

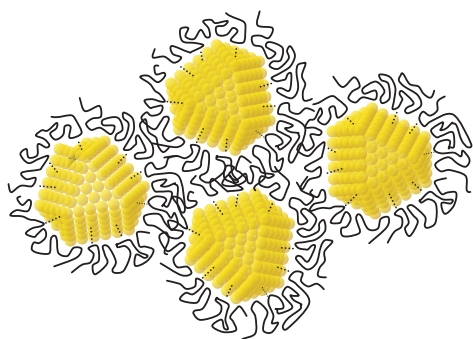
DIRECT EVIDENCE OF FERROMAGNETIC SPIN POLARIZATION IN GOLD NANOPARTICLES

It is believed that bulk gold metal is chemically inert and the most stable metal in nature. However, its properties in the nanosize region might be different from its bulk nature because the electronic structure may be modified significantly. In fact, recent experiments have shown that gold nanoparticles exhibit an enhancement in catalytic activity at a diameter of approximately 2 nm [1]. Moreover, superparamagnetic behavior has been reported for gold nanoparticles stabilized by a polymer (Fig. 1) for diameters below 3 nm [2], although bulk gold metal has non-magnetic (diamagnetic) properties. This indicates that individual Au particles possibly have ferromagnetic moments. However, no clear evidence has been provided showing that the ferromagnetism of Au particles is intrinsic because conventional magnetometry may include magnetization from trivial origins, such as magnetic impurities. Therefore, it is essential to measure the element-specific magnetization of gold atoms to confirm that their magnetism is intrinsic.

In this study, we have presented direct evidence of the intrinsic ferromagnetism of Au nanoparticles protected by polyallyl amine hydrochloride (PAAHC) (abbreviated as PAAHC-Au) by means of element-specific magnetization (ESM) measurements based on the X-ray magnetic circular dichroism (XMCD) technique. The XMCD technique allows the detection of the magnetic moments of a particular element through sensitivity to the difference between the up- and down-spin densities at approximately the Fermi level. This element selectivity is the most important advantage of this technique over conventional magnetometry and is essential in the present study of extracting the magnetization of Au nanoparticles.

XMCD spectra were recorded using a highly sensitive spectrometer installed at beamline **BL39XU**. External magnetic fields up to 10 T were applied along the X-ray beam direction using a split-type superconducting magnet. The experimental resolution was high enough to detect XMCD signals of 10^{-5} parts of the spin-averaged X-ray absorption coefficients. This high sensitivity is achieved through the helicity modulation technique based on lock-in detection [3], and the high brilliance of a third generation synchrotron radiation source. We emphasize that the modulation technique is crucial for the detection of very small ferromagnetism in Au nanoparticles because this technique markedly improves the signal/noise ratio of the XMCD signal.

Figure 2 shows the X-ray absorption spectroscopy (XAS) and XMCD spectra of Au at the L_{3-} ($2p_{3/2}$



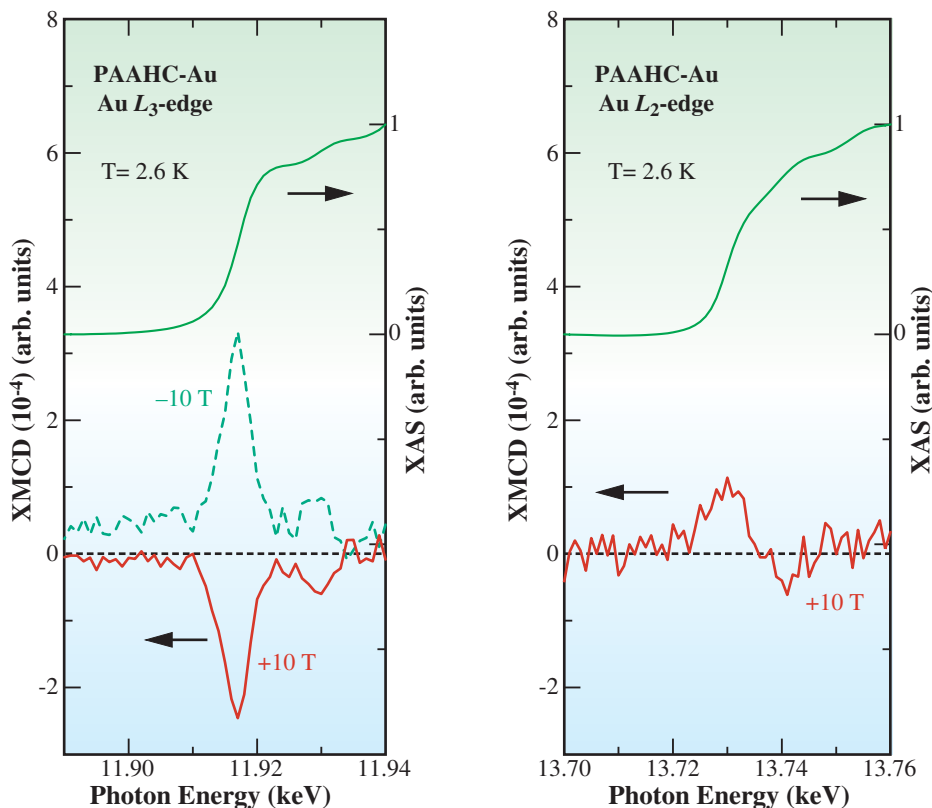


Fig. 2. XMCD and XAS spectra at Au L_3 - and L_2 -edge with applied magnetic fields of 10 T (red solid line) and -10 T (broken line). The XMCD and XAS spectra include the same scale factor so that the heights of the edge jumps of the XAS spectra (solid lines) are unity.

contradict the characteristics of the superparamagnetic model. If one assumes that superparamagnetism and Pauli paramagnetism arise from surface atoms and core atoms in Au nanoparticles respectively, the observed mixture of superparamagnetism and Pauli paramagnetism is reasonably explained.

In summary, our XMCD and ESM experiments have

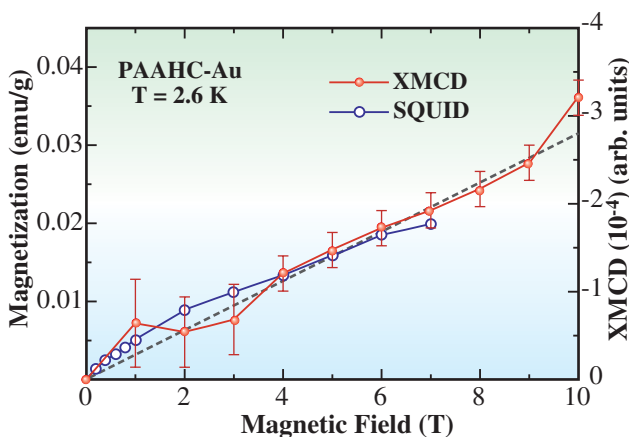


Fig. 3. ESM of PAAHC-Au as a function of applied magnetic field and magnetization process obtained using SQUID magnetometer. The integral of the peak intensity yields similar results. The dashed line is the fit to the data assuming a Langevin function plus a linear field-dependent term.

revealed the intrinsic magnetic polarization in Au nanoparticles with a mean diameter of 1.9 nm [4]. The external magnetic field and temperature dependences of the ESM signal suggest that the magnetization of Au nanoparticles consists of a superparamagnetic part and a temperature-independent Pauli paramagnetic part. The mixture of these components is reasonably explained by the picture that the surface atoms are ferromagnetic and the core atoms are Pauli paramagnetic.

Y. Yamamoto* and H. Hori

School of Materials Science, Japan Advanced Institute of Science and Technology (JAIST)

*E-mail: y-yamamo@jaist.ac.jp

References

- [1] M. Valden *et al.*: Science **281** (1998) 1647.
- [2] H. Hori *et al.*: Phys. Lett. A **263** (1999) 406.
- [3] M. Suzuki *et al.*: Jpn. J. Appl. Phys. **37** (1998) L1488.
- [4] Y. Yamamoto, T. Miura, M. Suzuki, N. Kawamura, H. Miyagawa, T. Nakamura, K. Kobayashi, T. Teranishi and H. Hori: Phys. Rev. Lett. **93** (2004) 116801.