

X-ray magnetic circular dichroism at IrL_{2,3} edges in Fe_{100-x}Ir_x and Co_{100-x}Ir_x alloys: Magnetism of 5d electronic states

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Abstract. The formation of induced 5d magnetic moment on Ir in Fe_{100-x}Ir_x ($x=3, 10$ and 17) and Co_{100-x}Ir_x ($x=5, 17, 25$ and 32) alloys has been investigated by X-ray magnetic circular dichroism (XMCD) at Ir L_{2,3} absorption edges. Sum rule analysis of the XMCD data show that the orbital moment of Ir is in the range of $-0.071(2)\mu_B$ to $-0.030(1)\mu_B$ in Fe–Ir alloys and $-0.067(2)\mu_B$ to $0.024(1)\mu_B$ in Co–Ir alloys. We find that the total moment of Ir in Fe–Ir alloys is approximately 1/5 of the total 3d moment on Fe at all the three compositions. In contrast, the total moment on Ir in Co–Ir alloys varies between 1/6 to 1/16 of the 3d moment on cobalt. The observed trends of Ir moments and the role of interatomic exchange interactions in 5d moment formation are discussed.

Keywords. Magnetic dichroism; *d* electrons; magnetic moments.

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1. Introduction

5d atoms are known to develop induced magnetic moments in dilute alloys with Fe [1–5]. Less is known about the magnetic behavior of 5d atoms in dense alloys and in Co–Ir alloys. Therefore, it is interesting to investigate the magnetic behavior of the 5d electronic states in dense alloys and their correlation with the host 3d moment and the alloy composition. To understand the correlation between the 5d moment and the host 3d moment, element specific measurement of 5d moments is necessary. X-ray magnetic circular dichroism (XMCD) technique and its sum rules [6] give a scope for determining element specific magnetic moments in ferromagnets. With the availability of undulator beam from high-brilliance 3rd generation synchrotron radiation sources, it is now become possible to obtain highly monochromatic and well-collimated X-rays for polarization-dependent X-ray absorption measurements using helicity modulation technique [7]. In light of these technical developments, it is possible to precisely determine the composition dependence of the magnetic moment of a specific *d* or *f* ion in alloys.

Fe_{100-x}Ir_x alloys order ferromagnetically below the critical Ir composition x_c of 25 at% for antiferromagnetic ordering. The Curie temperature of the alloys with $x=3, 10$ and

17 are higher than the room temperature. $\text{Co}_{100-x}\text{Ir}_x$ also order ferromagnetically in the Ir composition range of $x = 0-35$ with a Curie temperature much higher than the room temperature [8]. Presently, there is no direct information on the magnetic behavior of Ir as a function of Ir composition in these alloys. Therefore, it is desirable to obtain a detailed information on the spin polarization in the $5d$ states of Ir, the magnitude of the orbital and the spin magnetic moments of Ir as a function of alloy composition. With this motivation, we have investigated the magnetic behavior of the $5d$ electronic states of Ir in bcc $\text{Fe}_{100-x}\text{Ir}_x$ ($x=3, 10$ and 17) alloys and hcp $\text{Co}_{100-x}\text{Ir}_x$ ($x=5, 17, 25$ and 32) alloys using Ir $L_{2,3}$ edge XMCD spectroscopy. Our results show that Ir has a composition dependent $5d$ magnetic moment in Fe–Ir and Co–Ir alloys.

2. Experimental

Disordered alloys of $\text{Fe}_{100-x}\text{Ir}_x$ ($x = 3, 10$ and 17) and $\text{Co}_{100-x}\text{Ir}_x$ ($x = 5, 17, 25$ and 32) were prepared by arc melting the desired composition of the alloy starting from high purity Ir(4N) and Fe(4N) or Co(3N) in an argon atmosphere. The sample thickness was optimized for the jump in X-ray absorption at L edge of Ir. XMCD measurements were carried out in a field of 1.15 Tesla in the transmission mode at the undulator beamline BL29XU which is equipped with a liquid N_2 -cooled Si (111) double crystal monochromator at SPring8 [9]. The Si(111) monochromator was slightly detuned to avoid the contribution of higher harmonics in the 11–13 keV region. Left-circularly polarized and right-circularly polarized X-rays were generated by a diamond diffractive phase retarder set to make bistable oscillations around the Bragg angle θ_B . The degree of circular polarization $|P_C|$ for the experimental set up was over 90%. The XMCD spectra $\Delta\mu t$ were recorded by switching the helicity of the X-rays at a rate of 40 Hz while keeping the direction of the magnetic field fixed [7]. The data were collected at room temperature.

3. Results

All the X-ray absorption spectra (XAS) were normalized such that the height of the L_3 XAS was unity. An arc tangent function, which smoothly connects the pre-edge and after-edge baselines of XAS, was subtracted from normalized XAS. The resulting difference spectra consisted of a Lorentzian shaped white line and a broad satellite. The white line intensity was obtained by integrating the difference spectra and the normalized XMCD integrals for L_3 and L_2 edges were obtained with the integration range of ± 30 eV around the E_0 of the edge, where $|\Delta\mu t|$ is maximum.

Figure 1 displays the examples of the XAS measured with left-circularly polarized and right-circularly polarized X-rays and the difference, i.e., the XMCD spectra at Ir $L_{2,3}$ edges in $\text{Fe}_{100-x}\text{Ir}_x$ alloys at $x = 3$ and 17 . The white line intensity is significant around E_0 of L_3 and L_2 edges of Ir in all the three alloys. Such a feature is indicative of large $5d$ density of states at Fermi energy. The signs of XMCD at L_3 and L_2 edges are opposite and therefore indicate ferromagnetic coupling of Ir spin moment with the $3d$ moment of Fe in all the three alloys. The variation of peak intensity of XMCD spectra $|\Delta\mu t|_{\text{max}}$ with the Ir composition of the alloy x suggests the reduction of the local moment and the spin-orbit coupling of Ir. The magnitudes and signs of our $L_{2,3}$ edge XMCD spectra agree with the previous

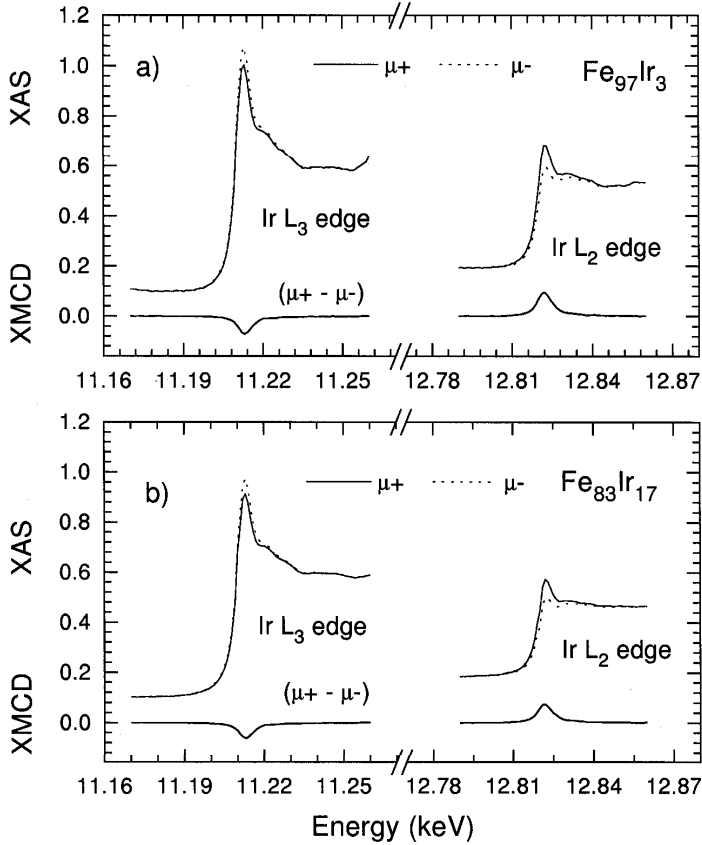


Figure 1. Ir L_3 edge and L_2 edge XAS ($\mu+$, $\mu-$) and XMCD ($\Delta\mu t = \mu+ - \mu-$) signal in (a) $\text{Fe}_{97}\text{Ir}_3$ and (b) $\text{Fe}_{83}\text{Ir}_{17}$ alloys.

$L_{2,3}$ edge XMCD data measured in $\text{Fe}_{97}\text{Ir}_3$ [4] as well as with the Korringa–Kohn–Rostor Green’s function calculations of Ebert and Zeller [10]. The orbital magnetic moment μ_{orb} and the spin magnetic moment μ_{spin} could be extracted from the XAS and XMCD spectra using the magneto-optic sum rules [6].

We assume $5d^8$ electronic configuration for Ir in all the three alloys. The threshold energy E_{th} of the L_2 and L_3 XAS was determined by the maximum derivative method. The derived values are $E_{\text{th}}(L_3) = 11210.25$ eV for the L_3 edge and $E_{\text{th}}(L_2) = 12821.00$ eV for the L_2 edge. Both the values of the threshold energies are independent of the alloy composition and support the $5d^8$ electronic configuration assumed for the valence shell of Ir in all these alloys. Applying the L_Z sum rule, μ_{orb} of Ir could be extracted as $-0.071(2)$, $-0.031(1)$ and $-0.032(1)$ μ_B per atom in $\text{Fe}_{97}\text{Ir}_3$, $\text{Fe}_{90}\text{Ir}_{10}$ and $\text{Fe}_{83}\text{Ir}_{17}$ alloys respectively. To extract μ_{spin} from the spin angular momentum sum rule [6], we approximate the expectation value of the magnetic dipole operator $\langle T_Z \rangle$ by $(1/3)S_Z$, i.e., the local Lorentz field [11,12]. The resulting value of μ_{spin} , and the total moment μ_{tot} are listed along side μ_{orb} in table 1. These results show that the μ_{tot} of Ir decreases with the increase of Ir content

Table 1. Orbital magnetic moment μ_{orb} , spin magnetic moment μ_{spin} and the total magnetic moment μ_{tot} of Ir in Fe–Ir alloys extracted from the XMCD data. μ_{Fe} is the magnetic moment/Fe atom in the alloy and $\mu_{\text{tot}}/\mu_{\text{Fe}}$ is the ratio of the magnetic moments of Ir and Fe.

Alloy	μ_{orb} ($\mu_{\text{B}}/\text{atom}$)	μ_{spin} ($\mu_{\text{B}}/\text{atom}$)	μ_{tot} ($\mu_{\text{B}}/\text{atom}$)	μ_{Fe}^* ($\mu_{\text{B}}/\text{atom}$)	$\mu_{\text{tot}}/\mu_{\text{Fe}}$
Fe ₉₇ Ir ₃	−0.071(2)	0.511(15)	0.440(13)	2.18	0.202(6)
Fe ₉₀ Ir ₁₀	−0.030(1)	0.405(12)	0.375(11)	1.98	0.189(6)
Fe ₈₃ Ir ₁₇	−0.032(1)	0.377(11)	0.345(10)	1.83	0.189(6)

*Values obtained by scaling the magnetic moment of Fe [11] with the average number of Fe atoms in the nearest neighbor (1NN) shell around an Ir atom in Fe–Ir alloys.

x suggesting that the virtual bound state of $5d$ electrons of Ir gradually shifts from Fermi energy to higher energies in the Ir rich alloys.

Both the sign and the magnitude of total moment obtained for Ir in Fe₉₇Ir₃ from the present XMCD measurement are in very good agreement with the value of $\approx 0.41(5) \mu_{\text{B}}$ reported for the total magnetic moment of Ir in this alloy from an earlier XMCD measurement by Schütz *et al* [4]. The sign and the total moment of Ir in Fe₉₇Ir₃ alloy from the present experiment also agrees with an earlier result of $0.3(3) \mu_{\text{B}}$ derived for the Ir moment by Campbell [1,2] from the neutron diffraction data of Collins and Low [13] and support the local Lorentz field approximation used above for the magnetic dipole operator $\langle T_Z \rangle$ of Ir. The positive sign of the total moment on Ir in Fe host is also in agreement with the density functional theoretical calculation of Akai [3], but the magnitude of the Ir moment derived in the present work is about 19% higher than the value obtained from the density functional calculations.

Figure 2 displays the XAS measured with left-circularly polarized X-rays and right-circularly polarized X-rays and the XMCD spectra at Ir $L_{2,3}$ edges in Co_{100− x} Ir _{x} alloys at $x = 5$ and 17. Significant white line intensities with their peaks centered near the respective threshold energy of the edges are observed in the XAS. Magnetic circular dichroism is observed at the L_3 and L_2 edges of Ir in all the alloys, suggesting significant density of states and exchange splitting in the $5d$ band of Ir.

The orbital and spin magnetic moments of Ir in Co–Ir alloys could be extracted from the XAS and XMCD spectra, following the procedure described above for Fe–Ir alloys by assuming a $5d^8$ electronic configuration for Ir. The resulting values of μ_{orb} , μ_{spin} and μ_{tot} are listed in table 2. The orbital moment of Ir comes out to be $-0.067(2)$, $-0.054(2)$, $-0.034(1)$ and $-0.024(1) \mu_{\text{B}}$ at $x = 5, 17, 25$ and 32 respectively. Both the orbital moment and spin moment of Ir decrease systematically with the Ir composition. The spin moment is the highest, i.e., $0.328(10) \mu_{\text{B}}$ in Co₉₅Ir₅ and the lowest, i.e., $0.095(3) \mu_{\text{B}}$ in the Co₆₈Ir₃₂ alloy. The composition dependence of the spin moment of Ir is mostly associated with the oscillatory RKKY interaction between Ir moments located in different shells. The reduction of the Ir spin moment with increasing Ir composition in Co_{1− x} Ir _{x} alloys indicate that the strength of the Ir–Ir antiferromagnetic coupling is larger at higher x . The total moment of Ir μ_{tot} in Fe_{100− x} Ir _{x} and in Co_{100− x} Ir _{x} alloys decreases systematically with the Ir composition x .

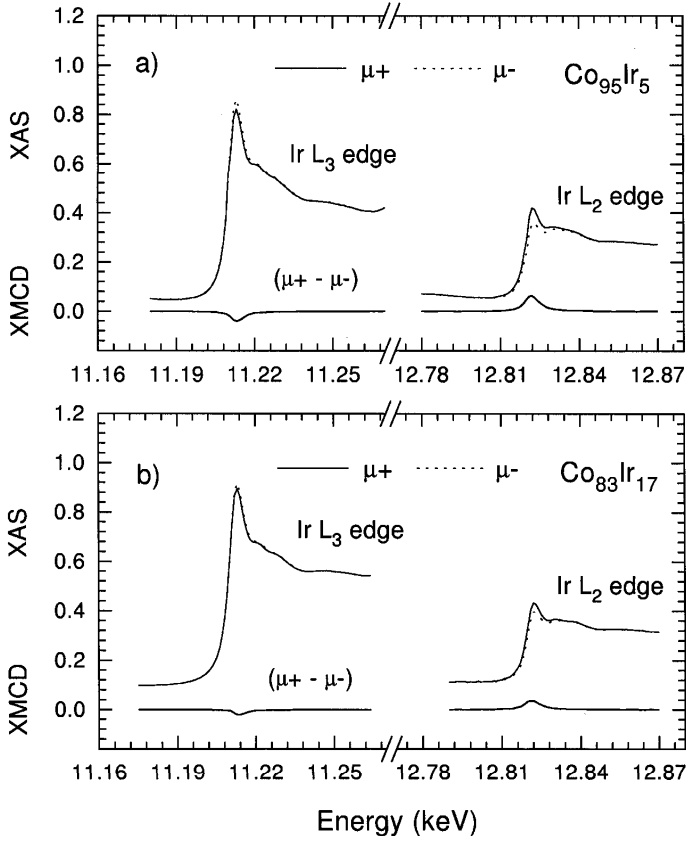


Figure 2. Ir L_3 edge and L_2 edge XAS ($\mu+$, $\mu-$) and XMCD ($\Delta\mu t = \mu + -\mu-$) signal in (a) $\text{Co}_{95}\text{Ir}_5$ and (b) $\text{Co}_{83}\text{Ir}_{17}$ alloys.

Table 2. Orbital magnetic moment μ_{orb} , spin magnetic moment μ_{spin} , their ratio $\mu_{\text{orb}}/\mu_{\text{spin}}$ and the total magnetic moment μ_{tot} of Ir in Co–Ir alloys determined from the XMCD data by applying the sum rules. μ_{Co} is the magnetic moment per Co atom in the alloy and $\mu_{\text{tot}}/\mu_{\text{Co}}$ is the ratio of the magnetic moments of Ir and Co.

Alloy	μ_{orb} ($\mu_{\text{B}}/\text{atom}$)	μ_{spin} ($\mu_{\text{B}}/\text{atom}$)	μ_{tot} ($\mu_{\text{B}}/\text{atom}$)	μ_{Co}^* ($\mu_{\text{B}}/\text{atom}$)	$\mu_{\text{tot}}/\mu_{\text{Co}}$
$\text{Co}_{95}\text{Ir}_5$	−0.067(2)	0.328(10)	0.261(8)	1.63	0.160(5)
$\text{Co}_{83}\text{Ir}_{17}$	−0.054(2)	0.194(6)	0.140(4)	1.43	0.098(3)
$\text{Co}_{75}\text{Ir}_{25}$	−0.034(1)	0.138(5)	0.104(3)	1.29	0.081(3)
$\text{Co}_{68}\text{Ir}_{32}$	−0.024(1)	0.095(3)	0.071(6)	1.14	0.062(2)

* Values obtained by scaling the magnetic moment of Co [8] with the average number of Co atoms in the nearest neighbor (1NN) shell around an Ir atom in Co–Ir alloys.

The reduction of μ_{tot} of Ir with the Ir composition in both these alloys also suggest that the spin polarization of $5d$ electrons of Ir gradually shifts to higher energies. This means an increasing tendency of itinerant behavior of the $3d$ band electrons in Ir rich alloys.

4. Discussion

We now discuss the correlation of the total moment of Ir with the total $3d$ moment in the alloy system. We approximate the total moment of Fe in $\text{Fe}_{97}\text{Ir}_3$ alloys as $2.17 \mu_B$, i.e., same as that of Fe in bcc Fe [14]. Then, we find that the total moment of Ir in $\text{Fe}_{97}\text{Ir}_3$ is about $1/5^{\text{th}}$ of the total $3d$ moment of Fe. Let us assume that the magnetic moment of Fe in Fe–Ir alloys scales with the average number of Fe in the nearest neighbor (1NN) shell and estimate the Fe moment. The resulting values are tabulated in column 5 of table 1. Column 6 shows the ratio of the total moment of Ir with the total moment of Fe. The ratio at the higher Ir compositions (up to 17 at% Ir) [12] also comes out to be very close to $1/5$ suggesting the scaling of total moment of Ir with the total moment of Fe in the alloy. This result also implies that the Fe moments in the 1NN shell of Ir mostly determine the size of the Ir moment in the alloy.

Similarly, taking the total moment of Co as $1.716 \mu_B$ [8], and scaling it with the number of Co in the 1NN shell, we obtain the magnetic moment μ_{Co} of Co in the alloys. These are listed in column 5 of table 2. The ratio of the magnetic moments of Ir and Co are listed in column 6. The total moment of Ir in $\text{Co}_{95}\text{Ir}_5$ then comes out to be $1/6$ of the total $3d$ moment of Co in the alloy. This ratio changes with the alloy composition and lowest value of $1/16$ is observed in the $x=32$ alloy. Therefore, unlike in the case of Fe–Ir alloys, the ratio is strongly composition dependent in Co–Ir alloys (see table 2). This difference suggests that the Co atoms located in the next near neighbor (2^{nd} and higher) shells also strongly contribute to the development of Ir moment in Co–Ir alloys through the RKKY exchange interaction. It is also likely that the RKKY exchange interaction between Ir spins located in different shells has an influence on the stability of the $5d$ moment of Ir.

The scaling factors found for Ir in Fe–Ir and Co–Ir alloys are comparable to the scaling factors found for the $4d$ moment on Rh, which is isoelectronic with Ir, in Rh–Fe and Rh–Co alloys, where the induced $4d$ moment on Rh is $1/3$ of the Fe or Co moment [15]. They are also comparable with the scaling factor of $1/4$ found for Ir in $\text{Ni}_{95}\text{Ir}_5$ alloy [16]. On the other hand, the scaling factor between the Ir moment and the $3d$ moment in $\text{Fe}_{1-x}\text{Ir}_x$ ($x = 0-17$) alloys and $\text{Co}_{1-x}\text{Ir}_x$ ($x \leq 25$) alloys is larger than the scaling factor of $1/13$ observed for the Ru $4d$ moment with respect to the Co $3d$ moment in $\text{Ru}_{71}\text{Co}_{29}$ alloy [15].

5. Summary

Magnetism of $5d$ electronic states of Ir in $\text{Fe}_{100-x}\text{Ir}_x$ ($x = 3, 10$ and 17) and $\text{Co}_{100-x}\text{Ir}_x$ ($x = 5, 17, 25$ and 32) alloys has been investigated by x-ray magnetic circular dichroism (XMCD) spectroscopy at Ir $L_{2,3}$ absorption edges. Sum rule analysis show that Ir develops a magnetic moment in all these alloys. Both the orbital magnetic moment and the spin magnetic moment of Ir are sizable and exhibit a strong dependence on the alloy composition. The total moment on Ir is $1/5$ of the magnetic moment of Fe at all the compositions suggesting that Fe atoms in the 1NN shell mostly control the size of the $5d$ moment on

Ir in Fe–Ir alloys. In contrast, the composition dependent scaling trends between the total moment of Ir and Co atoms suggest that the magnetic moment of Co atoms in the 1st, 2nd and higher shells, the RKKY exchange interaction between Ir and Co and the RKKY interaction between Ir moments located in different shells play a significant role in the development of 5d moment in Co–Ir alloys. It would be interesting to study other bcc and hcp alloy series containing 5d atoms using XMCD spectroscopy to know whether the *d*–*d* exchange coupling has a correlation with the crystal structure of the alloy.

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