Orbital contribution to the 3d magnetic moment in ferromagnetic Cu₃Au-type transition-metal-Pt alloys probed by soft-x-ray magnetic circular dichroism

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Magnetic circular dichroism in the soft-X-ray absorption spectrum in the 2p→3d excitation region of the transition-metal element is measured for ferromagnetic Cu₃Au-type alloys, MnPt₃, Fe₃Pt, and CoPt₃. The electronic state, especially the contribution of the spin and orbital angular momenta to the magnetic moment, is discussed by analyzing the results. The condition for the orbital angular momentum to make a large contribution to the magnetic moment in a metallic system is discussed in terms of the degree of the localization of the 3d orbital, the filling of it, and the symmetry around it. [S0163-1829(99)00213-1]

I. INTRODUCTION

3d transition metals and Pt make binary alloys in a wide range of concentration ratios and these alloys have various magnetic properties. At stoichiometric compositions, there often exist ordered phases. When the transition metal (represented by T) is one of the elements among Mn through Ni, ordered TPt has CuAuI-type (or L1₀) structure and TPt₃ and T₂Pt have Cu₃Au-type (or L₂₁) structure. Among the Cu₃Au-type ordered alloys with T=Mn–Ni, ferromagnetism is found for MnPt₃, Fe₃Pt, CoPt₃, and Ni₃Pt. This series is quite interesting in at least two points. The first point is the contrast between TPt₃ and T₂Pt, namely that the 3d electron of the transition metal is expected to be relatively localized in the former and itinerant in the latter. The second point is the change of the filling of the 3d orbital from T=Mn to Ni. From a view point of application, magneto-optical effect and magnetic anisotropy have been studied for films of MnPt₃ and CoPt₃. On the other hand, Fe₃Pt is known to show the Invar effect.

Magnetic circular dichroism (MCD) of core-level absorption spectrum (XAS), namely the difference of the spectra between parallel and antiparallel geometries of the sample magnetization and the photon spin of the incident circularly polarized light, has recently been used for the study of ferromagnetic materials. XAS is not only an element-specific method but it also yields information about a specific orbital, to which the core electron is strongly excited due to the selection rule and the transition probability. For the transition metal, the 3d orbital, which is the main origin of the magnetic moment, can be probed by 2p and 3p XAS.

The origin of the MCD in XAS can be summarized as follows. First, a circularly polarized photon selectively excites an electron with an orbital angular momentum parallel (antiparallel) to the photon spin when the azimuthal quantum number l is increased (decreased) by the photoexcitation. Second, the non-s core level has, in addition, spin-orbit interaction, which aligns the electron’s spin and orbital angular momenta parallel or antiparallel to each other. Now, in a ferromagnetic material, a valence orbital has a magnetic moment, which means that the occupation of the orbital is polarized in spin and/or orbital angular momenta. The photoabsorption transition can occur only when the state to which the electron is excited is empty. The unbalance of the occupation of the valence orbital in spin and orbital angular momenta is reflected in the dependence of the absorption intensity on whether the photon spin is parallel or antiparallel to the magnetization. XAS-MCD for a core level with a large spin-orbit splitting, for example, the 2p level of the transition-metal elements, is particularly a good tool since, in such a case, the circularly polarized photon select both orbital angular momentum and spin of the core electron.

The two sum rules known as the l_z sum rule and the s_z sum rule make use of these features of MCD and yield (l_z) and (s_z) of the valence orbital by integrating the XAS with each circular polarization. The s_z sum rule can only be used when spin-orbit splitting of the core level is large.

In T-Pt alloys, magnetic moments are carried mainly by T 3d electrons but the contribution of the Pt 5d electrons is not negligible. Spin and orbital angular momenta of the Pt 5d orbital were studied using the MCD in Pt 2p→5d XAS (Ref. 12) and Pt 4f→5d XAS. In this paper, we report MCD in T 2p→3d XAS of MnPt₃, Fe₃Pt, and CoPt₃. Our aim is to investigate the electronic and magnetic state of the T 3d orbital. By using the sum rules, contributions of the spin and orbital angular momenta to the magnetic moment are estimated. We discuss what determines the degree to which the orbital angular mo-
momentum contributes to the magnetic moment in a metallic system, and apply this argument to the present systems.

II. EXPERIMENT

The MnPt₃, Fe₃Pt, and CoPt₃ samples were prepared by the arc-melting method under an Ar atmosphere. The Cu₃Au ordered phase was realized by a suitable thermal treatment and was verified by x-ray powder diffraction.

The measurements of the MCD in the 2p XAS were performed at the beam-line NE-1B of the Accumulation Ring of the Photon Factory in the High Energy Accelerator Research Organization in Tsukuba, Japan. The clean surface of the sample was obtained by scraping in situ in an ultrahigh vacuum of about 5 × 10⁻¹⁰ Torr. The sample was cooled to below 120°K using a liquid-nitrogen cryostat. The circularly polarized soft x-ray from the helical undulator was monochromatized and incident normally on the sample. The degree of circular polarization was 95 ± 2% according to the calculation. XAS was obtained using the total photoelectron yield method by measuring the sample current and normalizing it by the photon current. The photon current was determined by measuring the sample current and normalizing by the total photoelectron yield of the gold mesh just before the measurement chamber. A magnetic field of 1.1 T was reversed at each photon energy to cancel a possible drift of the magnetization parallel to the photon spin.

III. RESULTS AND DISCUSSIONS

In Figs. 1(a)−1(c), the observed 2p XAS for the magnetization parallel to the photon spin (defined as the Iₚ spectrum) and that for magnetization antiparallel to the photon spin (Iₐ), and their differencespectra (IₓMCD=Iₚ−Iₐ) are shown for MnPt₃ [Fig. 1(a)], Fe₃Pt [Fig. 1(b)], and CoPt₃ [Fig. 1(c)]. We note that, by taking the magnetization direction as the quantization axis, the negative spin corresponds to the majority spin in this paper. Each spectrum has a two-peak structure due to the spin-orbit splitting of the 2p core level into 2p_{3/2} and 2p_{1/2} sublevels. The two main peaks mainly represent the 2p_{3/2} → 3d and 2p_{1/2} → 3d excitations. The origin of the relative photon energy was set at the boundary between the 2p_{3/2} and 2p_{1/2} regions (2p_{1/2} onset). The boundary was determined as the energy where the energy derivative of the absorption (dI/dE) rises abruptly. Iₐ was multiplied by a constant 1 + α so that Iₚ and Iₐ have the same intensity in the lowest photon energy region where 2p absorption should be absent. |α| was less than 4 × 10⁻³.

A. Line shape

The overall MCD features seen for the three compounds, namely positive MCD in the 2p_{3/2} region and negative MCD in the 2p_{1/2} region, are the common features for the MCD of the T 2p core in ferromagnets as long as the magnetic moment of the T is in the same direction as the net magnetization. The origin of these features is that the 3d orbitals with negative spin is more occupied than the positive spin. For example, in the 2p_{3/2} region, the 2p₂ electron with positive (negative) spin is mainly excited to the 3d orbital in Iₚ (Iₐ) due to the selection rule of the circularly polarized light and the spin-orbit interaction of the 2p core level. Since transition to an occupied state is forbidden, Iₐ is smaller than Iₚ in the 2p_{3/2} region.

Although multiplet structures are much less conspicuous than in ionic compounds, we can still see some remaining structures due to the intra-atomic electron-electron interaction in the final state of the x-ray absorption. In MnPt₃, for example, structures in both XAS and MCD around −7.5 and −4.5 eV in the relative photon energy resemble the structures found in the calculation for Mn^{2+}(3d⁶) assuming a moderate crystal-field splitting (10Dq=1 eV). It might seem strange that multiplet structure is quite prominent only in MnPt₃. For Fe₃Pt and CoPt₃, however, MCD spectra approach zero much more rapidly than the XAS spectra in the higher photon energy region of 2p_{3/2}. This is not the case in the 2p_{1/2} absorption region where both MCD and XAS equally have long tails on the higher photon energy side. These features are similar to those seen in the atomic calculation of MCD for high-spin d⁶ and d⁷ initial state without considering the 3d spin-orbit interaction (ζ = 0 and Δ = 1 in Ref. 14), where MCD changes sign from positive to negative in the higher photon energy region of 2p_{3/2} while MCD is monotonously negative for 2p_{1/2}. From these investigations, we can infer that the long tails seen in the 2p absorption of the metallic transition-metal compounds originate at least partially from the multiplet splitting of the 2p³3d⁶⁺ states due to the electron-electron interaction.

B. Sum-rule analysis

In order to estimate quantitatively the contribution of the spin and orbital angular momenta to the magnetic moment of the transition metal, we analyze the spectra by using the sum rules.¹⁰,¹¹

In the present case of 2p → 3d XAS, the Iₚ sum rule can be written as

\[ \langle Iₚ \rangle = -\frac{2}{\langle Iₚ + Iₐ + I₀ \rangle} \int d\varepsilon (Iₚ - Iₐ) \]

where \( \langle Iₚ \rangle \) is the average of the magnetic quantum number of the orbital angular momentum per 3d hole. I₀ is the XAS with the linearly polarized light whose polarization vector is parallel to the magnetization. The integration is taken over the whole 2p absorption region. The sₚ sum rule is written as

\[ \langle sₚ \rangle = \frac{3}{2} \langle tₚ \rangle \]

\[ = \frac{3}{2} \frac{\int_{2p_{3/2}} d\varepsilon (Iₚ - Iₐ)}{\int d\varepsilon (Iₚ + Iₐ + I₀)} \]

where \( tₚ \) is the z component of the magnetic dipole operator \( t = s - 3r(\mathbf{r} \cdot \mathbf{s})/|\mathbf{r}|^2 \). The integration \( \int_{2p_{3/2}} \langle f_{j=2p} \rangle \) is taken only over the 2p_{3/2}(2p_{1/2}) absorption region. By dividing Eq. (1) with Eq. (2), we obtain
We should note that this equation is quite efficient. This equation stands even if the circular polarization of the light is not perfect in \( I_+ \) and \( I_- \) so long as the degree of polarization is the same for both \( I_+ \) and \( I_- \). This equation also stands even if the magnetization of the sample is not saturated. Another advantage of this equation is that it is defined only by the difference spectrum of MCD. It is not affected by how the background of XAS is assumed, while Eqs. (1) and (2) do depend on the background.

In order to use Eqs. (1) and (2), we should subtract back-
groun...hence, we concentrate our discussion on the compound dependence of $\langle I_z \rangle / (\langle I_z \rangle + 2 \langle s_z \rangle)$.

Teramura et al.\cite{Teramura} argued the effect of the overlap between $2p_{3/2}$ and $2p_{1/2}$ final states on the $s_z$ sum rule. According to their results, the $s_z$ sum rule underestimates $\langle s_z \rangle$ by a factor which depends mainly upon the $3d$ electron number. The factor of the underestimation is reported to be 0.68, 0.88, 0.92, and 0.92 for $3d$ electron numbers of 5, 6, 7, and 8, respectively. According to the band-structure calculations by Shirai,\cite{Shirai} occupation of the $3d$ electronic state, i.e., the $3d$ electron number divided by the number of the $3d$ states within the muffin-tin sphere, is 55% for MnPt$_3$ and 76% for CoPt$_3$. We therefore assume that the $3d$ electron number is 5.5 and 7.6 for MnPt$_3$ and CoPt$_3$, respectively. We furthermore assume that it is 6.5 for Fe$_3$Pt. By linearly interpolating the values obtained by Teramura et al., we consider the factor of underestimation of $\langle s_z \rangle$ to be 0.78, 0.90, and 0.92 for MnPt$_3$, Fe$_3$Pt, and CoPt$_3$, respectively. Figure 2(b) shows the dependence of the values of $\langle I_z \rangle / (\langle I_z \rangle + 2 \langle s_z \rangle)$ on the integration region after correcting the $\langle s_z \rangle$ value by dividing it with the factors above.

The integration region dependence of $\langle s_z \rangle$ and $\langle I_z \rangle$ in Figs. 1(d)–1(f) indicates that convergence, especially of $\langle I_z \rangle$, is quite slow. The value of $\langle I_z \rangle / (\langle I_z \rangle + 2 \langle s_z \rangle)$ is free from error in the background, it is not free from that in the before-mentioned normalization between $I_+ \rightarrow I_-$ and $I_- \rightarrow I_+$. Therefore, it is desirable to take as wide an integration region as possible. The integration region region dependence of $\langle I_z \rangle / (\langle I_z \rangle + 2 \langle s_z \rangle)$, is free from error in the background, and $\langle I_z \rangle / (\langle I_z \rangle + 2 \langle s_z \rangle)$ obtained in this way are not accurate in an absolute sense. However, it is quite meaningful to compare them between different systems.
C. What determines the strength of the orbital angular momentum

Now, we discuss what determines the degree to which the orbital angular momentum is induced in metallic systems. We treat this issue from the following three points. One is the competition between itinerancy and localization of the 3d electron. Another is the occupancy of the 3d partial density of states, and the other is the symmetry of the system around the T site.

First, we consider the case where the system can be assumed to be spherically symmetric around the T atom. In this case, all the 3d orbitals, for example the $e_g$ and $t_{2g}$, are equivalent to each other. The 3d partial density of states (DOS) of such a ferromagnet may be represented by a model DOS in the upper panel of Fig. 3(a) in the absence of the spin-orbit interaction. Since we are taking the direction of the magnetic field as the quantization axis in this paper, $\downarrow$ corresponds to the majority spin and $\uparrow$ to the minority spin. When the spin-orbit interaction is switched on, each majority- and minority-spin partial DOS would split into subbands with a different magnetic quantum number of the orbital angular momentum, $l_z$. Here, we have assumed that the spin is still a good quantum number in the presence of the spin-orbit interaction. In other words, we only consider the $l_z$ term. This approximation can be justified when the exchange interaction is large enough so that the $l_zs_-$ and $l_zs_+$ terms that mix different spin states are negligible. The energy shift of the $l_z$ subband would be $\xi l_z$, where $\xi$ is the spin-orbit interaction constant of the 3d orbital which takes a positive value. The resultant shift of the subbands is illustrated in the lower panel of Fig. 3(a), where the subbands with positive (negative) $l_z$ are represented by the thickest (thinnest) lines.

The consequence of the present shift would be as follows. When the 3d partial DOS is less than half-filled, $l_z$ subbands with positive $l_z$ and negative (majority) spin are more occupied than the negative $l_z$ bands. Hence, orbital angular momentum with antiparallel direction as the spin is induced in this case. When the 3d partial DOS is nearly half-filled, the positive $\langle l_z \rangle$ induced in the majority-spin band is cancelled by the negative $\langle l_z \rangle$ induced in the minority-spin band, which leads to very small orbital angular momentum. When the 3d partial DOS is more than half-filled, negative $\langle l_z \rangle$ is induced and hence the orbital angular momentum is parallel to the spin.

Now, what happens when the degree of itinerancy, and hence the bandwidth, is changed in the present case? The energy splitting due to the spin-orbit coupling is not likely to depend much upon the bandwidth. Therefore, the induced orbital angular momentum would be larger for the narrower band which has larger DOS. In other words, orbital angular momentum is more induced in a system where 3d electrons are more localized.

Next, we should consider the case where the symmetry around the T atom is lower than the spherical symmetry. The 3d orbitals are no longer equivalent to each other. Here, we consider as an example that the system is octahedral or tetrahedral around the T atom. The partial density of states of $t_{2g}$ and that of $e_g$ are then different from each other.

![FIG. 3. Model 3d partial density of states (DOS) for (a) a spherically symmetric case, (b) a case where the symmetry around the transition-metal atom causes the bandwidth of the partial DOS to depend upon $|l_z|$, and (c) a case where the symmetry causes a splitting of the partial DOS into subbands. In each case, the upper panel shows the partial DOS without the spin-orbit interaction. The lower panel shows those with the spin-orbit interaction, where the thickest (thinnest) line corresponds to positive (negative) $l_z$.](https://example.com/figure3.png)
erant, depending upon the crystal structure. If the $t_{2g}$ orbital is more itinerant than the $e_g$ orbital, for example, the $l_z = \pm 1$ states are the most itinerant since these states consist purely of $t_{2g}$ states. $l_z = \pm 2$, which are linear combinations of the $t_{2g}$ and $e_g$ states, are the next and $l_z = 0$ is the most localized. This is schematically shown in the upper panel of Fig. 3(b). When the spin-orbit interaction is switched on, these bands split by energies proportional to $|l_z|$ as shown in the lower panel of Fig. 3(b). In this case, the contribution to the orbital angular momentum comes mostly from $l_z = \pm 2$, since the spin-orbit splitting of these states is stronger and the band width is narrower than $l_z = \pm 1$.

When the ionicity of the system is strong, the center of gravity of the $t_{2g}$ and $e_g$ partial DOS would be quite different. The upper panel of Fig. 3(c) illustrates the partial DOS for a case where the energy of the $e_g$ band is significantly lower than that of the $t_{2g}$ band as when the $T$ atom is tetrahedrally surrounded by negative ions. Linear combinations between two of the $t_{2g}$ orbitals, $\varphi_y$ and $\varphi_x$, lead to states with $(l_z) \neq 0$. Namely, the $(l_z) = \pm 1$ state is realized as $Y_{d \pm 1} \propto \sqrt{3}(\varphi_y \pm \varphi_x)$. Therefore, when the spin-orbit interaction is switched on, the $t_{2g}$ partial DOS split into sub-bands, namely, $Y_{d+1}$, $Y_{d-1}$, and $\varphi_y$, partial DOS’s as shown in the lower panel of Fig. 3(c). On the other hand, $(l_z)$ of any linear combination of $e_g$ states is always zero. Therefore, the $e_g$ partial DOS would not be affected. In this situation, only the $t_{2g}$ states contribute to the orbital angular momentum. Therefore, $(l_z)$ is zero if the $t_{2g}$ band is totally full or totally empty. Discussion about these aspects based on an atomic point of view was reviewed by Kanamori.18

D. Discussion about the present result

Now, we apply the model above to the present systems. In the Cu$_3$Au structure, Au is on the corner site of the fcc structure and Cu is on the face-centered site. Therefore, in both the Cu and Au sites, the $t_{2g}$ orbital hybridizes stronger with the surrounding orbitals than the $e_g$ orbitals. Since the structure is nearly close-packed and these systems are presumably quite metallic, the $3d$ partial DOS is considered to be like Fig. 3(b). This is qualitatively well reproduced by the band-structure calculation by Shirai.17 Hence the orbital angular momentum should come mainly from the $l_z = \pm 2$ orbitals. This is quite consistent with the argument on $TP_3$ by Iwahita et al.19 They discussed the orbital angular momenta of the $T$ 3$d$ and Pt 5$d$ orbitals on the basis that the $l_z = \pm 2$ give the largest contribution. This was deduced from their band-structure calculation based on the scalar-relativistic full-potential linear-augmented plane-wave method within the local-spin-density approximation (LSDA) with the additional inclusion of the spin-orbit interaction as a perturbation.

In MnPt$_3$ and CoPt$_3$, all the nearest neighbors of the transition-metal site are Pt sites. On the other hand, in Fe$_3$Pt, 2/3 of the nearest neighbors are the Fe sites and the other 1/3 are the Pt sites. Generally speaking, the Pt 5$d$ partial DOS is distributed in the energy region with a significantly larger binding energy than the $T$ 3$d$ partial DOS. Therefore, the $3d$ electrons are relatively localized in MnPt$_3$ and CoPt$_3$ whereas they are quite itinerant in Fe$_3$Pt.

In MnPt$_3$, although the $3d$ orbital is relatively localized, it is nearly half-filled. Therefore, from our discussion in the last section it follows that the orbital angular momentum of the $3d$ electrons is expected to be small. In Fe$_3$Pt, although the $3d$ orbital is more than half-filled, it is quite itinerant and the orbital angular momentum is also small. In CoPt$_3$, the $3d$ orbital is more than half-filled and is relatively localized and therefore the orbital angular momentum is expected to be larger than the other two systems. This argument well explains our experimental results that the contribution of the orbital angular momentum to the magnetic moment of the $3d$ orbital is larger in CoPt$_3$ than in MnPt$_3$ and Fe$_3$Pt.

Finally, we quantitatively compare the contribution of the orbital angular momentum, $(l_z)/((l_z)+2(s_z))$, obtained in Sec. III B with that obtained by Iwashita et al.19 According to their calculation, $(l_z)/((l_z)+2(s_z))$ values of the $3d$ electrons are 0.005 and 0.025 for MnPt$_3$ and CoPt$_3$, respectively. These values are significantly smaller than our values, 0.044 and 0.063, respectively. One of the origins of this discrepancy is that $(l_z)$ is omitted in our analysis since Wu et al. showed that $(l_z)/s_z$ is overestimated by the sum-rule analysis without $(l_z)$.15 Another origin, of course, might be that the band-structure calculation within LSDA underestimates $(l_z)$ since it cannot treat $(l_z)$ self-consistently.

IV. SUMMARY

We measured the MCD in the transition-metal 2$p$ absorption of the ferromagnetic Cu$_3$Au-type transition-metal-Pt ordered alloys, MnPt$_3$, Fe$_3$Pt, and CoPt$_3$. By combining the $l_z$ and $s_z$ sum rules, we derived $(l_z)/((l_z)+2(s_z))$, the portion of the orbital angular momentum’s contribution to the magnetic moment of the transition-metal $3d$ orbital, for the three compounds. This quantity is not only physically important but also experimentally more reliable in the sense that it is less affected by possible extrinsic errors such as the ambiguity in the background subtraction and imperfectness in magnetization and circular polarization than individual $(l_z)$ and $(s_z)$. The estimated $(l_z)/((l_z)+2(s_z))$ values, 0.044, 0.031, and 0.063 for MnPt$_3$, Fe$_3$Pt, and CoPt$_3$, respectively, are still not very reliable in an absolute sense, but they are quite meaningful in a relative sense.

What determines the degree of the orbital contribution to the magnetic moment in metallic ferromagnets was discussed. The orbital contribution is enhanced when the $3d$ electrons are localized and when the $3d$ filling is far from either empty, half-filled, or fully filled. The fact that the orbital contribution is the largest in CoPt$_3$ is explained by that the $3d$ electrons are relatively localized and the $3d$ orbital is more than half-filled in it, whereas the $3d$ electron is quite itinerant in Fe$_3$Pt and the $3d$ orbital is nearly half-filled in MnPt$_3$.

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