Two-photon photoemission magnetic circular dichroism and its energy dependence

Takeshi Nakagawa, Isamu Yamamoto, Yasumasa Takagi, Kazuya Watanabe,*
Yoshiyasu Matsumoto,* and Toshihiko Yokoyama†
Institute for Molecular Science, The Graduate University for Advanced Studies (Sokendai), Myodaiji-cho, Okazaki 444-8585, Japan
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We report an observation of two-photon photoemission (2PPE) magnetic circular dichroism (MCD) near the Fermi level. The 2PPE MCD asymmetry from a perpendicularly magnetized Ni film on Cu(001) at the normal-incidence geometry gives a significant intensity (~6%) comparable to that of the one-photon photoemission. The energy dependence of the 2PPE MCD asymmetry is essentially similar to that of the 1PPE MCD, which indicates that the initial and final states involved, not the intermediate state, play a dominant role for the MCD asymmetries. For the 2PPE MCD measurements the asymmetry shows a maximum of as much as ~28% at the light incident angle of ~45°.

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Magnetic circular dichroism (MCD) has been an important experimental method since its innovation and has been developed into various techniques; the magneto-optical Kerr effect using the visible light[1,2] and x-ray magnetic circular dichroism (XMCD) (Refs. 2 and 3) are widely used to study magnetic properties of thin films due to their high sensitivities to thin films. Since the MCD effect depends on the spin-orbit coupling and the spin polarization, XMCD from a core shell usually gives much larger MCD asymmetry than the Kerr effect in the valence band. For the valence-band photoemission MCD, however, angle- and energy-resolved experiments revealed that the MCD effect in valence band often shows more than 10% asymmetry at the maximum, which is comparable to the XMCD case.[4] Such a large MCD effect is ascribed to the high spin polarization in valence bands and the angle-resolved detection of emitted electrons from a specific band. Recently, Nakagawa and Yokoyama[5] reported that the valence-band MCD using the total electron yield mode without a specific energy- or angle-resolved detection method gives drastically high MCD asymmetry when measured near the photoemission threshold. This enhancement is also attributed to the spontaneous restriction of the energy and angle for emitted electrons near the threshold.[5,6]

On the other hand, with the advent of intense pulse lasers, magnetization-induced second-harmonic generation (MSHG) has been developed,[7] which is a nonlinear process. MSHG detects only the magnetism at interfaces and surfaces since it requires breaking of inversion symmetry. Moreover, MSHG is advantageous in its large rotation angle of the light polarization. Except MSHG, multiphoton MCD effects in thin film and bulk materials have not been attempted. The two-photon photoemission (2PPE) MCD should be a possible candidate. In the 2PPE MCD, the selection rule is more strict than that of the one-photon photoemission (1PPE) MCD. Although there have been reported no experimental studies concerning the 2PPE MCD, a recent theoretical 2PPE MCD calculation[8] predicted that Ni atoms in a strong magnetic field should provide XMCD asymmetry for the transition from 1*s* to 3*d* state, the magnitude of which is similar to that of the 1PPE MCD.

In this Brief Report, we report the experimental results of the valence-band 2PPE MCD near the photoemission threshold. The observed 2PPE MCD asymmetry from perpendicularly magnetized Ni films on Cu(001) is so large that we can measure magnetization hysteresis curves. The photon energy dependence of the 2PPE MCD asymmetry resembles the 1PPE MCD one, indicating that the intermediate state during the transition process may not be important for threshold photoemission. In contrast, the angle dependence of the 2PPE MCD shows drastic differences between the 1PPE and 2PPE. The 2PPE MCD asymmetry is found to give a maximum as much as ~28% at the grazing incident angle of ~45°. On the other hand, the 1PPE MCD asymmetry is rather monotonic and follows the profile expected ordinarily from the magneto-optical Kerr effect.

Experiments were performed in an ultrahigh vacuum chamber with a base pressure of $<2\times10^{-10}$ Torr. A Cu(001) surface was cleaned by repeated cycles of Ar^+ sputtering and subsequent annealing at 825 K. All the measurements were performed at room temperature for perpendicularly magnetized Ni films, which were epitaxially grown on Cu(001) showing sharp (1×1) diffraction spots by low-energy electron diffraction. The Ni films have a tetragonal distorted face-centered structure, with 3.2% compressed toward the surface normal,[9] with out-of-plane magnetization easy axis between 10 and ~50 ML. The emitted photoelectrons were measured via the drain current from the sample by placing an anode plate (1 kV) in front of the sample.[10] The electron yield is measured with the linear polarized light with the incident angle normal to the surface, and defined as I_s/I_0 for 1PPE and I_s/I_0^2 for 2PPE, where I_s and I_0 represent the sample current and laser power, respectively. An electromagnet with a maximum magnetic field of 3000 Oe was used to measure the MCD asymmetry and the magnetization hysteresis curves. The work function was estimated by the relationship between the sample current and the photon flux for 1PPE [Fig. 1(b)]. When the difference between the photon energy and the work function was less than 1 eV, we found linear relation between the sample current and the photon energy, which enables us to determine the threshold within the accuracy of 0.1 eV.

Photoelectrons were excited by an ultrashort pulse and broadband laser (<100 fs, 80 MHz, 680–1020 nm) and its second- and fourth-order harmonics generated by BaB_2O_4 (BBO) crystals. The second-order harmonics was used for

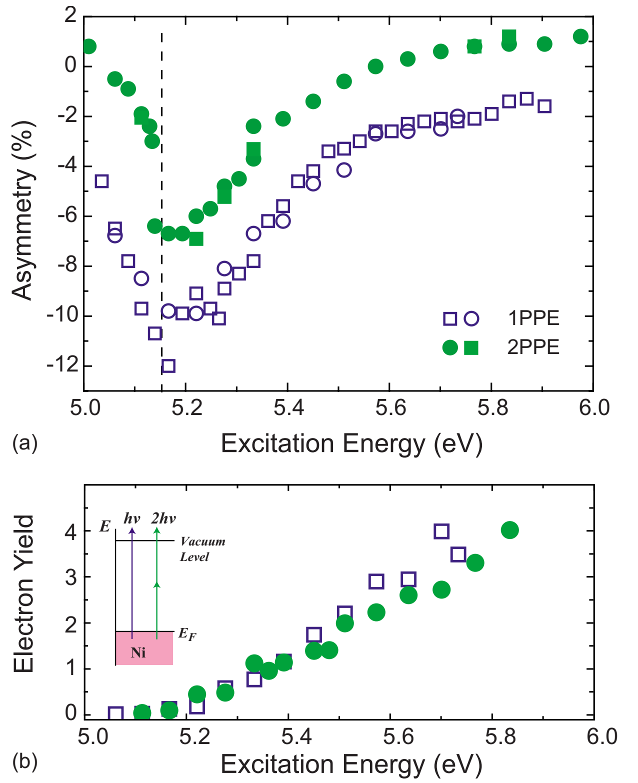

FIG. 1. (Color online) (a) 1PPE and 2PPE MCD asymmetries on the Ni(15 ML)/Cu(001) surface as a function of photon energy. The excitation energy corresponds to single and doubled photon energies for the 1PPE and 2PPE, respectively. The 1PPE and 2PPE MCD are plotted in the same scale. The work function of the sample is estimated to be 5.15 eV, as indicated by the vertical dashed line. Different symbols are the results from separately prepared samples. All the MCD asymmetries are measured in normal incidence with the external magnetic field (±100 Oe) parallel to the light propagation direction. (b) Electron yield as a function of photon energy for 1PPE and 2PPE. The electron yield for 2PPE is shown as electron/photon^2. Note that the electron yield and MCD are taken separately, and that the measurement time is longer for the smaller electron yield.

the 2PPE, while the fourth-order one for the 1PPE. The photon energy for the 2PPE was much lower than the sample work function and thus gives no 1PPE yield. The 2PPE process was verified by the sample current dependence on the square of input laser power. The photon density for the 2PPE experiment was set low enough to give a true MCD effect because we observed deformation of magnetization hysteresis curves for higher photon densities. The polarizations were controlled by quarter-wave plates. The incidence angle of the laser was usually set normal to the surface, otherwise mentioned below.

Figure 1 shows the energy dependence of the 1PPE and 2PPE MCD asymmetries and electron yield, where the work function of the Ni film is 5.15±0.1 eV. The MCD asymmetry is defined here by $A=(I^+-I^-)/(I^++I^-)$, where I^+ (I^-) is sample current for parallel (antiparallel) orientation between the angular momenta of photons and electrons. The 1PPE MCD spectrum shows a negative asymmetry with the minimum of −12% around the photoemission threshold. With in-

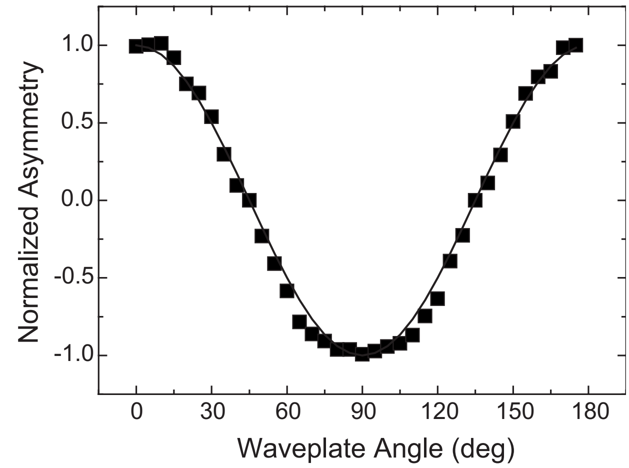

FIG. 2. The 2PPE MCD asymmetry as a function of the azimuthal angle of a quarter-wave plate. Rotating the wave plate varies the circular polarization from right (0°) to linear (45°) and left (90°). The fitted line is a cosine curve.

creasing the photon energy, the asymmetry is suppressed and approaches zero around the photon energy of ~0.75 eV away from the threshold. Note that the asymmetry slightly above the threshold originates from the thermal broadening at 300 K and energy spread of the pulse laser. The energy dependence of the 1PPE MCD is similar to our previous experiment,[5] where the photon energy is fixed and the work function is changed with the deposition of Cs. The rapid suppression of the MCD asymmetry with the photon energy demonstrates that the threshold photoemission is crucial for large MCD asymmetry.

The 2PPE MCD asymmetry is subsequently measured on the same sample as the 1PPE MCD one. The asymmetry is again large near the threshold, giving ~6% asymmetry. With increasing the photon energy, the asymmetry decreases and inverts its sign around $2\hbar\omega=5.6$ eV. Although the sign inversion is not observed for the 1PPE on the same sample, it was reported that for $\hbar\omega=3.8$ eV and the work function less than 2.8 eV, the asymmetry changes from a negative to positive value. The sign inversion is also observed for the 2PPE MCD with $\hbar\omega=1.55$ eV.[11] The rapid decrease in the 2PPE MCD asymmetry with the photon energy resembles the 1PPE MCD, and the asymmetries for 1PPE and 2PPE are of the same order of magnitude for the present Ni film. Also the electron yield curves for the 1PPE and 2PPE in Fig. 1(b) show monotonous increase, indicating that the density of the state is almost constant in this narrow region. The similarity of the 1PPE and 2PPE MCD will be discussed later.

Figure 2 represents the helicity dependence of the 2PPE MCD, plotting the asymmetry as a function of the azimuthal angle of a quarter-wave plate. With the rotation of the wave plate, the polarization of the incident light changes from right circular (0°) to linear (45°) and left circular (90°). The thin solid line in Fig. 2 shows a fitted cosine curve, in good agreement with the experimental result. The dependence of the 2PPE MCD asymmetry on the cosine law implies that the photon helicity is delivered to Ni and the process is similar to the 1PPE. This result also confirms that our 2PPE result is definitely attributed to MCD.

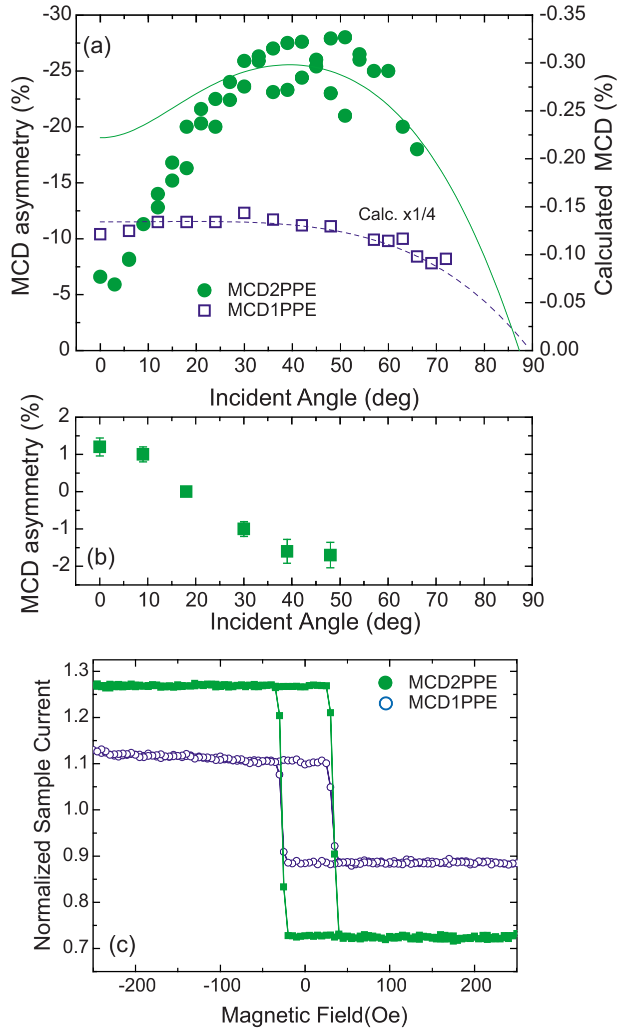

FIG. 3. (Color online) (a) Light incident angle dependence of the MCD asymmetry near the threshold on Ni(12 ML)/Cu(001) for the 2PPE (circles) and 1PPE (squares) MCD. The photon energies used for the 2PPE and 1PPE are 2.65 eV and 5.3 eV, respectively, and the work function is estimated to be ~5.15 eV. The dotted and gray lines show the calculated MCD asymmetries for $\hbar\omega=5.2$ and 2.6 eV, respectively (see text). (b) 2PPE MCD asymmetry away from the threshold ($\hbar\omega=2.95$ eV). (c) Magnetization hysteresis curves for the 2PPE and 1PPE MCD taken near the threshold at the incident angle of 33°, demonstrating a huge change of the electron yield (as much as 70%) in the 2PPE MCD.

Figure 3 shows incident angle dependence of the MCD asymmetry near the threshold for the 1PPE and 2PPE on Ni(12 ML)/Cu(001) and displays the comparison of magnetization curves at the incident angle of 33°. The photon energy for the 1PPE and 2PPE are 5.3 and 2.65 eV, respectively, while the work function is fixed at 5.15 eV. The 1PPE MCD asymmetry is nearly constant up to 60° and decreases slightly above 60°. On the contrary, the 2PPE MCD asymmetry shows drastic increase with an inclination of the incidence angle and gives a maximum of as much as 28% at 45°, exceeding the 1PPE MCD asymmetry.

We compared the observed MCD with the calculated results based on the magneto-optical theory.[12] The present MCD asymmetry, A_M, can be expressed as $A_M \sim -2(\varepsilon_K R + \varepsilon_F T)/(1-R-T)$, where ε_K, ε_F, R, and T, respectively, represent the Kerr and Faraday ellipticities, reflectivity, and transmittance.[6,12] Although usually the transmission term does not appear in absorption MCD of a magnetic film on a substrate, it should be here included since the present photoemission MCD is surface sensitive and detects dominantly the Ni 3d electrons only. Instead of using an empirical dielectric tensor of Ni to evaluate the MCD asymmetry, density-functional calculations[13,14] for bulk Ni were performed, where electronic excitations below the vacuum level are omitted to account for the limited transitions in energy. The empirical dielectric constants of Cu were used without modification. The angle dependence of the 1PPE MCD shows a typical trend of the Kerr effect and is in good agreement with the theory except its magnitude.[15] The angle dependence of the 2PPE MCD resembles more closely the calculation with $\hbar\omega=2.6$ eV rather than with $\hbar\omega=5.3$ eV because the MCD maximum at ~45° is well reproduced. This indicates that the first photoexcitation process is important for the 2PPE MCD. Figure 3(b) shows the angle dependence of the 2PPE MCD when the photon energy is set away from the threshold ($2\hbar\omega=5.9$ eV). By increasing the incident angle, the MCD asymmetry monotonically decreases and changes its sign at ~20°. Although the sign inversion was not reproduced in the preliminary calculation with $\hbar\omega=2.95$ eV, the sign of A_M could be inverted in the present model because of significant compensation between $\varepsilon_K R$ and $\varepsilon_F T$.

Let us here discuss the enhancement of MCD and the similarity between the 1PPE and 2PPE MCD. The comparison in the 1PPE and 2PPE measurements for their energy dependence shown in Fig. 1 indicates that the excitation processes involved are not so different. For the 1PPE process, the excitation from 3d and 4sp states to free-electron states close to the vacuum level gives photocurrent for threshold photoemission. In case of threshold photoemission, not only the energy but also the momentum of the emitted electrons are limited. The kinetic energy (E_K) of the measured electrons is given by $E_K < \hbar\omega - \Phi$, and its momentum parallel to the surface ($k_\parallel$) is restricted as $|k_\parallel| < \sqrt{2mE_k/\hbar^2} = 0.16$ Å^{-1} for $E_k=0.1$ eV, corresponding to 1.7% of the surface Brillouin zone. For the momentum along the surface normal ($k_\perp$), the initial state for $\hbar\omega=3-6$ eV lies around the X point along the ΓX direction. Thus only the electrons near the X point are excited near the threshold, giving spontaneous angle and energy-resolved measurements. This is the reason for the large MCD asymmetry near the photoemission threshold, and the 1PPE MCD results with $\hbar\omega=5.3$, 3.8, and 1.95 eV give similar asymmetries (~10%). Although the high spin polarization near the Fermi level for Ni is also important for the MCD enhancement, comparable situations hold for other ferromagnetic materials.[5]

For the 2PPE process, both the direct and indirect transitions should be considered. For the indirect transition, where the intermediate state is virtual, the MCD asymmetry may resemble that of the 1PPE since electronic bands with different orbital and magnetic quantum numbers in the final states are not separately observed for bulk metals in normal photoemission. The difference between the 1PPE and 2PPE should be attributed to the direct transition, where the intermediate state is not virtual. Even for the intermediate state in the direct transition, however, band structures with different magnetic quantum numbers are practically unresolved since the spin-orbit interaction is much weaker for the free-electron-like state above the Fermi level, possibly providing similarities between the 1PPE and 2PPE MCD. Thus it is suggested that the first excitation process governs the MCD effect mostly and that the second excitation process gives less important effect since the spin-orbit coupling above the Fermi level is much weaker than that below the Fermi level. The fact that the angular dependence of the 2PPE MCD ($2\hbar\omega$=5.3 eV) is better explained by the calculation with $\hbar\omega$=2.6 eV [Fig. 3(a)] also supports this interpretation. While the explanation based on established magneto-optical effect could give insight into the similarity between 1PPE and 2PPE MCD asymmetry, theoretical calculations including photoemission process and momentum space limitation is necessary to account for the 2PPE MCD mechanism in detail.

Finally we will discuss the 2PPE MCD asymmetry in the angle-dependent measurement. As mentioned, the magneto-optical theory including the light reflection and penetration could qualitatively explain the angular dependence of the 2PPE MCD. Higher MCD asymmetry is obtainable in grazing incidence for perpendicularly magnetized films, which is the case for the 2PPE MCD in Fig. 3. Although the phenomenological model is proposed to account for the angular dependence of the 2PPE MCD, other mechanisms in term of electronic band structure may also be important. Selective electronic excitation of Ni occurs in case of threshold photoemission, not included in the present magneto-optical theory. Moreover, the electronic field component normal to the surface is substantially enhanced at grazing incidence, which could further enhance the 2PPE process since the transition probability depends on the square of the electric field.[16]

In summary, we have observed the 2PPE MCD near the photoemission threshold on Ni films, giving 6% MCD asymmetry at normal incidence. The energy dependence of the 2PPE MCD is similar to the 1PPE MCD. This indicates that the 2PPE MCD process normally mimics the 1PPE process since the intermediate and final states incorporated in the transition does not significantly affect the MCD selection rule due to the negligible energy splitting between the different magnetic quantum number. The 2PPE MCD near the threshold shows as much as 28% MCD asymmetry at grazing incidence of ~45°. A large 2PPE MCD asymmetry at grazing incidence is practically useful for the 2PPE MCD photoelectron microscope, enabling microscopic imaging in laboratories.[10,17] Further experimental studies on the energy- and angle-resolved 2PPE MCDs will quantitatively observe the electronic origin for the drastic enhancement of the threshold 2PPE MCD at grazing incidence. Although we explain the angular dependence using semiemperical calculation and show that the first photoexcitation process governs the MCD effect mainly even in 2PPE MCD, a theoretical calculation including multiphoton photoexcitation processes and momentum space limitation is demanded to reveal the fundamental mechanism behind the 2PPE MCD.

A 2PPE MCD experimental result as presented in this Brief Report was shown recently for Heusler alloys,[18] where the MCD asymmetry is an order of 10^{-3}, which was measured with ~3 eV higher photon energy than the work function. Higher MCD asymmetry would be expected near the photoemission threshold.

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*Present address: Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan.
†yokoyama@ims.ac.jp

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