

Exploitations of Novel Spectroscopic Methods for Material and Surface Science

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For the developments of novel functional materials, it is quite important to exploit simultaneously new analytical methods based on advanced technology. Novel materials and devices often require spatial and/or time resolved analysis to optimize their qualities. In our group, we have been exploiting spectroscopic methods for material and surface science using mainly synchrotron radiation (SR) and partly lasers.

The first subject in our group is the spectroscopic analysis systems of magnetic thin films. In 2006, we successfully invented a novel magnetic nanoscope using ultraviolet magnetic circular dichroism photoelectron emission microscopy, which allows us to perform real-time and ultrafast magnetic imaging to investigate magnetic dynamics. We have also constructed in situ x-ray magnetic circular dichroism (XMCD) system using a ultrahigh vacuum superconducting magnet and a liq. He cryostat, which is installed at Beamline 4B of the IMS SR facility UVSOR-III. The XMCD apparatus is extensively open for public usage and many domestic and foreign researchers visit every year. We are currently interested in transition-metal phthalocyanine monolayers on nonmagnetic and ferromagnetic surfaces, whose electronic and magnetic properties are tunable by changing the central metal atom and/or modifying the ligand. Our recent achievement will be presented in the next page.

The second subject is the exploitation of near-ambient pressure hard x-ray photoelectron spectroscopy (HAXPES) for

polymer electrolyte fuel cells (PEFC) under working conditions. Although usually photoelectron spectroscopy is believed to be done under ultrahigh vacuum, recent material science requires in situ measurements under working conditions. We have installed nearly ambient pressure (up to 5000 Pa) HAXPES apparatus in Beamline 36XU of SPring-8. We have successfully investigated Pt 3d HAXPES of Pt/C, PtCo/C and PtNi/C cathode catalysts in PEFC under working conditions to reveal degradation mechanism of PEFC. This work is supported by the NEDO Fuel Cell project.

The third subject is the pico- and femtosecond pump-and-probe time resolved x-ray absorption fine structure (XAFS) spectroscopy. XAFS is a quite powerful technique for investigating quantitative local structures of very low concentrated element by using the *energy-resolved* x-ray fluorescence detection technique. Fast time resolved XAFS measurements are, however, usually difficult since the frequencies between normal SR (probe) and pumping lasers are far different, requiring pulse picking of the SR probe and resultantly time resolved detection of *energy-integrated* x-ray fluorescence. To solve this problem, a picosecond laser with high repetition rate (up to 1 MHz) was installed in Photon Factory Advanced Ring with single bunch operation (794 kHz). This allows us to investigate XAFS of low concentration elements using a slow but energy-resolved x-ray fluorescence detector.

Selected Publications

- K. Eguchi, T. Nakagawa, Y. Takagi and T. Yokoyama, *J. Phys. Chem. C* **119**, 9805 (2015).
- K. Eguchi, Y. Takagi, T. Nakagawa and T. Yokoyama, *J. Phys. Chem. C* **118**, 17633 (2014).
- Y. Takagi, H. Wang, Y. Uemura, E. Ikenaga, O. Sekizawa, T. Uruga, H. Ohashi, Y. Senba, H. Yumoto, H. Yamazaki, S. Goto, M. Tada, Y. Iwasawa and T. Yokoyama, *Appl. Phys. Lett.* **105**, 131602 (2014).
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1. Synthesis and Structural/Magnetic Properties of Vanadium Phthalocyanine¹⁾

Controlling a wide range of functionalities of metal complexes on substrate surfaces for the applications such as molecular spintronics, molecular devices, and molecular catalysis is of special importance. Metal phthalocyanine (MPc) is one of the most promising materials. Although most 3d transition metal Pcs have been synthesized, ScPc or VPc has never been obtained because of high air sensitivity during the chemical synthesis. In this work, we have successfully prepared VPc monolayer and multilayer on Ag(111) in a ultrahigh vacuum (UHV) deposition technique. Moreover, we investigated structural and magnetic properties of monolayer and multilayer VPc using XAFS and XMCD.

VPc was synthesized by depositing H₂Pc and subsequent V metal on a clean and ordered Ag(111) surface. Monolayer VPc did not require any annealing process to complete the reaction $V + H_2Pc \rightarrow VPc + H_2$, while multilayer VPc needed annealing at 450 K. The identification of VPc was carried out by in-laboratory N1s XPS. The N1s XPS of H₂Pc shows two peaks assigned to iminic (–N=) and pyrrolic (–NH–) nitrogen, while that of metal Pc exhibits a single peak. The present observation of a single N1s peak clearly elucidate the successful synthesis of monolayer and multilayer VPc. From the V2p XPS, V is found to be divalent, as expected, although some amount of charge transfer from the substrate Ag(111) was observed in monolayer.

Linear polarization dependence of the N K-edge XAFS of VPc on Ag(111) has revealed flat-lying orientation of monolayer VPc and rather random orientation of multilayer. The V L-edge XAFS and XMCD have indicated complicated electronic structure of VPc due to strong configuration interaction between 2E_g ($3d_{xy}$)²($3d\pi$)¹ and other configurations as ($3d_{xy}$)²($3d_z^2$)¹, similarly to other transition metal Pcs. The V L-edge XMCD spectra shown in Figure 1 suggest the doublet state in monolayer on Ag(111) and embedded in H₂Pc multilayer, while multilayer exhibits antiferromagnetism due to intermolecular exchange interaction.

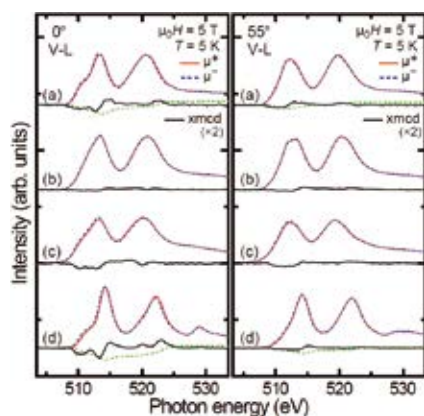


Figure 1. V L-edge XMCD of VPc on Ag(111) at incident x-ray angles of 0° (normal incidence, left panel) and 55° (grazing incidence, right panel): (a) monolayer embedded in multilayer H₂Pc, (b) multilayer, (c) monolayer and (d) VOPc monolayer as a reference.

2. Anomalous Structural Behavior in Metamagnetic Transition in FeRh Films

The FeRh intermetallic compound with ordered CsCl structure is known to exhibit an interesting metamagnetic transition from antiferromagnetic (AFM) to ferromagnetic (FM) phase with the temperature rise ($T_C \sim 385$ K), which would be applicable to thermally assisted recording/memory media. In this work, FeRh thin films have been investigated via temperature dependent XAFS spectroscopy in order to gain correlations between the magnetization and the local electronic and geometric structures.

According to the Fe and Rh K-edge XAFS, strong hybridization was found to exist between Fe and Rh. This Fe–Rh hybridization was revealed to decrease during the phase transition from the systematic change observed in the Fe K-edge XAFS. On the other hand, only the Debye-Waller factor of the Fe–Fe pair in the AFM phase was found to be considerably enhanced when compared with that in the FM phase, which was ascribed to local structural fluctuation inherent in the AFM phase itself. This anomalous feature is interpreted in consistent with the recent theoretical study proposing the local fluctuations of spin and structure by considering the different features of the exchange interactions in Fe–Rh and Fe–Fe. Therefore, we consider that the local Fe–Fe distance and the spin fluctuations play an important role for driving the metamagnetic transition, whereas the Fe–Rh hybridization is important for determining the static stability of each magnetic phase.

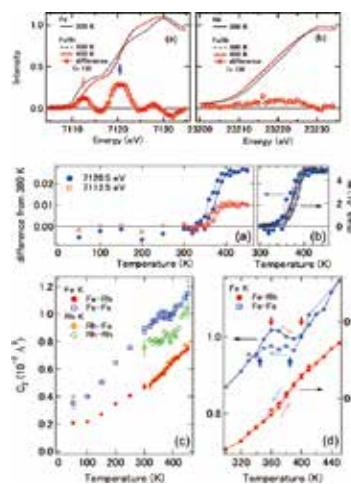


Figure 2. (a) Fe K-edge XAFS intensity at 7120.5 (blue) and 7112.5 (red) eV. (b) SQUID magnetization (black) compared to XAFS (7120.5 eV, blue). A slight T_C difference between SQUID and XAFS implies a difference in the phase transition nature between macroscopic and microscopic origins. (c,d) Debye-Waller factors for the atom pairs of the first nearest neighbor Fe–Rh and the second nearest neighbor Fe–Fe and Rh–Rh. Only the Fe–Fe pair exhibits an interesting anomaly.

Reference

- 1) K. Eguchi, T. Nakagawa, Y. Takagi and T. Yokoyama, *J. Phys. Chem. C* **119**, 9805 (2015).