Unveiling the hidden paramagnetic nature of diamagnetic bulk gold

Since ancient times, gold has presented a "magnetic" attraction to people owing to its eternal brilliance. At the beginning of the 21st century, by using X-ray spectroscopy with circularly polarized synchrotron radiation, scientists revealed that gold is actually capable of being magnetic.

Gold (Au) is one of the noble metals that humans are most familiar with, and its physical and chemical properties are the most studied among the 5*d*-electron systems. Regarding its magnetic properties, it is well known that elemental Au (bulk state) is a typical diamagnetic material with negative magnetic susceptibility. However, Au can have spontaneous magnetic moments when it forms alloys or stacked-film structures with 3*d* transition metals. Furthermore, it has been reported that Au nanoparticles (NPs) modified by some organic polymers at the NP surface exhibit superparamagnetism at low temperature [1] and even ferromagnetism at room temperature [2,3]. Spontaneous magnetization in Au NPs is possibly caused by a modification of the electronic states near the Fermi level. Thorough investigation of magnetism in elemental Au (parent material of Au NPs) would provide us with useful knowledge for elucidating the origin of magnetism in special forms of Au, i.e., NPs. X-ray magnetic circular dichroism (XMCD) spectroscopy is one of the promising techniques for studying the electronic and magnetic states of Au [1,3]. This element-specific tool can detect an imbalance in the density of electronic states with respect to the spin or orbital magnetic moments. It has a high sensitivity to ferromagnetic and paramagnetic moments but no sensitivity to diamagnetic moments. In this article, it is reported that XMCD spectroscopy at SPring-8 successfully unveiled Pauli paramagnetism in bulk Au hidden in a diamagnetic response that is larger than the intrinsic paramagnetic response [4].

A 5-μm-thick polycrystalline Au foil with a purity of 99.99% was studied using the high-resolution XMCD spectrometer at **BL39XU**. The beamline was equipped with a split-type superconducting magnet, and sample environments with a high magnetic field up to 10 T and temperatures as low as 2 K are available. An XMCD signal, the difference in the X-ray absorption spectra (XAS) for right- and left-circularly polarized X-rays, was recorded in the transmission mode by the helicity-modulation (lock-in detection) technique [5], which provided a detection sensitivity of a few parts in 10^5 for dichroic signals with respect to polarization-averaged XAS signals.

The XMCD results present clear and direct evidence of the magnetic response of bulk Au [4]. Figures 1(a) and 1(b) show XMCD spectra of Au foil at the L_3 and L_2 edges, respectively. The measured XMCD amplitude was on the order of 10^{-4} compared with the XAS signal (Figs. 1(c) and 1(d)), but the experiments produced clear dichroism signals with excellent precision owing to the helicity-modulation technique. The negative XMCD structure *A* at the L_3 edge and the positive structure *B* at the L_2 edge indicated that the Au 5*d* moment was aligned parallel to the external magnetic field. The field dependence of the XMCD signal demonstrated a paramagnetic-like response; the signs of the XMCD spectra were reversed for positive and negative magnetic fields of the same magnitude (±10 T), and the spectra for +2, +6, and +10 T were shown to change linearly with applied field.

Figure 2(a) shows the element-specific magnetization curve of the Au foil, i.e., the amplitude of the XMCD structure *A* as a function of the external magnetic field. The linear dependence of the signal on the external field supported the paramagnetic behavior of bulk Au. The slope of XMCD magnetization (Fig. 2(b)) was independent of temperature between 2 and 300 K. From measurements at variable temperatures and magnetic fields, the XMCD amplitude of Au was found to respond linearly with the external magnetic field and to be constant with respect to temperature. These results presumably indicate that bulk Au exhibits Pauli paramagnetism.

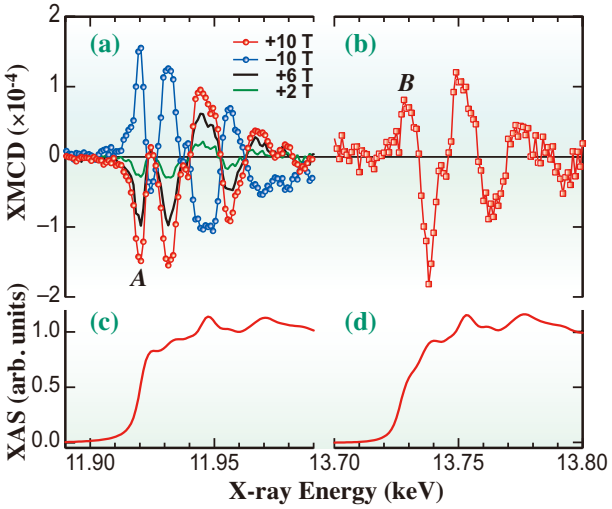

Fig. 1. X-ray magnetic circular dichroism (XMCD) spectra of Au foil measured at Au **(a)** L_3 and **(b)** L_2 edges at 2.3 K. X-ray absorption fine structure (XAS) spectra for (a) and (b) corresponding to the XMCD are shown in **(c)** and **(d)**, respectively. XMCD spectra recordead for different magnetic fields are shown in (a).

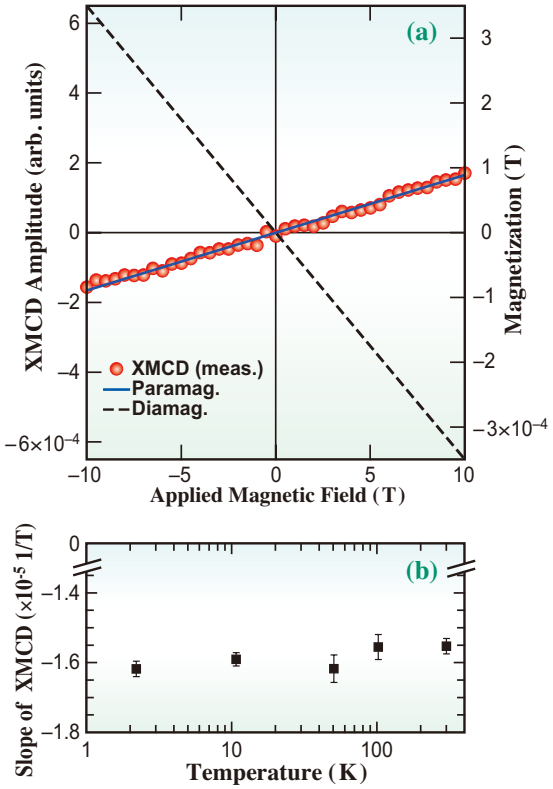

Fig. 2. **(a)** Element-specific magnetization curve of Au foil at 2.2 K, i.e., the amplitude of the XMCD structure at the L_3 threshold as a function of the external magnetic field. The dots represent measured values, and the blue line shows the fitted result using a linear function representing a paramagnetic response. The dashed line shows the diamagnetic response assumed from the reported value of the susceptibility of Au. Note that the sign of the XMCD signal was reversed for clarity. **(b)** Slope of element-specific magnetization curve as a function of temperature.

The spin and orbital magnetic moments of Au 5*d* electrons were determined to be $m_S = 9.8 \times 10^{-5}$ m_B / atom and $m_L = 2.8 \times 10^{-5}$ m_B/atom, respectively, at 10 T and at 2.3 K, using the sum rule analysis. The total moment $m_S + m_L = 1.26 \times 10^{-4}$ m_B/atom corresponds to paramagnetic susceptibility $\chi_{para} = 8.9 \times 10^{-6}$. Figure 2(a) shows the paramagnetic response of bulk Au, deduced from XMCD magnetization curves, and the diamagnetic response determined using the reported value of the diamagnetic susceptibility of Au, -3.5×10^{-5}. The signals originating from Pauli paramagnetism are weaker than those from diamagnetism. In conventional macroscopic magnetometry using a superconducting quantum interference device (SQUID), the Pauli paramagnetic response in Au is hidden by the stronger diamagnetic signal. In contrast, the XMCD spectroscopy measurement successfully yielded the intrinsic paramagnetic state.

The XMCD results for bulk Au provided a useful hint towards understanding the mechanism behind the emergence of magnetism in Au NPs. Figure 3 shows the XMCD spectra of bulk Au and Au nanoparticles protected by poly(allylamine hydrochloride) (PAAHC-Au NPs) [1]. For the NPs, structures *A* and *B* at the thresholds are enhanced at both the L_3 and L_2 edges compared with bulk Au. The strong XMCD features confined at the thresholds suggest that the spontaneous spin polarizations of 5*d* electrons are responsible for the superparamagnetism observed in PAAHC-Au NPs. In bulk Au, the magnetic moments were found to have a considerable orbital contribution, $m_L/m_S = 0.28$. Because a similar value ($m_L/m_S = 0.31$) was obtained for PAAHC-Au NPs, the large orbital contribution in elementary gold was suggested to be one of the possible origins of the spontaneous spin polarization in Au nanoparticles.

In summary, the XMCD study under high magnetic field, at various temperatures, and with a high signal-to-noise ratio, revealed that bulk Au exhibits both Pauli and orbital paramagnetism. XMCD spectroscopy, because of its extremely high sensitivity, is a powerful technique for exploring weak but exotic magnetism in noble metal compounds and nanoparticle systems.

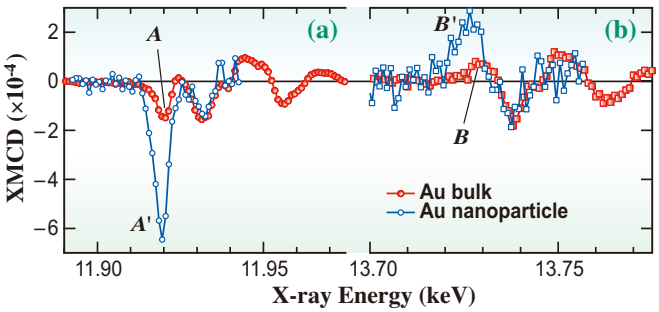

Fig. 3. XMCD spectra at Au **(a)** L_3 and **(b)** L_2 edges in PAAHC-Au nanoparticles (NPs) with mean diameter of 1.9 nm and in bulk Au foil. The data were taken at a temperature of 2.3 K in a magnetic field of 10 T.

Motohiro Suzuki

SPring-8/JASRI

Email: m-suzuki@spring8.or.jp

References

[1] Y. Yamamoto *et al.*: Phys. Rev. Lett. **93** (2004) 116801.
[2] P. Crespo *et al.*: Phys. Rev. Lett. **93** (2004) 087204.
[3] J.S. Garitaonandia *et al.*: Nano Lett. **8** (2008) 661.
[4] *M. Suzuki, N. Kawamura, H. Miyagawa, J. S. Garitaonandia, Y. Yamamoto and H. Hori, Phys. Rev. Lett.* ***108*** *(2012)047201.*
[5] M. Suzuki *et al.*: Jpn. J. Appl. Phys. **37** (1998) L1488.