Electrochemically Doped Oxides

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Using electrochemistry in order to change the concentration of light alkaline ions in transition metal oxides is an alternative way to alter the charge carrier doping in transition metal oxides. By extraction and insertion of Li and Na, as utilized in modern state of the art rechargeable power sources, it is possible to prepare transition metal oxides with unusual oxidization states and anomalous physical properties. So far, we have applied this method (i) to change the formal valence state of Cu in low-dimensional cuprates, (ii) to change the Na content in high quality single crystals of the well known Na_xCoO_2 system and (iii) to incorporate Li in VO_x nanotubes. In all cases drastic changes of the electronic and/or magnetic properties are observed. In the talk some aspects of the physical properties of both, the pristine materials as well as the electrochemically doped compounds will be presented and discussed.
In the case of the cobaltates the electrochemistry is an alternative way to determine the phase diagram of this chemically very complex class of materials. Evidence is presented that electrochemistry is a possibility to realize different doping levels in high quality single crystals. Concerning the physical properties we have studied the charge ordering using high energy x-ray diffraction [1]. In addition, several spectroscopic methods (XAS, ARPES) have been used in order to study the electronic structure of the pristine compounds [2,3]. The results will be discussed and compared to recent DFT calculations.
Very spectacular changes of the properties are found by intercalating Li in VO_x nanotubes. While the pristine materials exhibit a large spin gap, a ferromagnetic state is observed if Li ions are incorporated in the nanotubes. From EELS studies we find a mixture of V ions with different oxidation state, which changes as a function of the Li content [4]. The magnetism has been studied using magnetization measurements and studies of the NMR. For the pristine material both methods give a consistent result concerning the number and distribution of magnetic and non-magnetic V sites [5]. Moreover, the results from the magnetic studies are in qualitative agreement with the EELS data. For the Li doped nanotubes the magnetization shows a pronounced ferromagnetic response up to room temperature. However, so far no clear-cut signatures of the ferromagnetism are found in our NMR measurements.

References

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