

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 are 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) and the visible-light magneto-optical Kerr effect (MOKE) techniques. 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 Ni/Cu(001) Stabilized by Chemisorption of NO

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Spin reorientation transitions (SRT) of ultrathin Ni/Cu(001) films induced by adsorption of nitric oxide (NO) have been investigated by means of MOKE. A wedge-shaped Ni film (4–11 ML) was grown on a clean and ordered Cu(001) surface at room temperature, and was dosed with NO after cooling down to 90 K. The M-H curves were measured using both the polar and longitudinal MOKE geometries. Figure 1 show the observed coercivity (H_c) of the Ni film at 90 K as a function of Ni thickness. On the clean surface H_c abruptly increases at ~ 9 ML, implying that the SRT occurs at this coverage. On the other hand, the NO-adsorbed Ni film shows a clear shift of the SRT coverage at ~ 7 ML. It is concluded that the Ni/Cu(001) film with 7–9 ML thickness exhibits the SRT from in-plane magnetization to perpendicular after NO adsorption. This finding is consistent with the previous works on CO- and H-adsorbed Ni/Cu(001) films.

Let us here compare the coercivity between before and after NO adsorption at the Ni thickness where the SRT does not occur: less than 7 and more than 9 ML. Although the differences are not so large, it is found that in the in-plane magnetized films H_c is suppressed after NO adsorption while H_c is enhanced at the perpendicu-

larly magnetized ones. These results again imply that NO adsorption stabilizes perpendicular magnetization. It is known that the surface magnetic anisotropy constant K_{2s} is negative and favors in-plane magnetization on clean Ni/Cu(001). After NO adsorption, $|K_{2s}|$ is reduced, this leading to the stabilization of perpendicular magnetization, the suppression of H_c for the in-plane magnetization, and the enhancement of H_c for the perpendicular magnetization.

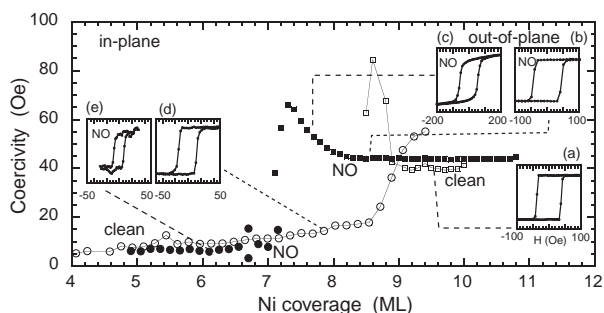


Figure 1. Coersivity of the Ni film at 90 K as a function of Ni thickness before (open circles and squares) and after (filled circles and squares) NO adsorption, obtained by the polar (open and filled squares) and longitudinal (open and filled circles) MOKE measurements. Typical M-H curves are inserted as (a)–(c) (polar) and (d)–(e) (longitudinal).

II-H Local Structures in Photoinduced States of Transition Metal Complexes

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 several kinds of transition metal complexes 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 Metastable Photoinduced Phase of Cu(II) Ethylenediamine Complexes Studied by X-Ray-Absorption Fine-Structure Spectroscopy

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Recently, a new type of the photoinduced (PI) metastable phase was reported in $\text{Cu}(\text{dieten})_2\text{X}_2$ (dieten = *N,N*-diethylethylenediamine, $\text{X} = \text{BF}_4$ and ClO_4) complexes. These materials are known to exhibit thermochromic phase transitions. From the color change the PI transition is expected to be similar to the thermally driven phase transition. The powder X-ray diffraction patterns of the PI phase were, however, found to be different from those of the HT phase, although no correspondence between the structure and diffraction patterns was deduced. In this work, Cu *K*-edge XAFS has been measured and analyzed in order to clarify the molecular structure in the PI phase.

The sample was irradiated by the UV lights (Hg lamp) at 30 K. The Cu *K*-edge near-edge structure indicates that the CuN_4 unit in the PI phase is distorted tetrahedrally, being similar to the HT phase. On the contrary, EXAFS shows a different finding in the second-nearest neighbor Cu–C shells], indicating that the configuration of the surrounding C atoms in the PI phase should be closer to the LT phase rather than to the HT phase.

We can conclude that the PI phase is a new metastable state, whose intramolecular structure is not equivalent to the one of either the HT or LT phase; the CuN_4 unit exhibits tetrahedral distortion, while the atomic configuration of ethylene and ethyl groups is similar to the LT one. One can thus propose a possible model structure shown in Figure 1. The $\text{Cu}(\text{dieten})_2$ ion has an inversion center in the LT phase (point group C_i), while it has a C_2 axis in the HT phase (point group C_2). We can suppose that when the LT phase is transformed to the PI phase upon UV irradiation, the CuN_4 plane is distorted tetrahedrally with less reconstruction of the dieten ligand compared to the LT phase. This might be a reasonable hypothesis since the transformation of the configuration of the ethyl groups and also the anions would require too much activation energy to complete at low temperature like 30 K.

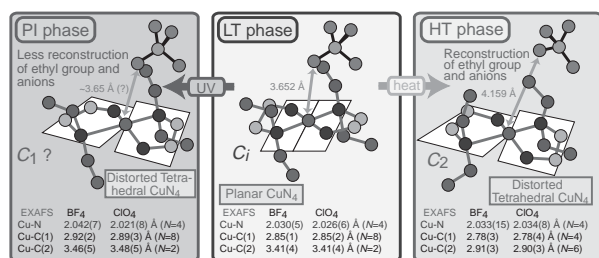


Figure 1. Proposed structure transformation in the PI phase transition.