

X-ray magnetic circular dichroism on Co monodispersive cluster assemblies

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2000 J. Phys.: Condens. Matter 12 3451

(<http://iopscience.iop.org/0953-8984/12/14/320>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.221

The article was downloaded on 16/05/2010 at 04:47

Please note that [terms and conditions apply](#).

X-ray magnetic circular dichroism on Co monodisperse cluster assemblies

H Sakurai[†], F Itoh[†], H Oike[†], T Tsurui[‡], S Yamamuro[§], K Sumiyama^{§||} and T Hihara[§]

[†] Department of Electronic Engineering, Gunma University, 1-5-1 Tenjin-cho, Kiryu, Gunma 376-8515, Japan

[‡] Satellite Venture Business Laboratory, Gunma University, 1-5-1 Tenjin-cho, Kiryu, Gunma 376-8515, Japan

[§] Core Research for Evolution Science and Technology (CREST) of Japan Science and Technology Corporation, Japan

^{||} Institute for Material Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

E-mail: sakuraih@el.gunma-u.ac.jp

Received 28 June 1999, in final form 29 December 1999

Abstract. X-ray absorption near edge structure (XANES) spectra and x-ray magnetic circular dichroism (XMCD) spectra at the Co K edge have been measured for Co clusters with the mean diameter $d = 6$ –13 nm. The spectral analysis indicates that the fcc phase is predominant for $d = 6$ nm, while the hcp phase gradually increases with increasing d in agreement with the results of transmission electron microscopy. The 4p orbital moments of clusters tend to decrease in the smaller cluster, but the reduction is small compared with the case of the multilayers, suggesting the importance of surface effects of the Co cluster system.

1. Introduction

Nanometre-scale geometrical and chemical controls can lead to fascinating new phenomena related to phase stability, the observation of macroscopic quantum phenomena and technical application such as information storage [1, 2].

From the viewpoint of applied magnetics, it is essential to stabilize the hcp phase and tailor nanoscale domains. The hcp Co phase has a smaller critical size, d_c , of the transition from the ferromagnetic state to the superparamagnetic state at room temperature compared with the critical size of fcc Co ($d_c = 10$ nm for the hcp phase and $d_c = 17$ nm for the fcc phase). It is well known that small Co particles always crystallize in the high-temperature fcc phase that is only stable above 693 K in bulk form. However, there have been only a few studies on the qualitative relationship between the Co cluster size and the crystal phase [2–4].

Furthermore, the orbital magnetic moment of the cluster is of great importance for induced magnetic anisotropy with an easy magnetization direction perpendicular to the substrate. It has been demonstrated that the orbital moments $\langle L_z \rangle$ of Co clusters is directly linked to hybridization and localization of 3d electrons [5]. For nanoscale clusters, this can lead to interesting features.

Photo- and electro-lithography techniques permit the fabrication of submicrometre-scale magnetic dots, wires and their arrays. The smallest size of fabricatable region is about 20 nm

[6, 7]. However, we have succeeded in production of monodispersed transition metal clusters whose sizes are controllable between 6 and 13 nm in diameter with standard deviation less than 10% of the mean size using newly constructed plasma-gas-condensation type (PGC) cluster deposition equipment [8, 9]. Thus it is desired to discuss the electronic structure of Co clusters closely related to the phase transition and the 3d magnetic moments.

In this report, we describe the experimental results of x-ray absorption near edge structure (XANES) spectra and x-ray magnetic circular dichroism (XMCD) spectra at the Co K edge for monodisperse Co cluster assemblies with mean diameter $d = 6\text{--}13$ nm. Then the size effects on the phase transition and electronic structure are discussed.

2. Experiment

Co clusters were deposited on polyimide substrate at room temperature using the PGC apparatus. The mean diameter, d , was controlled to 6, 8 and 13 nm by varying the Ar gas flow rate and the mixing ratio of Ar to He gas. The total thickness of each sample was adjusted to be about 1000 nm. The samples were coated by 50 nm Au film to avoid oxidization. A Co foil with 1000 nm thickness was prepared as a reference sample. The in plane magnetization curves were measured using a SQUID magnetometer (Quantum Design MPMS-5S) for the Co clusters and VSM (Riken Denshi BHV-50) for the Co foil. The magnetization of the samples was fully saturated below the magnetic field of 0.6 T at room temperature [10, 11]. X-ray diffraction showed hcp structure for the Co foil. However, the Co clusters did not have clear diffraction peaks due to the finite size effects of the diffraction.

The XANES and XMCD experiments were carried out for the Co together with the Co foil and CoO as the reference clusters on the beam line BL-28B at the Photon Factory, Institute of Materials Structure Science (KEK-PF), Japan. The XMCD and XANES spectra were measured using the circularly polarized x-rays emitted from the elliptical multipole wiggler. The measurements were made in a transmission mode under the applied magnetic field of 0.6 T parallel to the sample plane tilted by 45° away from the direction of the incident beam. The synchrotron light helicity was fixed, and the magnetization direction was reversed by an electro-magnet. The XANES and XMCD spectra were defined as follows

$$\mu_{XANES} = (\mu\uparrow + \mu\downarrow)/2 \quad (1)$$

$$\mu_{XMCD} = (\mu\uparrow - \mu\downarrow)/(P_c \cos 45^\circ). \quad (2)$$

Here $\mu\uparrow$ ($\mu\downarrow$) denotes the absorption coefficient with magnetization parallel (anti-parallel) to the direction of 45° . The value of P_c was evaluated on the basis of the dynamical diffraction theory at a monochromator using a calculated value of circular polarization of the incident x-rays emitted from an elliptical multipole wiggler [12]. The calculated value of P_c was about 0.90 over the measuring range. The edge jumps of the XANES spectra were normalized to unity. The XMCD spectra were also normalized according to the XANES spectra and Co metal fraction as discussed later.

3. Results and discussion

Figure 1 shows XANES spectra at the Co K edge on the Co cluster assemblies with three diameters together with the reference samples. When comparing the edge positions and structure of Co clusters with those of the Co foil, CoO and Co₃O₄ [13] in figure 1, a hump around 7.710 keV decreases and a peak around 7.725 keV appears with decreasing cluster diameter. These features can be ascribed to the existence of CoO. However, the pre-edge peak around 7.708 keV and the main peak around 7.728 keV, which are characteristic structures of

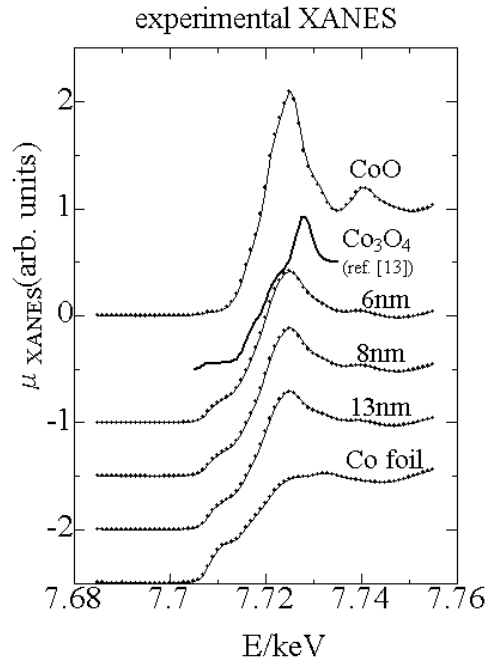


Figure 1. XANES spectra on Co clusters at the Co K edge (μ_{XANES}). XANES spectra of CoO (present experiment) and Co₃O₄ [13] are shown as reference spectra. The spectra are normalized to edge jump unity.

the XANES spectrum of Co₃O₄, cannot be observed in that of any Co cluster assemblies. This excludes the existence of Co₃O₄. This results are supported by the report that oxide-coated Co clusters fabricated by the PGC method have Co core and CoO shell structure and the oxide shell of the clusters is composed of the single CoO phase with no sign of the Co₃O₄ phase [14].

Since the Co clusters contain a Co metal phase and a CoO phase from figure 1, the XANES spectra of the Co cluster assemblies, μ_{XANES} , were decomposed into Co metal contribution and CoO contribution by the least squares fitting using the following equation

$$\mu_{XANES} = a\mu_{metal} + b\mu_{CoO}. \quad (3)$$

Here, μ_{CoO} and μ_{metal} denote the XANES spectrum of the CoO phase and the Co metal phase, respectively. We assume the XANES spectrum of the CoO phase is the same as that of bulk CoO shown in figure 1. This assumption is supported by Auger electron spectroscopy and photo-emission spectroscopy by Clemens *et al* [15], where they show that a photo-emission spectrum of surface CoO, which has the thickness of the probing depth (~ 1 nm), has the same binding energy and a very similar overall shape compared with that of bulk CoO phase. Furthermore, we assume that the XANES spectrum of the Co foil shown in figure 1 (hcp phase) can be used as the XANES of the Co metal phase, μ_{metal} . These two assumptions of μ_{metal} and μ_{CoO} allow us to estimate fractions of Co metal, a , and those of CoO, b , which are shown in table 1. The choice of fcc-phase Co (rapid quenched sample [16] or Pd(0.8 nm)/Co(0.4 nm) multilayer [17, 18]) instead of hcp-phase Co was found to make little change in the fitting results. From the consideration of the CoO oxide growth mechanism in the present cluster fabrication, it would be natural to assume the CoO layer coats the surface of Co metals in the present Co clusters. These results are summarized in table 1. The thickness of assumed

Table 1. CoO fraction and Co metal fraction obtained by least squares fitting using the XANES spectra in figure 1. Surface oxide layer thickness is estimated from CoO fraction assuming a Co metal core and CoO shell model [11, 14].

Cluster diameter (nm) (radius (nm))	Co metal fraction (%) <i>a</i>	CoO fraction (%) <i>b</i>	Co metal radius (nm)	Oxide thickness (nm)
6 (3)	57.6	42.4	2.50	0.50
8 (4)	61.1	38.9	3.40	0.60
13 (6.5)	69.9	30.1	5.77	0.73

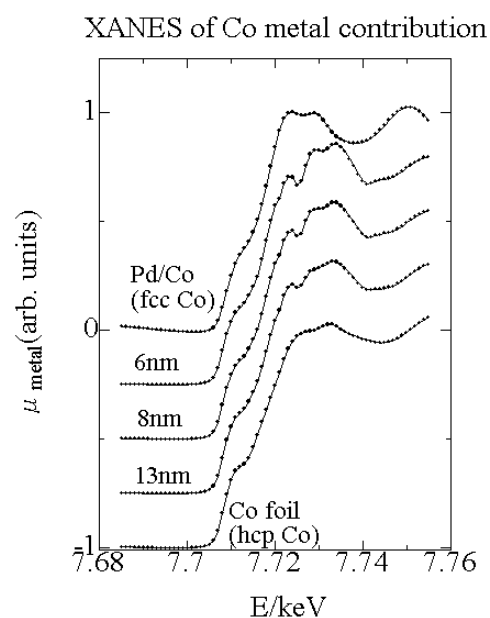


Figure 2. Separated XANES spectra of Co metal contribution by least squares fitting (see text).

surface CoO layers is found to be a constant value of about 0.6 nm irrespective of the cluster diameter. This result is consistent with TEM observations, which suggest the thickness of the surface oxide layer is less than 1–2 nm [11].

Since Yamamuro *et al* have also observed an fcc phase, an hcp phase and a CoO phase in the clusters from the electron diffraction patterns [11, 19], we re-define the Co metal contribution using the following equation:

$$a\mu_{metal} = \mu_{XANES} - b\mu_{CoO}. \quad (4)$$

Figure 2 shows the XANES spectra of the Co metal contribution, μ_{metal} , derived from equation (4). The μ_{metal} in figure 2 are normalized to give the edge jump of unity. For comparison, the XANES spectrum of the Pd(0.8 nm)/Co(0.4 nm) multilayer is shown as an fcc Co spectrum. The shapes of the XANES spectra in figure 2 slightly show cluster diameter dependence, which will come from a ratio of hcp phase to fcc phase.

The cluster size dependence of XANES spectra can be more emphasized by the first derivative spectra $d\mu_{metal}/dE$ as shown in figure 3. Concerning the peak around 7.718 keV in figure 3, the peak width (FWHM) decreases and the peak height increases with decrease in the cluster diameter. The parameters (peak width and peak height around 7.718 keV) of the smallest

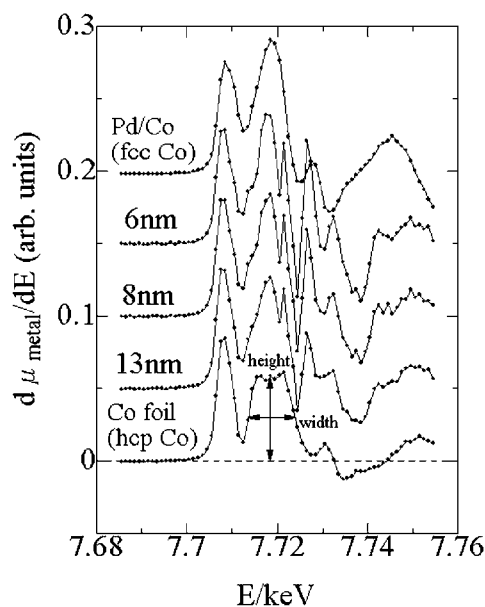


Figure 3. The first derivative spectra of figure 2. The fine structures around 7.718 keV are sensitive to the ratio of fcc phase to hcp phase. The fcc phase becomes dominant with decreasing cluster diameter.

cluster of 6 nm is almost the same as those of the fcc phase. These facts show that the μ_{metal} consists of the hcp phase and fcc phase of Co. The electron diffraction measurements [19] of these Co-cluster assemblies indicate that almost only fcc rings are observed for $d = 6$ nm. On the other hand, the hcp rings slightly appear for $d = 8$ nm and the hcp rings become more marked for $d = 13$ nm, even though the fcc rings are still predominant. Moreover, high-resolution TEM observation [11] has also shown the co-existence of fcc phase and hcp phase in the cluster assembly with $d = 8$ nm. These results indicate that the Co cluster assemblies with $d = 8$ –13 nm have fcc and hcp mixed structures in consistency with the present conjecture from figure 3.

The volume ratio of hcp phase to the fcc phase was quantitatively estimated from the peak heights and width in figure 3, and the results are shown in figure 4(a). The fcc fraction becomes predominant with decreasing cluster size and the fcc phase exists in the cluster with the diameter of 6 nm. These results are consistent with the x-ray diffraction experiment done by Kitakami *et al* [2] shown in figure 4(b).

Figure 5 shows the XMCD spectra of the cluster assemblies, μ_{XMCD} . These spectra are re-normalized by the Co metal fraction, a , in table 1. Figure 6 shows the first derivative of the XMCD spectra with respect to the energy, $d\mu_{XMCD}/dE$. The derivative spectrum of the hcp phase has a single peak with a shoulder at the energy of 7.710 keV, while that of the fcc phase (Pd(0.8 nm)/Co(0.4 nm)) has double peaks around 7.708 keV. The change from single peak with a shoulder to the double peaks is clearly observed with decreasing cluster diameter. The characteristic change of the XMCD spectra in this region corresponds to the phase transition from the hcp to fcc as discussed in the XANES spectra.

The XMCD spectrum on the Co K edge gives orbital moments of 4p electrons, which are induced by 3d spin-orbit interactions on the neighbouring sites through the 4p–3d hybridization [20–22]. Igarashi and Hirai have extended a sum rule for the XMCD on the K edge [20, 21],

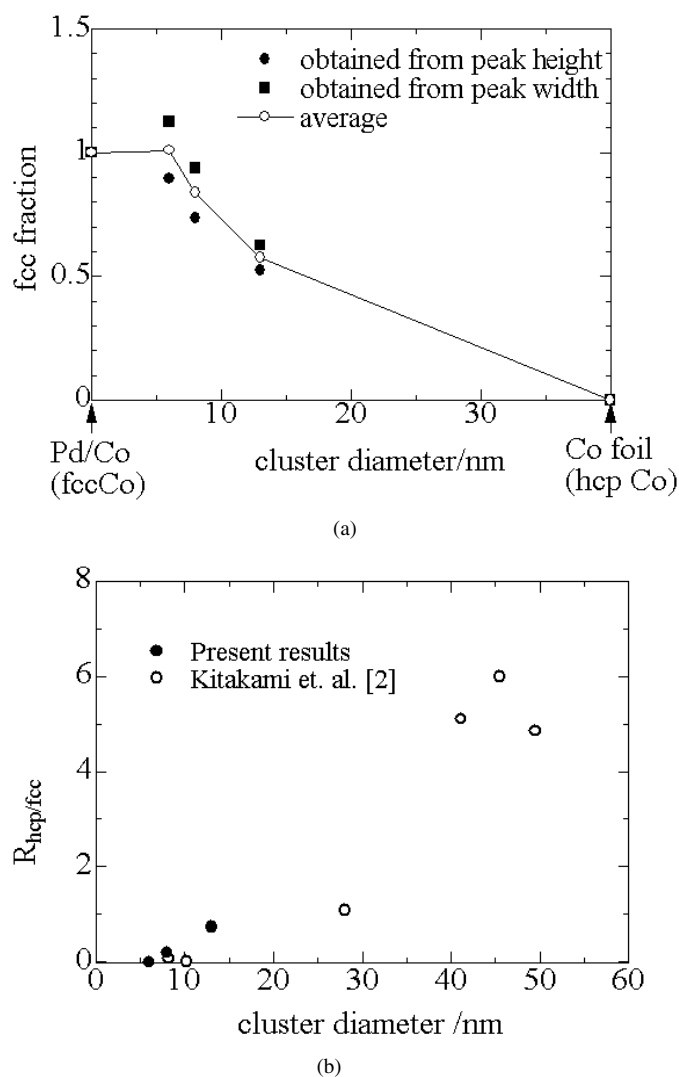


Figure 4. (a) Estimated fcc fraction obtained from an analysis of the fine structures in figure 3. The fcc phase is dominant in the smaller cluster diameter. (b) Fractional ratio, $R_{hcp/fcc} = (1 - R_{fcc})/R_{fcc}$. Fcc fraction, R_{fcc} , is obtained in figure 4(a).

which can be applicable even to a single absorption edge (corresponding to the case of $c = 0$ and $l = 1$ in the equation by Thole *et al* [23]), to give the orbital moments of p-symmetric states from the following equation:

$$B/\sigma_{4p} = 1.5\langle L_z \rangle/n_{4p} \quad (5)$$

where B is the integral over the dichroism at the K edge above Fermi energy; σ_{4p} is the integral over the absorption spectrum for $1s \rightarrow 4p$ transitions using unpolarized light. $\langle L_z \rangle$ denotes the orbital angular momenta of 4p states per atom along the spin axis, and n_{4p} is the hole number projected to 4p states per atom. The integration range of B and σ_{4p} is from ω_0 to ω_c , where ω_0 is the Fermi energy corresponding to the absorption edge and ω_c is the cut-off energy being roughly $\omega_0 + 12$ eV for Co. In the present experiment, the integration range was chosen

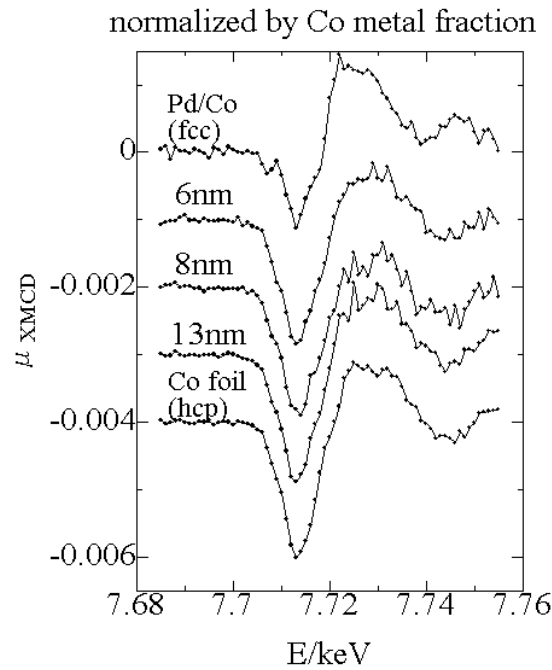


Figure 5. XMCD spectra normalized by the Co metal fraction obtained in table 1.

to cover an integrated intensity of a negative peak in an XMCD spectrum for two reasons. Firstly, the negative peak amplitude of XMCD spectra at the Co K edge has been reported to reflect the 4p polarization in the Co/Cu [24] and Fe/Co [25] multilayer system. Secondly, it has been theoretically pointed out that higher p-symmetric states other than 4p states dominate the spectra above $\omega_0 + 12$ eV [20]. Furthermore, the ratio n_{4p}/σ_{4p} in equation (6) can be regarded to be the same as the calculated value of pure Co [20] for the following reason. The σ_{4p} and n_{4p} are linked by Fermi's golden rule according to the relation $\sigma_{4p} = |M_{sp}|^2 n_{4p}$, where M_{sp} is the radial dipole transition matrix element, and the M_{sp} of Co can be regarded as being the same in the cluster and the Co foil. The similar analysis has been applied to the XMCD spectra at the Co $L_{2,3}$ edges [26]. The obtained $\langle L_z \rangle$ is shown as a function of cluster size in figure 7. The 4p orbital moments of clusters are seen to decrease in the smaller clusters.

Enhanced magnetic moment has been so far reported on Co clusters with small size experimentally [27–29] and theoretically [30–32]. Calculations on Co clusters have predicted 40% enhanced 3d magnetic moments and 70% reduced 4p magnetic moments at the surface [32]. This comes from the localization of 3d electrons in the peripheral atom sites with lower coordination number compared to the centre atom sites. This type of localization of 3d electrons could decrease the 4p–3d hybridization at the surface, resulting in reduced 4p orbital moments and enhanced 3d orbital moments [1, 31]. Concerning orbital moments, enhanced 3d orbital moments (20–100%) and reduced 4p orbital moments (30–70%) have been reported in multilayer systems such as Pd/Co [18, 33], Pt/Co [16, 34] and Cu/Co [24, 26]. The enhanced 3d orbital moments have been also reported in Co clusters embedded in copper [35] and Fe cluster assemblies [36]. From these considerations, 4p orbital moments are expected to reduce more and more in the smaller clusters, but the reduction of 4p

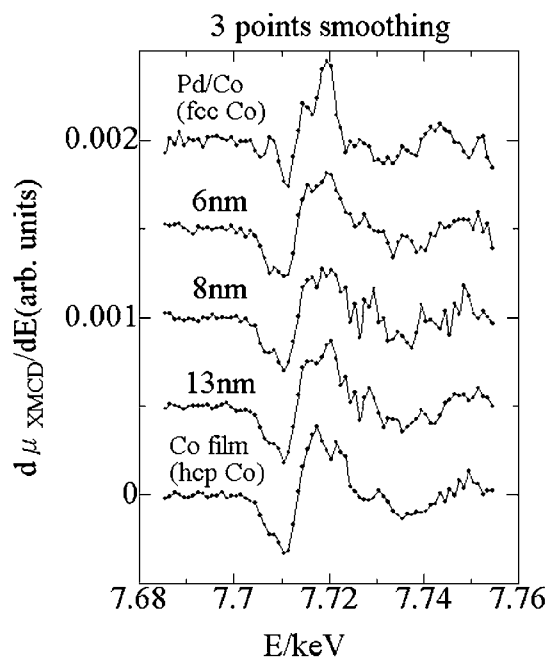


Figure 6. The first derivative spectra of figure 5. Fine structures around 7.708 keV are sensitive to the ratio of fcc phase to hcp phase, as discussed in the XANES spectra in figure 3.

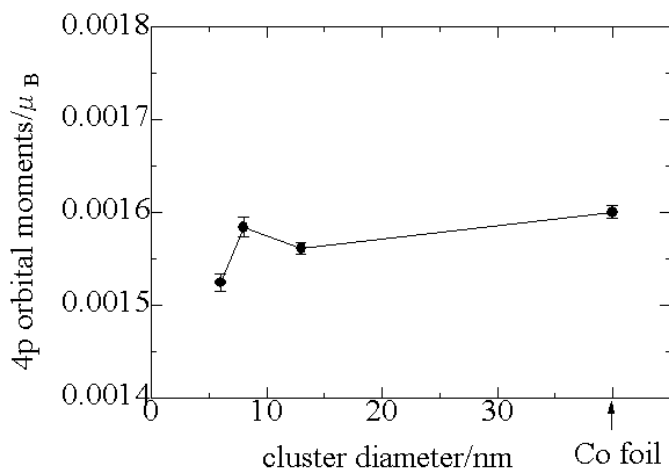


Figure 7. Estimated 4p orbital moments using a sum rule [20, 21].

orbital moments on the present clusters is small (within 6%) compared with the case of multilayers.

A possible explanation can be made from considering effects of the surface oxide layer. It has been reported theoretically [37] that surface enhanced spin moments can be suppressed by surface adsorbed oxygen in the Co cluster system. Then the surface CoO layer could suppress the enhancement of 3d magnetic moment and reduction of 4p orbital moment at the Co/CoO interface.

4. Conclusion

Co cluster assemblies with diameters 6, 8 and 13 nm have been prepared by the PGC method and studied via XANES and XMCD at the Co K edge. It is found that the cluster surface is oxidized with a thickness of about 0.6 nm. The fcc phase is predominant for a mean diameter of 6 nm, while hcp phase gradually increases with increasing diameter consistent with results of TEM and x-ray diffraction experiments. The 4p orbital moment of clusters is seen to decrease in the smaller clusters, but the reduction is small compared with the case of a multilayer system. These results suggest the importance of surface effects of the Co cluster system.

Acknowledgments

We thank Dr M Sakurai, Dr T J Konno (Institute for Material Research, Tohoku University) and Dr D L Peng (Evolutional Science and Technology (CREST) of Japan Science and Technology (JST) Corporation) for useful discussion. We also thank the Centre for Co-operative Research in Gunma University for the support of VSM measurements. This work was performed under the approval of the KEK-PF Program Advisory Committee (proposal No 98G025), and was supported by Core Research for Evolutional Science and Technology (CREST) of the Japan Science and Technology (JST) Corporation.

References

- [1] Durr H A, Dhese S S, Dudzik E, Knabben D, Van der Laan G, Goedkoop J B and Hillebrecht E U 1999 *Phys. Rev. B* **59** R701
- [2] Kitakami O, Sato H and Shimada Y 1997 *Phys. Rev. B* **56** 13 849
- [3] Suto H, Kitakami O, Sakurai T and Shimada Y 1997 *J. Appl. Phys.* **81** 1858
- [4] Takeno Y, Shimada Y, Takano H, Awano H and Sugita Y 1996 *Japan. J. Appl. Phys.* **35** 1724
- [5] Tischer M, Hjortstam O, Arvanitis D, Hunter Dunn J, May F, Baberschke K, Trygg J, Wills J M, Johansson B and Eriksson O 1995 *Phys. Rev. Lett.* **75** 1602
- [6] Chou S Y, Krauss P R and Kong L 1996 *J. Appl. Phys.* **79** 6101
- [7] Ye P D, Weiss D, Gerhardt R R and Nickel H 1997 *J. Appl. Phys.* **81** 5444
- [8] Yamamuro S, Sumiyama K, Hihara T and Suzuki K 1999 *J. Phys. Soc. Japan* **68** 28
- [9] Yamamuro S, Sumiyama K and Suzuki K 1999 *J. Appl. Phys.* **85** 483
- [10] Yamamuro S, Sumiyama K, Kamiyama T and Suzuki K 1999 *J. Appl. Phys.* **86** 5726
- [11] Yamamuro S, Sumiyama K, Konno T J and Suzuki K *Mater. Trans. JIM* submitted
- [12] Iwazumi T, Koyama A and Sakurai Y 1995 *Rev. Sci. Instrum.* **66** 1691
Kitamura H 1993 *Synchrotron Radiation Program for PC-98 SPECTRA* version 2.1
- [13] Bridges F, Boyce J B, Claeson T, Geballe T H and Tarascon J M 1989 *Phys. Rev. B* **39** 11 603
- [14] Peng D L, Sumiyama K, Konno T J, Hihara T and Yamamuro S 1999 *Phys. Rev. B* **60** 2093
- [15] Clemens W, Vescovo E, Kachel T, Carbone C and Eberhardt W 1992 *Phys. Rev. B* **46** 4198
- [16] Stahler S, Shutz G and Ebert H 1993 *Phys. Rev. B* **47** 818
- [17] Umeda K, Fujiwara Y, Matsumoto T, Nakagawa K and Itoh A 1996 *J. Magn. Magn. Mater.* **156** 75
- [18] Sakurai H, Itoh F, Okabe Y, Oike H and Hashimoto H 1999 *J. Magn. Magn. Mater.* **198–199** 662
- [19] Yamamuro S, Sumiyama K, Hihara T and Suzuki K 1999 *J. Phys.: Condens. Matter* **11** 3247
- [20] Igarashi J and Hirai K 1996 *Phys. Rev. B* **53** 6442
- [21] Igarashi J and Hirai K 1994 *Phys. Rev. B* **50** 17 820
- [22] Guo G Y 1996 *J. Phys.: Condens. Matter* **8** L747
- [23] Thole B T, Carra P, Sette F and van der Laan G 1992 *Phys. Rev. Lett.* **68** 1943
- [24] Pizzini S, Fontain A, Giorgetti C, Dartyge E, Bobo J F, Piecuch M and Baudalet F 1995 *Phys. Rev. Lett.* **74** 1470
- [25] Pizzini S, Fontain A, Dartyge E, Giorgetti C, Baudalet F, Kappler J P, Bohr P and Giron F 1994 *Phys. Rev. B* **50** 3779
- [26] Samant M G, Stohr J, Parkin S S P, Held G A, Hermsmeier B D, Herman F, van Schilfgarde M, Duda L-C, Mancini D C, Wassdahl N and Nakajima R 1994 *Phys. Rev. Lett.* **72** 1112
- [27] Bucher J P, Douglass D C and Bloomfield L A 1991 *Phys. Rev. Lett.* **66** 3052

- [28] Billas I M L, Chatelain A and de Heer W A 1996 *Surf. Rev. Lett.* **3** 429
- [29] Respaud M *et al* 1998 *Phys. Rev. B* **57** 2925
- [30] Li Z Q and Gu B L 1993 *Phys. Rev. B* **47** 13 611
- [31] Izquierdo J, Vega A and Bulbas C 1997 *Phys. Rev. B* **55** 445
- [32] Chuanyun X, Jinlong Y, Kaiming D and Kelin W 1997 *Phys. Rev. B* **55** 3677
- [33] Wu Y, Shohr J, Hermsmeir B D, Samant M G and Weller D 1992 *Phys. Rev. Lett.* **69** 2307
Weller D, Wu Y, Shohr J, Samant M G, Hermsmeir B D and Chappert C 1994 *Phys. Rev. B* **49** 12 888
- [34] Nakajima N, Koide T, Shidara T, Miyauchi H, Fukutani H, Fujimori A, Iio K, Katayama T, Nyvlt M and Suzuki Y 1998 *Phys. Rev. Lett.* **81** 5229
- [35] Eastham D A, Qiang Y, Maddock T H, Kraft J, Schille J-P, Thompson G S and Harberland H 1997 *J. Phys.: Condens. Matter* **9** L497
- [36] Edmonds K W, Binns C, Baker S H, Thornton S C and Norris C 1999 *Phys. Rev. B* **60** 472
- [37] Pick S and Dreyse H 1999 *Phys. Rev. B* **59** 4195