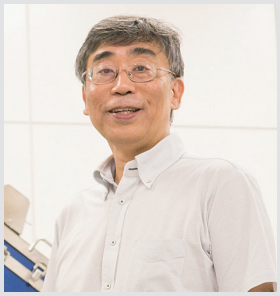
Exploitation of Novel Spectroscopic Methods for Material and Surface Science

Department of Materials Molecular Science
Division of Electronic Structure



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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 (UVMCD) photoelectron emission microscopy (PEEM), 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 an ultrahigh vacuum superconducting magnet and a liq. He cryostat, which is installed at Beamline 4B of the IMS SR facility UVSOR-III. The apparatus is extensively open for public usage.

The second subject is the exploitation of ambient pressure hard x-ray photoelectron spectroscopy (AP-HAXPES) for polymer electrolyte fuel cells (PEFC) under working conditions. In 2017, we succeeded in real ambient pressure (10^5 Pa) HAXPES measurements for the first time in the world using Beamline 36XU of SPring-8. These works were supported by the NEDO Fuel Cell project. More recently, the apparatus moved to BL46XU and is used for more general chemical reactions on heterogeneous catalysts and electrochemical cells such as CO_2 reduction.

The third subject is applications of the x-ray absorption fine structure (XAFS) spectroscopy, soft x-ray emission spectroscopy, and angle-resolved ultraviolet photoelectron spectroscopy for functional materials. These investigations include femto- and picosecond time resolved XAFS measurements using x-ray free electron laser SACLA, for the investigations of the geometric structure of the photoexcited state of photocatalytic systems and the spin dynamics of magnetic materials. Conventional temperature dependent EXAFS spectroscopy has been conducted for a very long time to elucidate thermal and dynamic properties of functional alloy materials as negative thermal expansion alloys.

Selected Publications

- T. Nakagawa and T. Yokoyama, "Magnetic Circular Dichroism near the Fermi Level," *Phys. Rev. Lett.* **96**, 237402 (2006).
- T. Yokoyama and K. Eguchi, "Anharmonicity and Quantum Effects in Thermal Expansion of an Invar Alloy," *Phys. Rev. Lett.* **107**, 065901 (2011).
- Y. Uemura *et al.*, "Dynamics of Photoelectrons and Structural Changes of Tungsten Trioxide Observed by Femtosecond Transient XAFS," *Angew. Chem., Int. Ed.* **55**, 1364–1367 (2016).
- Y. Takagi, T. Nakamura, L. Yu, S. Chaveanghong, O. Sekizawa, T. Sakata, T. Uruga, M. Tada, Y. Iwasawa and T. Yokoyama, "X-Ray Photoelectron Spectroscopy under Real Ambient Pressure Conditions," *Appl. Phys. Express* **10**, 076603 (2017).
- T. Koitaya, K. Yamamoto, T. Uruga and T. Yokoyama, "*Operando* Characterization of Copper–Zinc–Alumina Catalyst for Methanol Synthesis from Carbon Dioxide and Hydrogen by Ambient-Pressure Hard X-Ray Photoelectron Spectroscopy," *J. Phys. Chem. C* **127**, 13044–13054 (2023).

1. Local Thermal Expansion of Co-Containing Invar Alloys[1)]

Low thermal expansion materials are quite attractive from the viewpoints of both fundamental science and industrial technology. FeNi invar alloys are quite familiar and have been applied to precision equipment as telescope, microscope, and nanodevice, and also been employed as core cables of electric high-voltage power lines to avoid sagging due to heat on high current conduction. Recently, Fujii *et al.* developed a new stainless invar alloy, which is employed for the cryogenic infrared space telescope in National Astronomical Observatory. In this work, we measured and analyzed EXAFS spectra of Co-containing invar alloys of this newly developed stainless invar, together with Kovar $Fe_{53}Co_{17}Ni_{29}X_1$ for comparison. We will focus our attention on how Co plays a role in the invar effect from the local structure viewpoint, which is often different from the macroscopic points of view.

Two stainless invar foils with 10 μm thickness were prepared and the elemental compositions are found to be $Fe_{38.8}Co_{50.1}Cr_{9.2}Ni_{1.9}$ and $Fe_{37.8}Co_{51.3}Cr_{9.0}Ni_{1.9}$ by the x-ray fluorescence spectra. Cr, Fe, Co, and Ni K-edge EXAFS spectra of commercially available Kovar (10 μm) and the stainless invar foils were recorded with the transmission mode in BL9C of Photon Factory, High Energy Accelerator Research Organization (KEK-PF) at 30–300 K using a He gas-circulating refrigerator installed at the beamline. The lattice thermal expansion coefficients of Kovar and stainless invar were measured by the laboratory dilatometer. We have also recorded Cr, Fe and Ni K-edge EXAFS of FeNi invar alloys $Fe_{64}Ni_{36}$, $Fe_{58}Ni_{42}$, and $Fe_{55}Ni_{45}$, stainless steel SUS304 ($Cr_{18.09}Fe_{71.98}Ni_{9.07}X_{0.86}$) and the Ni spanC Elinvar alloy ($Cr_{5.49}Fe_{49.66}Ni_{42.38}Ti_{2.47}$).

Temperature dependent EXAFS spectra were analyzed with the standard method including the third-order cumulant to yield thermal expansion for the first-nearest neighbor (NN) shells correctly. Since the first-NN shell includes different atom pair contributions, the analysis yields only the average distances. Nevertheless, assuming that the interatomic distance is given as a sum of the atomic radii, all the interatomic distances are evaluated as long as all the corresponding EXAFS spectra provide the average distances. Figure 1 shows the thermal expansion at 200 K thus obtained for the interatomic distances and the lattice constant as a function of corresponding distances. Since the two stainless invar alloys exhibit essentially the same results and the average values are given here. In FeNi invar, the Fe–Fe pair shows significant reduction of the interatomic distance and thermal expansion going from 42 and 45 invar to 36 invar, while the Ni–Ni one exhibits little suppression of thermal expansion and negligible distance contraction. This clearly implies that Fe exclusively contributes to the invar effect in $Fe_{64}Ni_{36}$. In stainless invar in Figure 1(b), it is found that thermal expansions of Fe–Fe, Fe–Co, and Co–Co are significantly smaller than in Kovar, associated with shortening of the corresponding interatomic distances. This implies a much more significant invar effect on Co as well as Fe in stainless invar, while the invar effect on Co is negligibly small in Kovar. The path-integral effective classical potential simulations exhibit qualitative agreement with this finding, indicating that the Co magnetization is more noticeably suppressed with a temperature rise in stainless invar, because of a smaller lattice constant and interatomic distances and also of the presence of Cr in stainless invar, both of which favor antiferromagnetic coupling. The present study clearly demonstrates importance of local structure point of view to understand detailed low thermal expansion mechanism, in which microscopic local thermal expansion noticeably differs from macroscopic lattice thermal expansion.

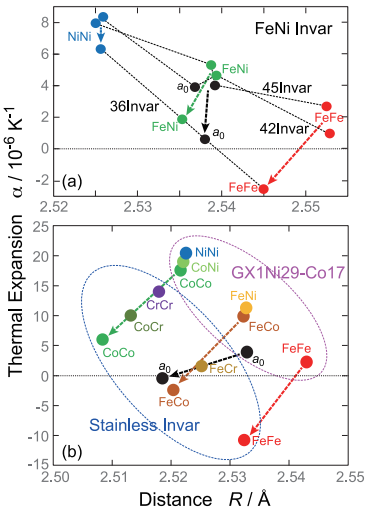

Figure 1. Thermal expansion coefficients α (10^{-6} K^{-1}) at 200 K for the first-NN interatomic distances determined by EXAFS and the lattice constant a_0 versus corresponding distances of (a) FeNi invar and (b) Kovar and stainless invar.

2. Synchrotron Radiation Based Spectroscopic Characterization of Functional Materials

In FY2023, we have been investigating following research subjects. The first one is continuous collaboration with Prof. Toshio Miyamachi in Nagoya University using high-field, low-temperature and ultrahigh-vacuum XMCD system installed at BL4B in UVSOR-III. Interesting magnetic properties such as magnetic anisotropy of ferromagnetic ultrathin films decorated organic molecules are being studied. Second, AP-HAXPES investigations are being conducted for working electrochemical cells on CO_2 reduction. This is a collaboration with Prof. T. Koitaya in Kyoto University and Dr. Y. Takagi in JASRI (both were previous assistant professors in this research group in IMS). Third, research assistant professor Dr. N. Kurahashi is studying peculiar water motion in Nafion solid electrolyte that shows abrupt phase transformation around 15°, using soft x-ray absorption and emission spectroscopy and AP-HAXPES. Fourth, research assistant professor Dr. N. Maejima is investigating a novel 2-dimensional Dirac-cone-like blue phosphorene using angle-resolved photoelectron spectroscopy and low-energy positron diffraction.

Reference

1) T. Yokoyama, H. T. Fujii, S. Matsumura, N. Sakaguchi, N. Kurahashi and N. Maejima, P*hys. Rev. Mater.* **8**, 083603 (2024).