

X-ray Magnetic Circular Dichroism of Size-Selected, Thiolated Gold Clusters

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Size reduction of bulk gold into the nanometer regime gives rise to novel electronic, optical, and catalytic properties due to the quantum size effect and a large surface-to-volume ratio.¹ A recent example of the size effect was the emergence of ferromagnetism in gold nanoparticles (NPs),^{2–4} whose bulk counterpart is diamagnetic. However, the origin of magnetic properties in the gold NPs has been controversial: two diametrically opposite views have been presented on the effect of chemisorption of thiol, a well-known passivating agent. Crespo et al. have shown by SQUID that gold NPs capped with weakly interacting reagents are diamagnetic, but those protected by thiolates become ferromagnetic due to 5d-localized holes generated through Au–S bonding.² A recent theoretical study has predicted induction of spin polarization of Au₁₃ by chemisorption of C₆H₅–X (X = O, S, Se).³ In contrast, Hori and co-workers have observed ferromagnetic spin coupling in weakly stabilized gold NPs, which has been ascribed to the ferromagnetic nature of the surface atoms due to the so-called Fermi hole effect.⁴ They have reported that thiol passivation quenches spin polarization through electron pairing in Au–S bonding, as in the case of nickel carbonyl cluster compounds.⁵ To help elucidate the origin of magnetism in gold NPs, we report herein magnetic moments of thiolated gold clusters whose chemical compositions are well defined. The samples used here were a series of gold clusters protected by glutathione (GSH), whose synthesis and mass spectrometric characterization have been reported previously.⁶ Their magnetic moments were systematically measured by X-ray magnetic circular dichroism (XMCD), which is known to be an element-selective magnetic probe.⁷

The samples used here included Au_N(SG)_M with (N, M) = (10, 10), (15, 13), (18, 14), (22, 16), (25, 18), (29, 20), (39, 24) and a sodium gold(I) thiomalate (SGT) as a reference. Pellets fabricated by pressing mixtures of solid samples and boron nitride powder were used for the XMCD measurement. The mixing ratios were optimized so that the Au L₃ edge jumps exhibited nearly unity heights. The XMCD spectra were recorded using a spectrometer installed at BL39XU of SPring-8 Synchrotron Radiation Facilities.⁸ External magnetic fields of –10 to 10 T were applied along the X-ray beam direction using a split-type superconducting magnet. The temperature of the sample was varied in the range of 2.7–273 K. The detection efficiency was high enough to record XMCD signals as small as ten-thousandth of the spin-averaged X-ray absorption coefficients. Such a high sensitivity is achieved by the helicity modulation technique based on a diamond phase plate, lock-in detection, and high brilliance of the third generation synchrotron

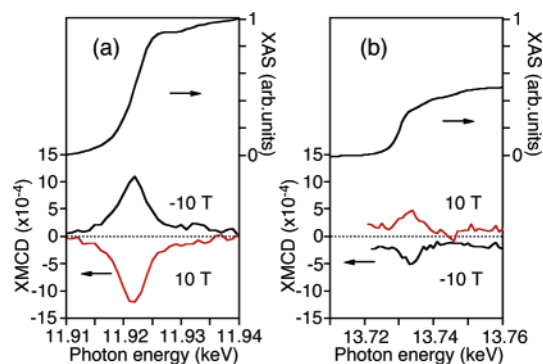


Figure 1. XAS (top) and XMCD (bottom) spectra of Au₁₈(SG)₁₄ at the (a) Au L₃ and (b) L₂ edges with an applied field of 10 T at 2.7 K. The XMCD signals are scaled with the edge jumps of the XAS spectra.

radiation source.⁸ Sample degradation due to synchrotron radiation was assessed by repeated acquisition of XMCD spectra from the same spot. For example, after six acquisitions, the XMCD signals from the Au₁₈(SG)₁₄ sample increased by ~50% as compared with that from a fresh spot. Thus, the scanning procedure and beam exposure time were optimized to ensure that the data were not from a radiation-damaged sample, but from the original clusters.

The top panels of Figure 1 show X-ray absorption spectra (XAS) of Au at the L₃ (2p_{3/2} → 5d_{5/2}, 6s_{1/2}) and L₂ edges (2p_{1/2} → 5d_{3/2}, 6s_{1/2}) of Au₁₈(SG)₁₄ at 2.7 K under a field of 10 T. Shown in the bottom panels are the XMCD spectra of Au₁₈(SG)₁₄ recorded under the same conditions. Negative and positive peaks are observed at the L₃ (11.922 keV) and L₂ (13.733 keV) edges, respectively. The XMCD amplitudes are on the order of a thousandth of the XAS step height. The XMCD intensities described hereafter are normalized by the corresponding XAS heights so that they are proportional to magnetic moments per Au atom. The sign of the XMCD signal is reversed when the magnetic field is switched to –10 T, confirming that these peaks are not from an experimental artifact but originate from real XMCD signals. The XMCD spectra of all the other Au:SG clusters and SGT complex exhibit similar spectral features. Note that the Au:SG clusters studied here are chemically pure as previously confirmed by mass spectrometry.⁶ Even if magnetic impurities are present, these are not directly incorporated into the gold cores⁹ so that they cannot contribute the XMCD signals at the Au L_{2,3} edges. Thus, these observations verify that *the Au atoms in the Au:SG clusters are inherently spin-polarized*. The XMCD peak height at the L₃ edge is 2.5 times larger than that at the L₂ edge. This asymmetry of the spectra indicates a considerable orbital magnetic moment of the Au 5d electrons; the ratio of the orbital to the spin magnetic moment is estimated to be 12% by application of the sum rules.^{10,11}

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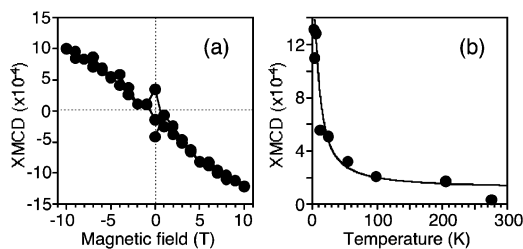


Figure 2. (a) Magnetization curve of $\text{Au}_{18}(\text{SG})_{14}$ recorded at the Au L_3 edge at 2.7 K. (b) Temperature dependence of the XMCD peak intensity of $\text{Au}_{18}(\text{SG})_{14}$ recorded at the Au L_3 edge at 10 T. The curve represents the fitted result assuming a Langevin function.

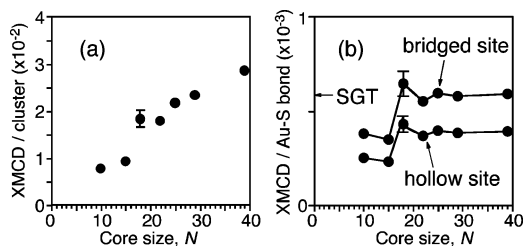


Figure 3. Core size dependences of XMCD intensities per (a) Au:SG cluster and (b) Au–S bond.

The magnetization behavior was studied by monitoring the XMCD signals at the L_3 edge as functions of the external field and temperature. Figure 2 shows the results of $\text{Au}_{18}(\text{SG})_{14}$. The XMCD signals exhibit a nearly linear relationship with magnetic field in the range from -10 to 10 T. No appreciable hysteretic behavior is observed in Figure 2a. This behavior is reproduced in the SQUID measurements.¹² Curie-type behavior is clearly seen in the temperature dependence of the magnetization (Figure 2b).

The XMCD signals of $\text{Au}_N(\text{SG})_M$ (2.7 K, 10 T) multiplied by the number of the constituent Au atoms, N , are plotted in Figure 3a. The ordinate of Figure 3a is proportional to a magnetic moment per cluster. Gradual increase in the magnetic moments with the core size suggests that the quantum size effect is not the direct cause of the magnetism. This inference is supported by the observation of magnetism in self-assembled monolayers of thiolate on a “bulk” gold surface.¹³ The authors proposed that the phenomenon is related to charge transfer between the organic layer and the gold substrate. Recent experimental and theoretical studies on the Au:SR clusters corroborate that the hole in the Au(5d) orbital created by Au–S bonding is responsible for the spin polarization.^{2,3} Since the XPS spectra of $\text{Au}_N(\text{SG})_M$ show partial electron transfer at the Au–S interface,⁶ a similar mechanism may be at play in the magnetization observed here.

The validity of the spin-polarization mechanism proposed above is checked by evaluating the magnetic moments per Au–S bonding. According to recent theoretical studies on the structures of $\text{Au}_{38}(\text{SCH}_3)_{24}$,¹⁴ it is plausible that the GS ligands coordinate to bridged or hollow sites of the Au core surface. Namely, the number of the Au–S bonds in $\text{Au}_N(\text{SG})_M$ is given by $2M$ or $3M$, respectively. In the framework of these coordination models, the XMCD intensities per cluster (Figure 3a) can be converted to those per Au–S bond as plotted in Figure 3b. The magnetic moments per Au–S bond for $\text{Au}_N(\text{SG})_M$ appear nearly constant for $N \geq 18$. Also shown in Figure 3b is the XMCD intensity per Au–S bond for SGT having a polymer structure with a $-\text{Au}-\text{S}-$ repeated backbone.¹⁵ Both of the coordination models for $\text{Au}_N(\text{SG})_M$ give the XMCD intensities per Au–S bond comparable to that of SGT. We interpret these results to suggest that *the spin polarization due to the Au(5d) hole^{2,3,16} created by GS ligation contributes additively to that of $\text{Au}_N(\text{SG})_M$.* Since the structural models employed here are over-

simplified, we must await further studies on geometrical structures of $\text{Au}_N(\text{SG})_M$ to fully understand the origin of the magnetism.

Although our conclusion qualitatively agrees with those of SQUID studies on $\text{Au}:\text{SC}_{12}$ clusters (1.4 nm) by Crespo et al.,² there is a significant difference at the quantitative level. Crespo et al. observed a hysteresis in the magnetization curve at room temperature and concluded that the clusters were ferromagnetic. The magnetic moment per Au–S bond was estimated to be $0.036 \mu_B$.² On the other hand, the present XMCD results shown in Figure 2a reveal that $\text{Au}_{18}(\text{SG})_{14}$ is paramagnetic, which is consistent with the SQUID measurements.¹² The magnetic moment per Au–S estimated from our SQUID data is $0.0093 \mu_B$,^{12,17} which is slightly larger than the theoretical value ($0.0025 \mu_B$)³ but is appreciably smaller than that reported by Crespo.² The origin of these discrepancies is not clear at present.

In summary, we have conducted XMCD measurements at the Au $L_{2,3}$ edges of $\text{Au}_N(\text{SG})_M$ clusters with well-defined chemical compositions. Magnetic moments per cluster were found to be increased with core size, whereas those per Au–S bond were nearly constant for $N \geq 18$. It is tentatively concluded that a localized hole created by Au–S bonding, rather than the quantum size effect, is responsible for the spin polarization of gold clusters.

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Supporting Information Available: SQUID data of $\text{Au}_{18}(\text{SG})_{14}$ (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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