Strong Fano effect in the magnetic circular dichroism of the Pt $N_{6,7}$ core absorption of ferromagnetic CoPt$_3$

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We report the core photoabsorption (XAS) and magnetic circular dichroism (MCD) spectra in the Pt $N_{6,7}(4f\rightarrow5d)$ region of the ferromagnetic CoPt$_3$. The measured XAS spectra have shown typical Fano line shapes, and the MCD spectrum has shown very unusual features that cannot be explained within the framework of the conventional selection rule for the dipole transition. It is revealed from a theoretical analysis that the strong Fano effect is essential to interpret these MCD features. We will discuss in detail the influence of the Fano effect on the Pt $N_{6,7}$ MCD line shape.

I. INTRODUCTION

The ordered alloys $M$Pt$_3$ ($M=$V, Cr, Mn, Fe, Co) have a Cu$_3$Au-type crystal structure and have attracted much interest due to their wide variety of magnetic properties. In these intermetallic compounds, the Pt sites have induced magnetic moments due to the hybridization with the spin-polarized 3$d$ states of transition metal sites. VPt$_3$ (Ref. 1) and CrPt$_3$ (Refs. 2 and 3) reveal ferrimagnetic ordering in the sense that the moment on the Pt sites is antiparallel to that on the 3$d$ transition metal sites. MnPt$_3$ (Refs. 3 and 4) and CoPt$_3$ (Ref. 5) are ferromagnets, whereas FePt$_3$ (Ref. 6) shows antiferromagnetic ordering. The contribution of the orbital moment to the total moment on the Pt sites is expected to be important, because the Pt atom is so heavy (atomic number $Z=78$) that the spin-orbit coupling of the Pt 5$d$ electrons is fairly large (coupling constant $\xi_{5d}=0.5$ eV). It is interesting to investigate the variation of both $\langle L_z \rangle$ (the orbital angular momentum) and $\langle S_z \rangle$ (spin) on the Pt sites through the series of MPt$_3$ to reveal the origin of their rich variety of magnetic orderings. Maruyama et al. have measured MCD spectra of $M$Pt$_3$ ($M=$Cr, Mn, Co) and ferromagnetic Fe$_3$Pt (Ref. 9) in the Pt L$_{2,3}$ edges (2$p\rightarrow5d$ transition by hard x ray). Using the magneto-optical sum rules, they have shown interesting variations of $\langle L_z \rangle$ and $\langle S_z \rangle$ on the Pt site. In CrPt$_3$, the $\langle L_z \rangle$ component dominates the magnetic moment on the Pt site, contrastingly, it disappears in MnPt$_3$. In the case of CoPt$_3$, the $\langle S_z \rangle$ contribution is predominant and the $\langle L_z \rangle$ is aligned parallel to the $\langle S_z \rangle$. Very recently, Iwashita et al. have calculated the electronic band structures of MPt$_3$ by using the full-potential linear augmented plane wave (FLAPW) method with including the spin-orbit interaction as a perturbation. Their calculation reproduces the experimental trend of the $\langle L_z \rangle$ and $\langle S_z \rangle$ well. The orbital moment of Pt in CoPt$_3$ is, however, underestimated by a factor of about two.

In this paper, we report on the MCD spectrum of ferromagnetic CoPt$_3$ observed in the photon energy range of $\hbar\omega=50–80$ eV. The observed MCD spectrum in the Pt $N_{6,7}(4f\rightarrow5d)$ region has shown very unusual features. This MCD spectral shape deviates completely from the one expected by considering the conventional selection rule of the dipole transition. From a detailed theoretical analysis, it is found that the unusual line shape of the MCD is caused by a strong interference effect (Fano effect) in the form of resonant photoemission.

In Sec. II, we describe the experimental results. In Sec. III, we present a theoretical framework and calculation done to explain the Pt $N_{6,7}$ MCD features of CoPt$_3$. Section IV is devoted to the concluding remarks.

II. EXPERIMENTAL RESULTS

The polycrystalline sample of ferromagnetic CoPt$_3$ was prepared by the arc-melting technique from 99.9% pure Co and Pt in argon atmosphere. To develop the ordered arrangement of atoms, the cast was annealed for 5 weeks at 680 °C. An x-ray diffraction study showed the Cu$_3$Au-type ordered structure. The Curie temperature was 367 K and the total magnetic moment was measured to be $2.71\mu_B$/CoPt$_3$ at 4.2 K. From the result of neutron scattering, it is known that the Pt site has an induced magnetic moment $M_{Pt}=0.26\mu_B$/atom and the Co site has a moment $M_{Co}=1.64\mu_B$/atom at 77 K. It is believed that they are coupled ferromagnetically.

Core photoabsorption spectra (XAS) and MCD spectra in the range of $\hbar\omega=50–80$ eV were measured at the beamline BL28A (Ref. 14) of the Photon Factory in the National Laboratory for High Energy Physics (KEK). The circularly
polarized light was supplied by a helical undulator. Almost completely polarized light was obtained at the peak of the first harmonic of the undulator radiation. The full bandwidth of the monochromatized incident photons was set to about 0.1 eV. A clean sample surface was obtained by in situ scraping with using a diamond file under ultrahigh vacuum condition (10^{-9} Torr). The sample was cooled down by liquid N_2. A magnetic field of about 1.1 T was applied to the sample by using an apparatus with two sets of permanent dipole magnets made of Nd-Fe-B alloy. XAS spectra were measured by the total photoelectron yield (TPY) method by directly measuring the sample current while scanning the photon energy (h\omega). It is widely known that the TPY spectrum well represents the photoabsorption in the core excitation region. MCD spectra were taken by reversing the direction of the magnetic field \( H \) applied to the sample at each h\omega while the helicity of the light was fixed. We define the MCD spectrum as \( I^+ - I^- \), where \( I^+ \) and \( I^- \) denote the absorption intensity with the photon spin (helicity) parallel and antiparallel to the direction of the applied magnetic field, respectively (note that our definition of MCD is opposite to the one in Ref. 16).

The experimental results obtained in the photon energy range of h\omega=50–80 eV are shown in Fig. 1. Here the solid and dashed curves represent the XAS spectra, \( I^+ \) and \( I^- \), respectively, and the dots show the MCD spectrum. One recognizes rather broad peaks in the XAS, which originate from the core excitations of the Pt 5p_{3/2}, Co 3p, Pt 5p_{1/2}, and Pt 4f states as indicated in the figure. Clear MCD signals are seen near each edge. The Pt 5p→5d XAS shows a large spin-orbit splitting (13 eV) with a positive and a negative MCD signals in the regions of the 5p_{3/2} and 5p_{1/2} components, respectively. Considering the selection rule for the \( p \rightarrow d \) dipole transition, we confirm from these MCD signals that the magnetic moment on the Pt site (\( M_{Pt} \)) is aligned parallel to the applied magnetic field (\( H \)), \( M_{Pt} \parallel H \). The magnetic moment on the Co site is confirmed to be parallel to \( H \), because \( M_{Co}(1.64\mu_B/\text{atom}) \) dominates the total magnetic moment of CoPt_3. Therefore, we can reach a conclusion that \( M_{Pt} \parallel M_{Co} \), which is consistent with the neutron scattering result.5

Noticeable MCD signals are observed in the higher energy region where the Pt 4f→5d absorption (4f XAS) arises. We have carried out a detailed measurement of the Pt 4f MCD in the narrow photon energy range of h\omega=70–80 eV. The results are shown in Fig. 2. In the \( I^+ \) and \( I^- \) XAS spectra, one can see broad peaks related to the 4f_{3/2} and 4f_{5/2} components at about 74 and 77.5 eV. In the prethreshold regions of both components, clear dips are observed. As a result, the XAS spectrum has a very asymmetric line shape. It is well known that such a characteristic line shape is caused by the Fano effect.13,17 The MCD spectrum displayed in the lower panel of Fig. 2 also shows characteristic features. Considering the direction of the Pt moment (\( M_{Pt} \parallel H \)) and the selection rule for the \( f \rightarrow d \) dipole transition, one expects that the MCD signal should become negative in the 4f_{3/2} and positive in the 4f_{5/2} region. The observed MCD spectrum deviates considerably from such an expectation and shows very unusual features, namely, a positive and a negative MCD signals in the 4f_{3/2} region with increasing h\omega, and a negative and a positive signals in the 4f_{5/2} region. As a whole, the MCD line shape is well represented by the letter ‘‘W.’’ It is known that the Fano effect gives rise to some characteristic features in MCD spectra. Muto et al.18,19 have measured MCD spectra in the \( M_{2,3} \) (3p→3d) edge of Ni metal and in the \( N_{4,5} \) (4d→4f) edge of rare-earth metals. In such a shallow core excitation, the Fano effect is not negligible and they observed characteristic ‘‘extended MCD’’ features. The overall line shape of their MCD, however, is well understood within the framework of ordinary \( p \rightarrow d \) (Ni) or \( d \rightarrow f \) (rare-earth) dipole transition. In the case of the present Pt 4f, the MCD line shape cannot even be qualitatively explained in the framework of the dipole selection.

![FIG. 1. Core absorption (XAS) and MCD spectra of CoPt_3 in the photon energy range h\omega=50–80 eV. The solid and dashed curves show the XAS spectra, \( I^+ \) and \( I^- \), measured by means of the total photoelectron yield method. The dots show the MCD spectrum, \( I^+ - I^- \). The horizontal dotted line represents the MCD zero.](image1)

![FIG. 2. Detailed XAS and MCD spectra taken in the Pt 4f→5d excitation region. The XAS shows asymmetric Fano line shape and the MCD spectrum reveals very unusual features. See text for details.](image2)
FIG. 3. A conceptual diagram representing the interactions in the Pt $4f$ XAS process. The vertical axis represents the total energy of the system. In addition to the $4f \rightarrow 5d$ dipole transition ($4f$ XAS), the $5d$ PES and $5p$ PES processes also occur. There is a configuration interaction between the discrete excited states and continuum states via the CK transitions, which leads to the Fano-type interference effect.

We suppose that an extremely strong Fano effect may be the origin of this unusual MCD. In the following section, we present basic concepts to treat this problem and perform a simplified theoretical calculation in order to discuss the influence of the Fano effect on the Pt $4f$ MCD spectrum.

The basic concepts concerned about the Fano effect in the Pt $N_{6.5}$ region are schematically illustrated in Fig. 3. First we regard the electron configuration of the Pt in the ground state as $5d^n$. The Pt $4f$ XAS leads to the quasidiscrete excited states $4f^{13}5d^{n-1}$. On the other hand, the Pt $5d$ photoemission [5d valence photoemission spectroscopy (PES)] process always occurs at any $h\omega$, producing the $5d^{n-1}e^{l}$ continuum states. Here, $e^{l}$ denotes the photoelectron state with energy $\epsilon$ and the orbital angular momentum $l$ ($l=p$ or $f$). The Pt $5p$ core level lies in the energy region between the $4f$ core and the $5d$ valence states, so that the $5p$ PES process also takes place for a photon energy corresponding to the $4f$ XAS excitation, resulting in the $5p^55d^{n-1}\epsilon l$ continuum states ($l^{*}=s$ or $d$). The discrete excited states ($4f^{13}5d^{n-1}$) are embedded in the various continua and will interact with them by Coster-Krönig transitions ($4f5d5d$ and $4f5p5d$ CK transitions). From these configuration interactions, the $4f$ XAS process ($4f \rightarrow 5d$), which is followed by the CK decay, will interfere with the direct PES processes and will lead to the asymmetric Fano line shape.

In order to clarify how the Fano effect works on the Pt $4f$ MCD spectrum of CoPt$_3$, we perform a simplified calculation in this section. The Fano effect is essentially an intratomic phenomenon, so that the information about the local electronic and magnetic states projected to one Pt site is needed. The Anderson impurity model is suitable for this purpose. We pick out one Pt atom which will be photoexcited and regard this atom as an impurity that has an atomic $5d$ orbital. The electronic states constructed by other Co and Pt atoms are considered to be Bloch states which would be well described by the band structure calculation. We regard these Bloch states as "electron reservoir orbitals" (hereafter denoted by $\nu$). We assume a hybridization between the impurity $5d$ orbital and $\nu$. Due to this hybridization, the impurity Pt would have a magnetic moment, reflecting the spin-polarized DOS of the reservoir state. The ground state of the system $|g\rangle$ is assumed to be symbolically expressed as

$$|g\rangle = c_1|5d^{10}\rangle + c_2|5d^9\nu\rangle.$$  (1)

Here, $|5d^{10}\rangle$ denotes the state where the impurity Pt has the $5d^{10}$ configuration and the reservoir states below the Fermi energy are occupied, and $|5d^9\nu\rangle$ is the state which can be created from $|5d^{10}\rangle$ by transferring one of the $5d$ electrons into the empty reservoir state above the Fermi energy. Other configurations ($5d^8\nu^2$, etc.) and the bandwidth of the unoccupied reservoir states are tentatively neglected. The point group symmetry around the Pt atom is assumed as $O_h$ for simplicity although it is actually $D_{4h}$ in CoPt$_3$. The Hamiltonian of the system is expressed as

$$H = \sum_{\mu} \epsilon_{d\mu} n_{d\mu} + \frac{1}{2} U_{dd} \sum_{\mu \neq \mu'} n_{d\mu} n_{d\mu'} + H_{dd}(\xi_d) + H_{f}(\xi_f)$$

$$+ \sum_{\sigma} \sum_{i} V_{Y_{i}}(\sigma) \gamma_{i} (a_{i\sigma}^{+} a_{i\sigma} + \text{H.c.}).$$  (2)

In Eq. (2), the origin of energy is taken at the reservoir level (Fermi energy). The first term represents the one-body energy of the $5d$ states. Here, $\mu$ denotes the combined index specifying the $5d$ magnetic quantum number and spin state. The second term represents the $5d$-$5d$ repulsive Coulomb interaction. The third and fourth terms represent the spin-orbit interaction of the $5d$ (with a coupling constant $\zeta_d$) and $4f$ core states $(\zeta_f)$, respectively. We use the Hartree Fock values $\zeta_d=0.52$ eV and $\zeta_f=1.00$ eV. The last term expresses the hybridization between the impurity $5d$ and reservoir states. The index $\sigma$ denotes the spin state and the index $\gamma_i$ runs over the basis of the $Y_i$ ($i_{2g}$ or $e_g$) irreducible representation of the $O_h$ group. The empirical relation $V_{e_g} = -2V_{i_{2g}}$ is assumed. The spin-dependent hybridization strength is considered to be related to the reservoir DOS by the relation of $V^2(\alpha)\propto \text{DOS}(\alpha)^{20}$ according to the LAPW band structure calculation of CoPt$_3$. The total DOS at the Fermi energy (constructed mainly by the Co $3d$ and Pt $5d$ states) shows the ratio of DOS(down)/DOS(up)$=0.45$ (the majority spin is the down spin in our definition), and we assume $V(\text{down})=0.7\times V(\text{up})$. Let us define the average energy difference between the two configurations as

$$\Delta = E(5d^{10}) - E(5d^9\nu).$$

It may be clear that $\Delta$ is positive because the Pt $5d$ electron number is close to 9 according to the band structure calculation. The free parameters in Eq. (2) are only $\Delta$ and $V_{e_g}(1)$. We choose the parameters so as to obtain the total magnetic moment $\langle M_z \rangle = -2\langle S_z \rangle + \langle L_z \rangle = 0.26\mu_B$, that is the Pt moment observed by neutron
scattering. From this restriction the number of the free parameters is reduced to only one, so that we treat $\Delta$ as the free parameter. In Table I, we show the calculated ground-state properties with varying $\Delta$. For larger $\Delta$, both $n_{5d}$ (the 5d electron number), $(g| \sum_{\mu} n_{\mu} | g\rangle)$ and $(L_z)/(S_z)$ become smaller.

We briefly explain the photoexcitation processes. Discretelike $4f/5d^{10}v$ states will be excited by the $4f \rightarrow 5d$ dipole transition from the ground state given by Eq. (1). We call these states the intermediate states because they will soon decay into various final states by the Coster-König transitions as shown in Fig. 3. Eigenvalues and eigenfunctions of the intermediate states are denoted as $E_m$ and $|m\rangle$, respectively. The final states can be reached not only via the intermediate states but also directly from the ground state by the 5d PES and 5p PES processes. Their eigenvalues and eigen functions are denoted as $E_{fe}$ and $|fe\rangle$. We ignore the interaction between the photoelectron and the rest of the system, so that $|fe\rangle$ can be expressed as a direct product $|fe\rangle = |f\rangle |e\rangle$ with $E_{fe} = E_f + \epsilon$; here $|e\rangle$ denotes the photoelectron state and $|f\rangle$ is the eigenstate of the rest of the system (symbolically, $|f\rangle = c_{5d}^1|5d^9\rangle + c_{5d}^2|5d^6v\rangle$.

We calculate the Pt N_{6,7} XAS spectrum using the $T$ matrix which is generally applied in the calculation of excitation spectra with interference effect. Our $T$ matrix is defined as

$$T(\omega) = V + \frac{1}{z-H-H_{pe}V}. \tag{3}$$

Here, $\omega = \omega + E_f + i \tau$ ($\tau \rightarrow 0$), $\omega$ is the incident photon energy, $E_f$ is the energy of the ground state $|g\rangle$, $H$ is given by Eq. (2), and $H_{pe}$ is the Hamilton of a photoelectron ($H_{pe}|e\rangle = \epsilon|e\rangle$). Based on the concepts illustrated in Fig. 3, the perturbation $V$ is given by

$$V = V_A^* + V_D^* + V_{CK} + H.c. \tag{4}$$

The superscript $\kappa$ denotes the photon helicity ($\kappa = \pm 1$). The operator $V_A^*$ is to represent the $4f \rightarrow 5d$ dipole transition ($4f$ XAS) which is expressed by the dipole matrix element $\langle 4f|r|5d\rangle$. The operator $V_D^*$ represents the direct photoemission processes. $V_D^*$ consists of two parts, $V_D^* = V_D^5(5d) + V_D^5(5p)$, where the two operators are described with the use of the matrix element $\langle 5d|r|e\rangle$ and $\langle 5p|r|e^{1/2}\rangle$, respectively. The operator $V_{CK}$ likewise represents the Coster-König (CK) transitions, $V_{CK} = V_{CK}^5(5d) + V_{CK}^5(5p)$, where $V_{CK}^5(5d)$ and $V_{CK}^5(5p)$ describe the $4f5d5d$ and $4f5p5d$ CK decays with the use of the radial integrals $R^4(5d,5d;4f,e^{1/2})$ and $R^4(5p,5d;4f,e^{1/2})$, respectively. We calculate the $T$ matrix by taking into account the perturbation up to the lowest order of $V_A^*$ and $V_D^*$, and to infinite orders of $V_{CK}$. Although the operators $V_{CK}$ and $V_D^*$ are actually depending on the photoelectron kinetic energy $\epsilon$, we disregard their $\epsilon$ dependences for simplicity. After some algebra, the $T$ matrix is expressed as

$$T(\omega) = (V_A^{\kappa^*} - i\pi V_D^{\kappa^*} V_{CK}) \frac{1}{z-H_m+i\Gamma} (V_A^{\kappa^*} - i\pi V_D^{\kappa^*} V_{CK} V_D^*) \tag{5}$$

Here, $H_m$ is the Hamiltonian of the intermediate state $(H_m|m\rangle = E_m|m\rangle)$, and $\Gamma = \pi V_{CK}^* V_{CK}$. The absorption spectrum $I^\kappa(\omega)$ is given by the optical theorem as

$$I^\kappa(\omega) = -\frac{1}{\pi} \text{Im}\langle g|T(\omega)|g\rangle. \tag{6}$$

We should first evaluate various matrix elements listed in Table II. The radial part of the one-electron wave function $\psi_{nl\sigma}(r, \theta, \phi) = P_{nl\sigma}(r)|r\rangle |\lambda\rangle |\lambda\rangle |\phi\rangle \chi(\sigma)$ is evaluated from the nonrelativistic atomic Hartree Fock approximation. The radial wave function of the continuum state is obtained from the following differential equation in the units of Rydberg and Bohr radius:

$$- \frac{d^2}{dr^2} + \left( l(l+1) - \frac{1}{r^2} \right) + V^{el}(r) P_{el}(r) = \epsilon P_{el}(r). \tag{7}$$

The normalization condition is

$$P_{el}(r) \xrightarrow{r \to \infty} \pi^{-1/2} e^{-1/4} \sin[\epsilon^{1/2} r - l \pi/2 - e^{-1/2} \ln(2 \epsilon^{1/2} r) + \delta_1], \tag{8}$$

where $\delta_1$ is a phase shift. The potential $V^{el}$ may be expressed as

$$V^{el}(r) = -2Zr + V_p(r) - [24 \rho(r)/\pi]^{1/3}. \tag{9}$$

Here the second term is the Hartree potential energy in the field of the $N=1$ bound electrons. The third term represents the exchange energy with the bound electrons of the electron-density $\rho(r)$. $V^{el}(r)$ was evaluated with using the nonrelativistic HF radial wave functions of the bound electrons, and Eq. (7) was solved. The absolute values of the calculated $\langle 5d|r|e\rangle$ and $\langle 5p|r|e^{1/2}\rangle$ were, however, too small to explain the interference effect. We suppose that this failure comes from the nonrelativistic treatment of the bound electrons. The Pt atom is rather heavy ($Z=78$), so that the core $s$ and $p$ electrons would be relativistically contracted toward the nucleus and the nuclear attractive potential $-2Zr$ would be strongly shielded. So, relativistic effects should be taken into account. Being based on the local density approximation (LDA), the scalar-relativistic LAPW potential $V_{APW}(r)$ of CoPt$_3$ was employed as the potential $V^{el}(r)$. It is known that a bold approximation of LDA in the treatment of the exchange-correlation term induces a wrong behavior of $V_{APW}(r)$ for large $r$. Namely $V_{APW}$ decreases very fast (exponentially) whereas it should behave as $-2/r$ for large $r$ in the units of Rydberg and Bohr radius. In order to eliminate such a shortcoming, $V_{APW}$ is modified as
TABLE II. Values of the matrix elements evaluated by using the HF radial wave functions for the bound states and the modified LAPW potential for continuum (See text for details). The employed units are $a_0$ (Bohr radius) for $\langle 4f| r | 5d \rangle$, $a_0/\sqrt{eV}$ for other dipole matrix elements and $\sqrt{eV}$ for $L_z^+$s. We chose the kinetic energy of the continuum electron as $e=70$ eV and $e^*=10$ eV.

| $\langle 4f| r | 5d \rangle$ | 0.2235 |
| --- | --- |
| $\langle 5d| r | ep \rangle$ | 0.02907 |
| $\langle 5d| r | e^s \rangle$ | 0.07636 |
| $\langle 5p| r | e^s \rangle$ | 0.07415 |
| $\langle 5p| r | e^s d \rangle$ | -0.1176 |

\[
R^k(5d,5d;4f,\ell) = \begin{cases} 
\text{if } rV_{\text{APW}} < -2 \\
-2 \quad (\text{otherwise}).
\end{cases}
\]

As for the bound states’ radial wave functions $P_{5d}$, $P_{5p}$, and $P_{4f}$ which appear in the required matrix elements, we tentatively used the nonrelativistic atomic HF radial wave functions (for $P_{5d}$, the HF result is almost the same as the LAPW radial wave function except for the behavior near the muffin-tin radius where the contribution of the neighboring muffin-tin sphere takes place). The matrix elements obtained by this way are listed in Table II. In the calculation of the spectra, the values of $R^k$ are reduced to 80% of the values in Table II in order to match the experimental spectral broadening.

Maruyama et al. have so far estimated the ratio $\langle L_z \rangle/\langle S_z \rangle$ of the Pt site of CoPt$_3$ as being about 0.6. In our theoretical framework, the same value of $\langle L_z \rangle/\langle S_z \rangle$ is obtained by choosing the parameter $\Delta=1.5$ eV (See Table I). Starting from this ground state, let us examine how the Fano effect works on the MCD spectrum. For this purpose, we introduce a coefficient $Q_D$ which scales the dipole matrix element of the direct photoemission processes as $Q_D \langle 5d| r | \ell \rangle$ and $Q_D \langle 5p| r | e^s \ell \rangle$. When $Q_D$ equals zero, there is no direct photoemission process so that the interference effect does not occur. As we increase $Q_D$ from zero, the Fano effect would become gradually stronger. The results calculated with varying $Q_D$ are shown in Fig. 4. The polarization-averaged XAS spectra, $(I^+ + I^-)/2$, are presented in the upper panel of the figure, and the MCD spectra, $I^+ - I^-$, are shown in the lower panel. In the case of $Q_D=0$, the XAS shows a simple two peak structure. Both $4f_{7/2}$ and $4f_{5/2}$ components show symmetric Lorentzian line shapes. For a finite $Q_D$, the XAS has an asymmetric line shape with a dip and a noticeable tail. For larger $Q_D$, these features are enhanced and the absorption peak moves to higher photon energies. The MCD spectrum also shows an interesting variation. For $Q_D=0$, the MCD spectrum shows a negative (denoted as “A” in the figure) and a positive (“B”) peak in the $4f_{7/2}$ and $4f_{5/2}$ region, respectively, as expected from the dipole selection rule. For larger $Q_D$, peak A becomes stronger and peak B becomes weaker. Both peaks shift to higher energies and additional structures A’ and B’ appear in the lower energy region of peaks A and B, respectively. A reasonable agreement with the experimental result is obtained by choosing the value of $Q_D=0.4$ as shown in Fig. 5. Here the dotted curves represent the experimental results and the solid curves represent the calculated results. A monotonously increasing background is subtracted from the experimental absorption spectrum. Although the calculated absorption spectrum reproduces the asymmetric Fano line shape well, a discrepancy can be seen in the region of absorption peaks. Namely the calculated spectrum is rather sharp compared to the experimental spectrum. As for the MCD spectrum, the calculation reproduces
best fit calculated and the
peak A and A' in the sense that the amplitude of the
calculated spectrum is too large. The negative MCD signal
of the Pt 5p_{1/2} component, not taken into account in the
present calculation, may partly cancel the positive MCD of
the A' peak. The possibility of another major reason for this
discrepancy will be discussed later.

Thus the unusual MCD line shape of the Pt 4f XAS in
CoPt3 can be qualitatively understood from the spectral func-
tion of Eqs. (6) and (5). We will further inspect the details
with taking the 4f_{7/2} 5d configuration, and with the assumption of a
constant Γ', Eq. (6) can be resolved into the following four terms:

\[ I^*(\omega) = \frac{1}{\pi} L(\omega) \sum_m |\langle m|V_A^*|g\rangle|^2 \]
\[ - \pi L(\omega) \sum_m |\langle m|V_C^+ V_D^*|g\rangle|^2 \]
\[ + D(\omega) \sum_m \langle g|V_A^{+1} V_C^*|m\rangle \langle m|V_C^+ V_D^*|g\rangle \]
\[ + \langle g|V_A^{+1} V_D^*|g\rangle. \]  

Here, \( L(\omega) \) is the Lorentzian function, \( L(\omega) = \Gamma/\omega^2 + \Gamma^2 \).
The function \( D(\omega) = 2\omega(\omega^2 + \Gamma^2) \) becomes zero at \( \omega = 0 \)
and has extremum values \( \pm \Gamma \) at \( \omega = \pm \Gamma \). Note that the origin of
\( \omega \) is taken at \( E_m - E_g \). The functions \( L(\omega) \) and \( D(\omega) \) deter-
mine the \( \omega \) (photon energy) dependence of each term in Eq.
(10). The fourth term represents the direct photoemission
process which just produce a background for both XAS
and MCD in the present framework. The first term represents
the normal photoabsorption process \( 4f \rightarrow 5d \), in which
\( F_1(\kappa) = \sum_m |\langle m|V_A^*|g\rangle|^2 \) gives a negative MCD signal in the
4f_{7/2} region according to the dipole selection rule, leading to
\( F_1(+1) < F_1(-1) \). The second term represents a “virtual”
process, in which the system is first excited from the ground
state into the continuum states (where either 5p or 5d
electron is excited) and then goes to the intermediate states by
the reverse process of the CK decay (where the excited electron
decays nonradiatively and the 4f electron is excited to the
5d state). Let us call this the second order process in the
sense that the system follows the two sequential paths to
reach the state \( |m\rangle \). This second term contains the operator
\( V_D^* \) and thus is proportional to \( Q_D \). It has the same \( \omega \) depen-
dence as the first term [due to the Lorentzian \( L(\omega) \)]. In this
term \( F_2(\kappa) = \sum_m |\langle m|V_C V_D^*|g\rangle|^2 \) which determines the \( \kappa \)
(helicity) dependence of the second term, has the same depen-
dence as the first term, namely, \( F_2(+1) < F_2(-1) \). The
first and the second terms have signs opposite to each other
and the sum of the two terms is almost canceled out at any \( \omega \)
for \( Q_D = 0.4 \) (the best fit value). As the result, the third term
almost determines the spectral shape of both the XAS
and MCD. This term contains both the normal absorption process
and the second order process and is called an interference
term. This has a unique \( \omega \) dependence, represented by \( D(\omega) \), whereas the \( \kappa \) dependence represented by
\( F_1(\kappa) = \sum_m |\langle m|V_A^*|g\rangle|^2 \) is the same as the preceding
two terms. Namely, \( F_1(+1) < F_1(-1) \) is realized. In Fig. 6
we show the behavior of the function \( D(\omega) F_1(\kappa) \) on the
supposition of \( F_1(+1) = 0.8, F_1(-1) = 1.0, \) and \( \Gamma = 0.5 \) eV. In
the upper panel of the figure, the solid (dashed) curve repres-
ts the spectrum for \( \kappa = +1(-1) \). The dotted chain curve in
the lower panel represents the MCD spectrum
\( D(\omega)[F_1(+1) - F_1(-1)] \). We recognize that a positive and
a negative MCD signals reproduce the experimental result in the
4f_{7/2} region well. The MCD in the 4f_{5/2} region is like-
wise reproduced by this treatment. From this inspection it
becomes clear that the observed unusual MCD features in the
Pt N_{6p} region are just reflecting the \( \omega \) and \( \kappa \) dependence of the
interference term.

The present theoretical approach has, however, two short-
comings. First of all, we obtained the best fit result by setting
\( Q_D = 0.4 \) (See Figs. 4 and 5), starting from the reasonable
ground state. The spectrum with $Q_D=1.0$ (not shown) cannot explain the experimental result because the peaks $A'$ and $B'$ become extremely enhanced. This suggests that our estimation of the dipole matrix elements $\langle 5d^p r|e l \rangle$ and $\langle 5p|e^* l^* \rangle$ is not satisfactory. A full relativistic HF treatment may reduce this disagreement. Secondly, the best fit result with $Q_D=0.4$ still has some discrepancies around the peak $A$ and $A'$. These discrepancies may be coming from the too simplified treatment of the continuum excitation processes. As shown in Fig. 3, three types of the continuum states, $5d^{p-1} e l$, $5p_{3/2} 5d^p e^* l^*$, and $5p_{1/2} 5d^p e^* l^*$, are considered. The intermediate states $4f^{54}d^p$ are assumed to interact with all kinds of continua. The $4f^{55}d^{n+1} \rightarrow 5p_{1/2} 5d^p e^* l^*$ states. As shown in Fig. 1, the Pt $5p_{1/2} \rightarrow 5d$ absorption occurs around $h\omega=72$ eV, and the largest part of the $5p_{1/2} e^* l^*$ continuum excitation absorption may be located at slightly higher energies than the Pt $4f_{7/2} \rightarrow 5d$ absorption onset. As a result, the $4f^{55}d^{n+1}$ states may not be heavily embedded in the $5p_{1/2} 5d^p e^* l^*$ continuum states. So the Fano effect around the photon energy of the $4f_{7/2}$ excitation threshold region would become much weaker compared to the present theoretical framework. Then the amplitude of the MCD around the $4f_{7/2}$ edge may be substantially reduced. These discrepancies should be removed in future.

Then we comment on magnetic sum rules. We cannot simply apply the sum rules to the Pt $N_{6,7}$ MCD of CoPt$_3$, because the coexistence of the direct photoemission process and the interference effect are not considered in deriving the sum rules. So we should rely on the line shape fitting analysis to determine the ratio $\langle L_z \rangle/\langle S_z \rangle$. Figure 7 shows the calculated MCD spectra for a fixed $Q_D=0.4$ with varying the value of $\langle L_z \rangle/\langle S_z \rangle$. Figure 7 shows the calculated MCD spectra for a fixed $Q_D=0.4$ with varying the value of $\langle L_z \rangle/\langle S_z \rangle$. As we have seen in Fig. 4, however, the MCD is more sensitive to the value of $\langle L_z \rangle/\langle S_z \rangle$. This fact suggests that it may be possible to determine the ratio $\langle L_z \rangle/\langle S_z \rangle$ from the line shape analysis. As we have seen in Fig. 4, however, the MCD is more sensitive to the change of $Q_D$ (the dipole matrix elements of the photoemission processes), so that the determination of $\langle L_z \rangle/\langle S_z \rangle$ from the line shape analysis is very difficult unless we accurately know the dipole matrix elements.

IV. CONCLUSIONS

We have measured the XAS and MCD spectra in the Pt $N_{6,7}$ region of ferromagnetic CoPt$_3$. The measured XAS

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26 M. Shirai (private communication).