

Induced Rh magnetic moments in Fe-Rh and Co-Rh alloys using x-ray magnetic circular dichroism

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The induced magnetic moment of Rh atoms in $\text{Co}_x\text{Rh}_{100-x}$ alloys ($x=77,49$) is investigated by x-ray magnetic circular dichroism (XMCD) at the Rh $M_{2,3}$ absorption edge. By comparing with the XMCD signal observed in an $\text{Fe}_{77}\text{Rh}_{23}$ alloy where the Rh magnetic moment is known, the value of the Rh magnetic moment in Co alloys can be determined ($0.6\mu_B$ for $x=77$ and $0.1\mu_B$ for $x=51$). We find that the Rh moment is about $\frac{1}{3}$ the Fe or Co moment for the alloys studied. Analogous measurements of XMCD from a $\text{Co}_{71}\text{Ru}_{29}$ alloy show Ru behavior very different from that of Rh, with an induced Ru moment $< \frac{1}{14}$ the Co moment.

Of all the transition metals, only the $3d$ elements whose d shell is at least half full are magnetic. However, it is well known that some $4d$ elements, such as Rh and Pd, are "nearly" ferromagnetic, in that small perturbations, of e.g., the lattice constant, give rise to a ferromagnetic state. One approach to the stabilization of magnetism in the $4d$ elements is the formation of layered structures with ferromagnetic transition metals (FTM's). For example, Pd has been found to have significant magnetic polarization in Pd/Fe multilayers.¹

Another, perhaps more straightforward way to polarize $4d$ elements is by the preparation of an intermetallic alloy with an FTM. Many studies of magnetic moments of each atomic species in intermetallic transition-metal alloys were made in the 1960s and 1970s using Mössbauer spectroscopy,² neutron diffraction,^{3,4} or NMR spin-echo measurements (see, e.g., Ref. 5). However, these studies were confined to Fe alloys, or in a few cases Ni alloys. Due to the high defect density and relative complexity of the hcp Co crystal structure,⁶ neither neutron diffraction nor NMR spin-echo measurements were pursued on the Co/ $4d$ alloys.

In the study of either alloys or multilayers of $4d$ elements and FTM elements, it is difficult to separate out the relatively small $4d$ magnetic moment from the large FTM moment. One promising approach is to use an element-sensitive technique, such as x-ray magnetic circular dichroism (XMCD) to sort out the magnetic moments on the different atomic species. In XMCD, variations in the absorption coefficient of circularly polarized x rays of different helicity give a measure of the average magnetic moment of particular atomic species in a complex material. The XMCD effect is proportional to magnetic moment, but requires "calibration"

through the measurement of one sample having known magnetization before absolute magnetic moments may be determined. XMCD would appear to be an ideal tool for the study of ferromagnetism in the $4d$ elements.

Although XMCD has been applied successfully to $3d$, $5d$, and rare-earth elements,⁷ applying XMCD to the $4d$ elements presents experimental difficulties, and until the present, no other work has used this approach. The reason for this is that for the transition metals, the $2p$ absorption edge is preferred for XMCD due to its high signal/background ratio and high sensitivity to the d -band valence levels (the latter being the most sensitive to spin polarization). However, for most x-ray crystal monochromators, the relevant diffraction angle for the $2p$ absorption edges of $4d$ elements is near 45° , and at this angle monochromators transmit only linearly polarized x rays, making XMCD impossible.

In the present work, we present the first XMCD measurements on a $4d$ element (Rh). These were obtained at the $3p$ absorption edge. Although possessing a lower signal/background ratio, the photon energy required for the $3p$ edge is such that highly circularly polarized x rays may be produced using conventional grating optics.⁸ Through the study of a $\text{Fe}_{77}\text{Rh}_{23}$ alloy, where the induced Rh magnetic moment is known, we determine the proportionality constant between the XMCD effect and magnetic moment for Rh. This permits absolute determination of the Rh magnetic moment in two $\text{Co}_x\text{Rh}_{100-x}$ alloys, with $x=77,49$. Finally, an examination of a $\text{Co}_{71}\text{Ru}_{29}$ alloy shows very little polarization of the Ru atoms, in sharp contrast to Rh. The importance of the present work is enhanced by demonstrating how element-specific magnetic polarization measurements can be performed on $4d$ transition metals, in, e.g., magnetic multilayers.

TABLE I. Summary of results of SQUID and XMCD magnetization measurements on various alloys discussed. For the $\text{Fe}_{77}\text{Rh}_{23}$ alloy, the XMCD Rh magnetic moment (asterisk) is deduced from literature values, and all other Rh moments are scaled to this value. Also for $\text{Fe}_{77}\text{Rh}_{23}$, neutron diffraction measurements (Ref. 3) are shown for comparison. Magnetization units are in μ_B per atom.

	$M_{\text{rem}}/M_{\text{sat}}$ SQUID	M_{sat} SQUID	M_{FTM} XMCD	M_{4d} XMCD	M_{sat} XMCD	M_{FTM}/M_{4d}
$\text{Fe}_{77}\text{Rh}_{23}$	0.82	1.70	$M_{\text{Fe}}=2.13$ (2.75 Lit.)	$M_{\text{Rh}}=0.75^*$ (1.0 Lit.)	1.82 (2.31 Lit.)	2.8
$\text{Co}_{77}\text{Rh}_{23}$	0.65	1.22	$M_{\text{Co}}=1.34$	$M_{\text{Rh}}=0.64$	1.18	2.1
$\text{Co}_{49}\text{Rh}_{51}$	0.38	0.34	$M_{\text{Co}}=0.45$	$M_{\text{Rh}}=0.11$	0.28	4.1
$\text{Co}_{71}\text{Ru}_{29}$	0.52	0.39	$M_{\text{Co}}=0.42$	$M_{\text{Ru}}<0.03$	0.30	>14

The measurements were carried out at the Synchrotron Radiation Center in Stoughton, Wisconsin. The alloy samples were prepared as 500–1000 Å films on fused quartz wafers by codeposition using magnetron sputtering with the substrate held at 500 °C. Alloy compositions were measured by electron microprobe and x-ray fluorescence analysis, and absolute magnetizations were measured by superconducting quantum interference device (SQUID) magnetometry. The samples were transported to the synchrotron in air. To remove the resulting surface impurity layer, the films were sputter-etched in vacuum and annealed to ~ 300 °C prior to measurement. Residual oxygen impurity levels were small (less than 1 equivalent monolayer) as determined from the oxygen 1s absorption peak. The samples were magnetized in-plane prior to the XMCD measurements, and were measured in remanence. We estimate the circular polarization at $85 \pm 5\%$,⁸ and the x rays were incident at $\pm 65^\circ$ from the surface normal upon the sample, with consecutive spectra taken at alternating angles. Absorption spectra were measured using a total electron yield technique.

Table I presents the results of the SQUID magnetometry and composition studies (the XMCD results are discussed below). The remanent magnetization fraction ($M_{\text{rem}}/M_{\text{sat}}$), and the magnetic moment per alloy atom are tabulated for each alloy. The remanent fraction is important for the XMCD determinations of magnetic moments, since the measured XMCD moments must be divided by this number to find their equivalent saturation values.⁹ Note that the moment per alloy atom of the $\text{Fe}_{77}\text{Rh}_{23}$ alloy is reduced by about 25% relative to literature values⁴ for the perfectly chemically ordered bulk alloy.¹⁰ This is somewhat larger than the expected errors inherent in magnetometry of such films ($\approx 10\%$). The reduction of magnetic moment might be due to imperfect chemical ordering in the present alloy films.

The XMCD results at the Fe edge [Fig. 1(a)] are consistent with this conclusion. Here the solid and dashed curves are the absorption coefficients, $\alpha_{\pm 65^\circ}$, taken in the two sample positions (magnetization 25° or 155° with respect to polarization, respectively), and the dotted curve their difference. All XMCD spectra are normalized such that below the absorption edge the intensity is zero and at one point above the absorption edge, the “edge jump” is equal to 1.¹¹ To obtain a measure of the magnetic moment per atom, M_γ , for a particular atomic species, γ , we use

$$M_\gamma = (2\langle S_z^\gamma \rangle + \langle L_z^\gamma \rangle) \\ = \mathcal{A}^\gamma \left(5 \int_{p_{3/2}} (\alpha_{+65} - \alpha_{-65}) - 4 \int_{p_{1/2}} (\alpha_{+65} - \alpha_{-65}) \right), \quad (1)$$

following the prescriptions of Refs. 12. The integrals are performed over the energy regions near the $2p_{3/2}$ and $2p_{1/2}$ absorption features in Fe and Co, and over the analogous $3p$ features for Rh and Ru. To determine the proportionality constant \mathcal{A}^γ for Fe and Co in Eq. (1), we use spectra from epitaxial films¹³ (not shown). For example, assuming the bulk magnetic moment ($2.18\mu_B$) for Fe in the epitaxial film, we obtain a remanent moment of $1.75\mu_B$ for the iron atoms in the $\text{Fe}_{77}\text{Rh}_{23}$ alloy. Dividing by the remanent fraction (0.82), this implies a saturation magnetic moment of $2.13\mu_B$ for Fe in this alloy.

The “calibration” films used were 25 ML Fe/Cu(100) (bcc), and 15 ML Co/Cu(100) (fcc), both of which have magnetic moments close to those of bulk Fe and Co, respectively. Implicit in this analysis, however, is the assumption that \mathcal{A}^γ is a constant for, e.g., Fe atoms, whether they are in Fe metal, or an Fe-Rh alloy. Although not rigorously true,

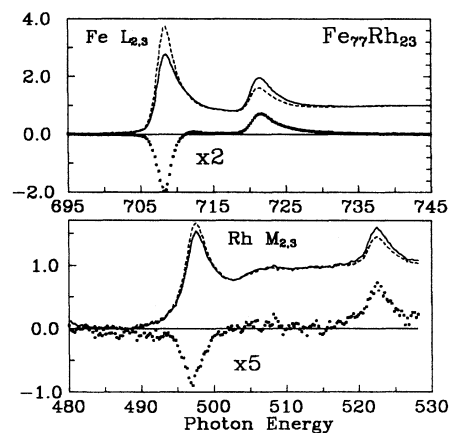


FIG. 1. X-ray absorption spectra from an $\text{Fe}_{77}\text{Rh}_{23}$ alloy at the Fe $2p$ and Rh $3p$ edges, taken with the sample magnetization at 25° (solid) and 155° (dashed) with respect to the photon helicity. The difference (dotted curve) of the absorption curves is plotted on an expanded scale.

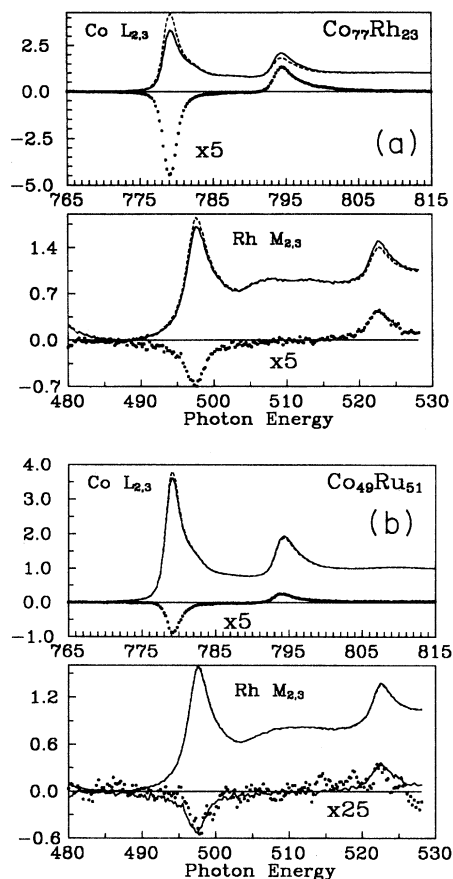


FIG. 2. Similar to Fig. 1, but for two Co-Rh alloys: $\text{Co}_{77}\text{Rh}_{23}$ and $\text{Co}_{49}\text{Rh}_{51}$.

this approximation is similar to (and probably better than) the “transferability” approximation mentioned in Ref. 14.

As seen in Fig. 1(b), the Rh $3p$ spectrum does indeed show dichroism, indicating a net Rh magnetic moment. To obtain a calibration of the Rh magnetic moment in XMCD, we must appeal to another technique. Neutron scattering⁴ on chemically ordered bulk alloys of this composition finds saturation moments of $2.75\mu_B$ and $1.0\mu_B$ for the Fe and Rh, respectively. Similar to the SQUID measurements of total magnetization, we find by XMCD an Fe moment which is reduced by about 25% relative to the chemically ordered bulk alloy. We shall assume that the Rh moment is also reduced by 25% in the present alloys, with a moment of $0.75\mu_B$ at saturation. Thus, we assume that the dichroism signal of Fig. 1(b) corresponds to a remanent Rh magnetic moment of $0.62\mu_B$.

Figure 2 shows the XMCD spectra from the $\text{Co}_{77}\text{Rh}_{23}$ and $\text{Co}_{49}\text{Rh}_{51}$ alloys. From these we may extract the Co and Rh remanent magnetic moments, leading to their respective saturation magnetic moments as tabulated in Table I. From these individual moments, the moment per alloy atom is calculated. In all the alloys, the moment per atom is in reasonably good agreement with that determined by SQUID magnetometry, providing a self-consistency check for our measurements. We estimate the error in the XMCD estimate of Fe or Co magnetic moments is $\approx 20\%$, while for Rh this error is $\approx 30\%$.

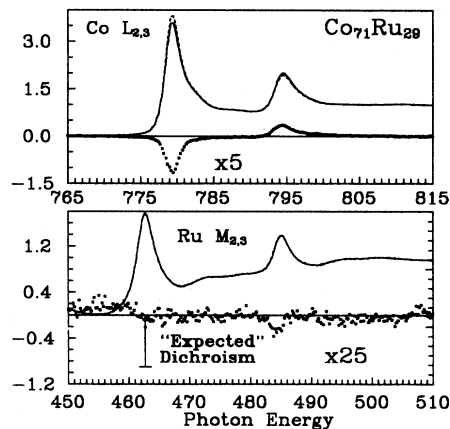


FIG. 3. Similar to Fig. 1, but for a $\text{Co}_{71}\text{Ru}_{29}$ alloy.

Note that the $\text{Co}_{49}\text{Rh}_{51}$ alloy has very low remanence and low overall magnetic moment. This is partly due to the fact the Curie temperature (T_C) of this alloy is close to room temperature.² Nevertheless, the dichroism signal is about three times the noise level, corresponding to a remanent magnetic moment of $\approx 0.04\mu_B$. As a guide to the eye, we have superimposed (solid line) a scaled version of the XMCD signal from the $\text{Co}_{77}\text{Rh}_{23}$ alloy, where the scaling factor is chosen such that both spectra give the same total magnetic moment.

It is of interest to compare the ratios of the magnetic moments of Fe and Co to the Rh magnetic moment in the various alloys. This is done in the last column of Table I. It is seen that this ratio varies around 3 for the Rh alloys.

This behavior is quite different from that observed in a $\text{Co}_{71}\text{Ru}_{29}$ alloy (see Fig. 3). Although the remanent Co moment is greater here than that in the $\text{Co}_{49}\text{Rh}_{51}$ alloy, no dichroism is observed in the Ru spectrum. Assuming that the calibration constant \mathcal{A}^{Rh} may be “transferred” to Ru,¹⁴ if Ru and Rh polarize similarly then the dichroism at the Ru $3p_{3/2}$ edge would be the size of the vertical bar drawn on the graph. From this we estimate that the remanent Ru magnetic moment in this alloy is at least three times smaller than the remanent Rh moment in the $\text{Co}_{49}\text{Rh}_{51}$ alloy. Hence, at saturation, $M_{\text{Ru}} < 0.03\mu_B$, and the Co to Ru moment ratio is > 14 (see Table I).¹⁵

We conclude therefore that Rh and Ru atoms polarize to much different degrees when placed in alloys with Co. This is in contrast to dilute Fe(Rh) and Fe(Ru) alloys, where the $4d$ atoms polarize to almost the same degree ($1.1\mu_B$ and $1.0\mu_B$, respectively).⁵ We speculate that this contrast is due to the change of the “host” ferromagnetic material from Fe to Co. It is well known (see, e.g., Ref. 16) that for transition element impurities in Fe, the impurity polarization varies with its d -band occupation number. Impurities with the same or higher occupation number than Fe generally polarize ferromagnetically with Fe. Impurities with occupation number less than that of Fe generally polarize antiferromagnetically with Fe, with the polarization passing through zero near the elements in the column to the left of Fe. The same trend seems to apply also to Co. In Co, Rh has the same d -band

occupation number, hence magnetizes ferromagnetically. Ru has occupation number one less than Co, hence showing little polarization.

It is also interesting to compare the present alloys with sputtered Co/Rh and Co/Ru multilayers. Both Co/Rh and Co/Ru multilayers exhibit oscillatory exchange coupling between adjacent Co layers. The first antiferromagnetic coupling peak in Co/Rh multilayers occurs at ≈ 3 ML Rh thickness.¹⁷ One expects that for such a multilayer, the Rh atoms in contact with the Co are polarized ferromagnetically with the Co, with the "middle" Rh atoms having only very small magnetic moments. This behavior is similar to what is observed in the Co-Rh alloys, where the Rh atoms are all in contact with Co atoms, and are polarized ferromagnetically.

In Co/Ru, however, the first antiferromagnetic coupling peak occurs near 1 ML Ru thickness. In this case, one might say that Ru atoms separating two Co layers prefer to have zero net magnetic moment, and arrange for this by aligning the adjacent Co layers antiferromagnetically. This is not unlike the $\text{Co}_{71}\text{Ru}_{29}$ alloy, where the Ru atoms polarize very little. Also, the magnetization and T_C of Co-Ru alloys are depressed compared with Co-Rh alloys. The disordered ar-

angement of atoms in the alloy does not permit simple antiferromagnetic alignment of Co atoms on either side of the Ru atoms. The system compensates by reducing the overall magnetization and T_C .

Based on these considerations, one might speculate on antiferromagnetic coupling in other ferromagnetic/nonmagnetic multilayer systems. For example, Tc impurities in Fe show very small induced magnetic moments. In analogy to Co/Ru then, Fe/Tc might be another case where antiferromagnetic coupling occurs between FTM layers separated by only 1 ML of 4d element.

In conclusion, we have observed XMCD at the Rh 3p edge in Fe-Rh and Co-Rh alloys. We find that the Rh atoms have a magnetic moment typically 1/3 as large as the moment of the ferromagnetic element. This is in contrast to a Co-Ru alloy, where the Ru atoms have magnetic moments less than 1/14 as large as the Co atoms.

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⁷See, e.g., G. Schütz, W. Wagner, W. Wilhelm, P. Keinle, R. Zeller, R. Frahm, and G. Materlik, *Phys. Rev. Lett.* **58**, 737 (1987); G. Schütz, M. Knülle, R. Weinke, W. Wilhelm, W. Wagner, P. Keinle, and R. Frahm, *Z. Phys. B* **73**, 67 (1988); G. Schütz, R. Weinke, W. Wilhelm, W. Wagner, P. Kienle, R. Zeller, and R. Frahm, *ibid.* **75**, 495 (1989).

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⁹Note that the samples are polycrystalline and have no in-plane anisotropy. Thus the in-plane direction along which the magnetic field is applied in the SQUID or XMCD measurements is unimportant.

¹⁰ $\text{Fe}_x\text{Rh}_{100-x}$ is a chemically ordered alloy with the CsCl crystal structure in the range $x=20-50$. The chemical ordering can be truly perfect only in the stoichiometric alloy ($x=50$), where in the bcc unit cell, Rh atoms occupy the body centers and Fe atoms the corner sites. For the Rh deficient alloys, perfect ordering is defined as the case where all Rh atoms occupy body center sites, and Fe atoms occupy all the corner sites as well as the remaining body center sites.

¹¹Note that for Rh, the data are unreliable above 528 eV due to the

presence of strong variations in the monochromator transmission at the position of the oxygen 1s edge (532 eV). The lack of data above the Rh edge introduces an additional error of $\approx 10\%$ in the measure of the Rh moment.

¹²Paolo Carra, B. T. Thole, Massimo Altarelli, and Xindong Wang, *Phys. Rev. Lett.* **70**, 694 (1993); B. T. Thole, Paolo Carra, F. Sette, and G. van der Laan, *ibid.* **68**, 1943 (1992).

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¹⁴It has been previously recognized that in the absence of a calibration standard, a "transfer" of calibration constants between near neighbors in the periodic table might be justifiable although such transfers introduce additional errors into the magnetic moment determination. This idea was introduced in an application to Cu [M. G. Samant, J. Stöhr, S. S. P. Parkin, G. A. Held, B. D. Hermsmeier, F. Herman, M. van Schilfgaarde, L. C. Duda, D. C. Mancini, N. Wassdahl, and R. Nakajima, *Phys. Rev. Lett.* **72**, 1112 (1994)], and has also been used to determine magnetic moments in V [G. R. Harp, S. S. P. Parkin, W. L. O'Brien, and B. P. Tonner, *Phys. Rev. B* **51**, 3293 (1995)].

¹⁵Like $\text{Co}_{49}\text{Rh}_{51}$, $\text{Co}_{71}\text{Ru}_{29}$ has a T_C near room temperature. Thus, a slight temperature elevation at the time of magnetization could reduce the remanent moment. Recall that just before magnetizing the alloys in vacuum, they were annealed to $\approx 300^\circ\text{C}$. It is possible that the slight differences between the SQUID and XMCD measurements of M_{sat} are partly due to incomplete cooling of the low- T_C samples. While incomplete cooling will affect the value of M_{sat} , it will not affect the ratios of the magnetic moments of constituent atoms in the alloys. Thus, our conclusion that, e.g., $M_{\text{Co}}/M_{\text{Ru}} > 14$ in the $\text{Co}_{71}\text{Ru}_{29}$ alloy is unchanged by such considerations.

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