ab initio DFT cluster studies for the $V'OV$ and $O_tV'O$ terminations — •Christine Kolczewski and Klaus Hermann — Fritz-Haber Institut der Max-Planck Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

In the present work we use model clusters and ab initio density functional theory (DFT) together with gradient corrected functionals to obtain theoretical 1s core excitation spectra of differently coordinated oxygen appearing near the V_2O_3(0001) surface. Here we consider both the intrinsic half metal layer, $V'OV$, and the vanadyl termination, $O_tV'O$. Comparison of the theoretical spectra with those from recent NEXAFS experiments [1] spectra yields overall good agreement. This allows us to assign spectral details in the experiment to specific O 1s core excitations where final state orbitals are determined by the local binding of the differently coordinated oxygen centers. The strong dependence of peak positions and relative intensities on the photon polarization direction found in experiment is also described well by the present theoretical spectra. As a result, a combination of the present theoretical spectra with experimental NEXAFS data enables an identification of differently coordinated surface oxygen species at the V_2O_3(0001) surface.

[1] A.-C. Dupuis, M. Abu Haija, B. Richter, H. Kuhlenbeck, and H.-J. Freund, Surface Science, 2003, vol. 539(1-3), 99-112

O 11.2 Fr 16:00 TU EB420

Electronic structure of alkaliated transition metal oxides used as battery cathodes — •Andreas Thissen[1], Francisco Javier Fernandez Madrigal[1], Qi-Hui Wu[2], Stefan Laubach[3], Peter C. Schmidt[3], and Wolfram Jaegermann[1] — [1]FB Material- und Geowissenschaften, FG Oberflächenforschung, TU Darmstadt, Petersenstr. 23, D-64287 Darmstadt — [2]Lehrstuhl für Physikalische Chemie I, Ruhr-Universität Bochum, Universitätsstr. 150, D-44780 Bochum — [3]FB Physikalische Chemie, FG Festkörpertheorie, TU Darmstadt, Petersenstr. 20, D-64287 Darmstadt

Electronic structure of (Li, Na)xV2O5 and (Li, Na)xCu2.33V4O11 has been studied by XPS, UPS, ResPES and XAS. V2O5 thin films have been prepared by PVD and RF magnetron sputtering. From ResPES partial valence band density of states has been derived, giving a V3d-admixture to the valence band of 12 percent, comparing well to recent DFT calculations. From that value real oxidation numbers are calculated to V+2.5 and O-1. Adsorption of lithium and sodium at room temperature leads to spontaneous intercalation until alkali saturation concentrations of Li2.4V2O5 and Na2V2O5 are reached. O.32 electrons per lithium and 0.42 electrons per sodium atom are transferred to V3d states, reducing the formal oxidation state of the V-ion from 5+ to 4+. The Fermi-level is shifted upwards due to the charge transfer and the V3d states are stabilized by localization indicating the breakdown of the rigid band model. A model is shown, to correlate the electronic structure to battery voltages against Li/Li+ from electrochemical measurements. This work is funded by DFG(SFB595), EU(INTERCALNET) and BMBF.

O 11.3 Fr 16:15 TU EB420

Electronic structure of Li-inserted V_6O_{13} battery cathodes: rigid band behaviour and effects of hybridization — •V. Eyert[1], U. Schwingenschlögl[1], T. Schmitt[2], and L.-C. Duda[2] — [1]Institut für Physik, Universität Augsburg — [2]Department of Physics, Uppsala University

The electronic properties of $Li_xV_6O_{13}$ battery cathodes are studied by means of resonant soft x-ray emission spectroscopy and *ab initio* calculations as based on density functional theory using the augmented spherical wave (ASW) method. For $x = 0, \ldots, 6$ we observe both experimentally and theoretically a rather rigid shift of the V 3*d* bands centered about the Fermi energy. However, lithiation leads to an overall weakening of the V 3*d*-O 2*p* hybridization. These findings conform with the observed high crystal structure stability upon insertion of Li, which is essential for the desired use as a battery cathode material.

O 11.4 Fr 16:30 TU EB420

Analysis of the $SrTiO_3$ Valence Band Structure by X-ray Standing Wave Measurements and Ab-Initio Calculations — •Sebastian Thiess[1], Tien-Lin Lee[1], François Bottin[2], Bruce C.C. Cowie[1], and Jörg Zegenhagen[1] — [1]ESRF, Grenoble, France — [2]CEA, Bruyères-le-Châtel, France

We have determined the Sr, Ti and O components of the $SrTiO_3$ valence band (VB) by site-specific X-ray photoelectron spectroscopy employing the X-ray Standing Wave (XSW) method. Decomposition into angular-momentum resolved density of states for each element was achieved by comparision with *ab initio* calculations based on norm-conserving pseudopotentials within the local density approximation.

Lattice site-specific electronic information - which is not available from standard XPS - is obtained by utilising the spatial intensity modulation of an XSW interference field, generated by the coherent superposition of an incident and a Bragg-reflected x-ray beam. By proper positioning the antinodes of the XSW within the STO unit cell, photoemission from specific lattice sites can be preferentially excited and their valence electronic contribution identified.

XSW fields were generated by the STO(111) and STO(112) reflections at photon energies of 2.75 and 3.89 keV. XSW modulated, high-resolution core and valence-electron emission spectra were recorded from an in-situ UHV annealed STO single crystal at beamline ID32 at the ESRF.

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Electronic Structure of decagonal Al-Cu-Co quasicrystals — •Jan Hugo Dil[1], JeongWon Kim[1], Eli Rotenberg[2], Karsten Horn[1], and Wolfgang Theis[3] — [1]Fritz-Haber-Institut der MPG, Berlin — [2]Advanced Light Source, Lawrence Berkeley Lab — [3]Fachbereich Physik der FU Berlin

An analysis of the electronic structure of quasicrystals is important for an explanation of the unusual structural and physical properties of these materials. Progress has been made in understanding the band structure in the lower s-p region of the valence levels in decagonal quasicrystalline alloys. However, an identification of the dispersion relation of bands near the Fermi level in these solids, which lack translational symmetry, is still missing. Here we characterize the electronic levels in decagonal Al-Cu-Co through photoemission data from the tenfold and twofold symmetric surfaces. Al-Cu-Co is a useful material from the point of view of photoemission experiments since the Cu and Co d bands are well separated, and the influence of either d metal can thus be identified. We compare strongly dispersing features in the region near E_F with LEED data to identify those reciprocal lattice vectors which give rise to dominant features in the photoemission intensity maps, and compare our data with results from Al-Ni-Co where the Ni and Co bands overlap.