II-G Spin Reorientation Transitions of Ultrathin Magnetic Films Induced by Chemisorption

Magnetic anisotropy of ultrathin metal films is one of the most attractive subjects in magnetism. When one considers magnetic anisotropy of thin films within the framework of the classical electromagnetic theory, one finds that in-plane magnetization is always more stable than perpendicular magnetization. Perpendicular magnetic anisotropy (PMA) is, however, sometimes observed in real systems and the understanding of the origin of PMA is important from the viewpoints of both fundamental physics and technological applications to new-generation high-density recording media. We have been investigating the microscopic mechanism of PMA that is stabilized by gaseous adsorption on magnetic film surfaces by means of the synchrotron radiation x-ray magnetic circular dichroism (XMCD) technique. A goal of these works is spin engineering by which the magnetization of ultrathin metal films can be controlled artificially.

II-G-1 Perpendicular Magnetic Anisotropy in Co/Pd(111) Stablized by Chemisorption of CO and NO

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Spin reorientation transitions of ultrathin Co/Pd(111) films induced by adsorption of atoms and molecules have been investigated by means of Co $L_{\mathrm{III,II}}$-edge x-ray magnetic circular dichroism (XMCD). We have examined CO, NO, O and H as chemisorbed species. Figures 1(a) and 1(b) show the Co $L_{\mathrm{III,II}}$-edge XMCD spectra on clean and CO-adsorbed 4.5 ML Co/Pd(111) at 200 K, respectively. In clean Co/Pd(111) [Figure 1(a)] the XMCD signal appears only in the grazing-incidence (θ = 30˚) spectrum, while in CO-adsorbed Co/Pd(111) the normal-incidence (θ = 90˚) spectrum gives a two-times more intense XMCD signal than the θ = 30˚ spectrum. These observation directly implies that the magnetization direction varies from in-plane to perpendicular upon CO adsorption. We observed a similar adsorbate-induced spin reorientation transition in the NO case as well, while in O or H adsorption no transitions took place. We have investigated detailed Co-thickness dependence in the case of CO. Figures 1(c) and 1(d) show the Co spin magnetic moments of clean and CO-adsorbed Co/Pd(111), respectively. The critical thickness of the spin reorientation transition in CO-adsorbed Co is found to be ~6.5 ML, which is by ~3 ML greater than that of clean Co (~3.5 ML), implying the stabilization of PMA by CO adsorption.

The most important information from XMCD is the orbital magnetic moments, which determine the magnetic easy axis in spite of very small contribution to the total magnetic moments. Figure 1(e) shows the orbital magnetic moments of Co on clean and CO-adsorbed Co/Pd(111). Below ~3.5 ML the *surface normal* orbital moment is found to be left *unchanged*, while above ~6.5 ML the *surface parallel* orbital moment is *reduced* significantly after CO adsorption. We conclude that the observed stabilization of perpendicular magnetic anisotropy due to adsorption is ascribed to *quenching* of the *surface parallel orbital* magnetic moment.

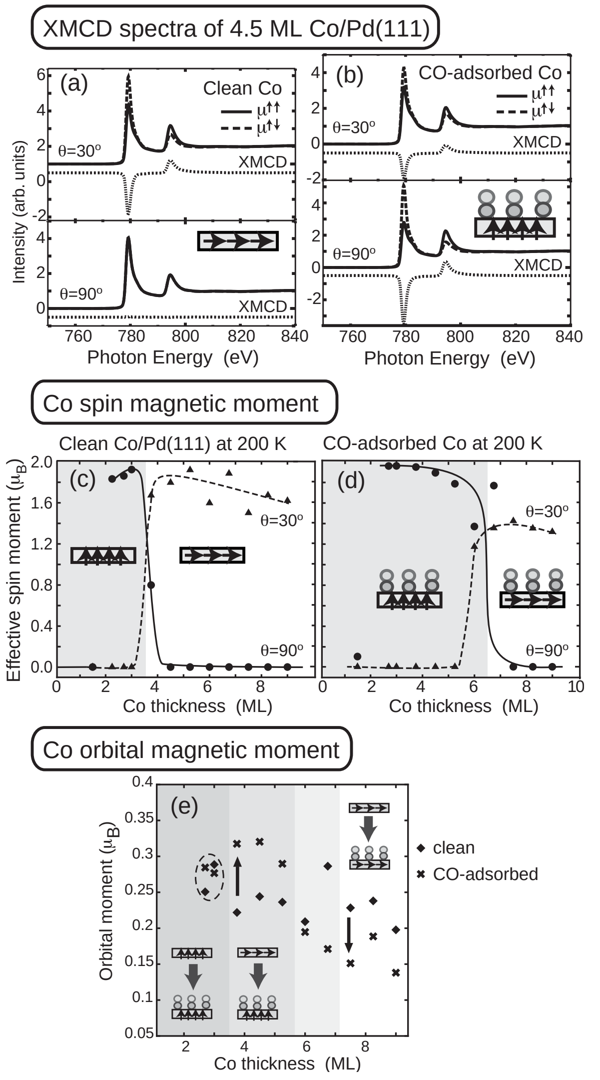

Figure 1. (a), (b): Co $L_{\mathrm{III,II}}$-edge circularly polarized (solid and dashed lines) and XMCD (dotted line) spectra of 4.5 ML Co/Pd(111) at 200 K before (a) and after (b) CO adsorption. θ is the angle between surface normal and the x-ray electric field (θ = 30˚ and θ = 90˚ correspond to grazing and normal x-ray incidence, respectively). It is found that the magnetic easy axis rotates from in-plane in (a) to perpendicular in (b).

(c), (d): Co thickness dependence of the Co spin magnetic moments at 200 K. Hatched areas indicate the PMA regions. The critical thickness for the spin reorientation transition is ~3.5 ML for clean Co (c) and ~6.5 ML for CO-adsorbed Co (d), this indicating that the perpendicular magnetic anisotropy is stabilized upon CO adsorption.

(e): Co thickness dependence of the Co orbital magnetic moments at 200 K. After CO adsorption, the perpendicular orbital moment does not vary so much (see the data below ~3.5 ML), while the in-plane orbital moment reduces significantly (see the ones above ~ 7 ML).

II-H Local Structures in Photoinduced States of Molecular-Based Magnetic Materials

Molecular-based magnets provide noble properties such as photoinduced magnetism. Photoinduced phase transition is closely related to bistability of the ground state in the material. Light irradiation stimulates the macroscopic phase transition between the ground state and the metastable state, although thermal fluctuation triggers the thermal phase transition. Although it has been believed that the photoinduced phase is the same state as the thermally induced phase, recent investigations have reported some differences in structure from the high-temperature phase. We have been studying local structures and electronic properties of photoinduced phases of Prussian-blue analogues and other metal-complex magnets by means of x-ray absorption fine structure (XAFS) spectroscopy. XAFS is one of the most suitable methods for these purposes since the technique does not require long-range order in the sample and provide element-specific information about each metal atom.

II-H-1 Photoinduced Phase Transition of RbMnFe(CN)$_6$ Studied by X-Ray-Absorption Fine Structure Spectroscopy

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A Prussian-blue analogue of RbMnFe(CN)$_6$ shows a thermally induced first-order phase transition ($T_{c\downarrow}$ = 231 K and $T_{c\uparrow}$ = 304 K) and also turns to a ferromagnetic phase below 12 K. Upon visible-light irradiation, the ferromagnetism is quenched and the phase is transformed to the metastable nonmagnetic state. In this work, we have investigated the photoinduced magnetic phase transition of RbMnFe(CN)$_6$ by means of XAFS spectroscopy.

Mn and Fe *K*-edge x-ray-absorption near-edge structure spectra have clarified that upon the phase transition, a Fe 3*d* electron is transferred to the Mn 3*d* level; the electronic state of Mn changes from trivalent (d^4, spin momentum S = 2) to divalent (d^5, S = 5/2), while the Fe state correspondingly varies from divalent (d^6, S = 0) to trivalent (d^5, S = 1/2). Such a tautomeric scheme in the photoinduced phase transition is exactly the same as in the thermally induced transition.

Local structures have been investigated by the extended x-ray-absorption fine-structure analysis for the photoinduced phase as well as for the low- and high-temperature phases. The low-temperature phase shows a significant Jahn-Teller distortion in the Mn(III) octahedron, where the Mn–N distances for four shorter and two longer bonds are 1.964 ± 0.008 Å and 2.21 ± 0.01 Å, respectively. The high-temperature phase gives a longer Mn–N distance of 2.211 ± 0.006 Å, although some minor contribution from a shorter distance still remains. It is also revealed that the atomic configuration of the –Fe–C–N–Mn– chain is essentially collinear and that the Rb ions locate at the center of the cubic lattice. The photoinduced phase was found to be structurally and electronically identical to the high-temperature phase. Summary of the present investigation is given in Figure 1.

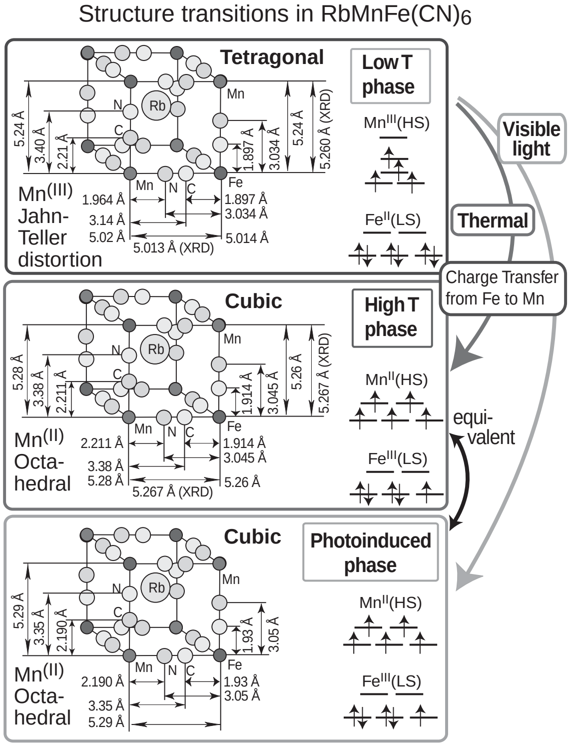

Figure 1. Summary of the present investigation for the phase transitions in RbMnFe(CN)$_6$.