Electronic and Magnetic Properties of Mn_3O_4/Fe_3O_4 Superlattices

C. L. Chen[1], G. Chern[2], H. J. Lin[3] and C. L. Chang[1*]

[1] Department of physics, Tamkang University, Tamsui, Taiwan
[2] Department of physics, National Chung-Cheng University, Chiayi, Taiwan
[3] National Synchrotron Radiation Research Center, Hsinchu, Taiwan

Abstract

Antiparallel interlayer magnetic coupling between layers of Fe_3O_4 and Mn_3O_4 , both ferromagnetic, was reported in a recent study. The interlayer magnetic coupling may be affected by the magnetic property at the interface. In order to understand the interplay between the electronic configuration, the atomic structure and the magnetic property at the interface, we have performed transition metal $L_{2,3}$-edges x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) measurements on a series of samples. Ferrimagnetic/ferrimagnetic Mn_3O_4/Fe_3O_4 superlattices of different thickness were studied. A piece of bulk $MnFe_2O_4$ was studied for comparison. Our results indicate the interface can be viewed as a layer of $MnFe_2O_4$ compound, which affects magnetic property of the Fe_3O_4/Mn_3O_4 superlattices.

Introduction

Transition metal oxide Fe_3O_4 (magnetite) and Mn_3O_4 have been investigated for decades due to their rich electromagnetic properties and application potential [1]. Both of these oxide materials are ferromagnetic with spinel structure. T_c of Fe_3O_4 and Mn_3O_4 are 863 and 43K, respectively. The antiparallel interlayer magnetic coupling between ferrimagnetic-ferrimagnetic Fe_3O_4/Mn_3O_4 superlattice was reported in a recent paper [2]. The interlayer magnetic coupling may be affected by the magnetic property at the interface, as reported by Ohldag *et al.* [3] in the study of Co deposited on NiO. They observed an ultra thin layer of CoNiO*x* formed at the interface, which affects the interlayer magnetic coupling between ferromagnetic Co and antiferromagnetic NiO. In order to look into the effect of interface on the magnetic coupling in Fe_3O_4/Mn_3O_4 system it is important to investigate the electronic and magnetic properties at the interface in details.

We have performed XAS and XMCD studies of a series of Fe_3O_4/Mn_3O_4 superlattice samples at room temperature. XMCD provides element specific local magnetic moment information, which enables quantitative determination of spin and orbital magnetic moments [4]. In addition to the superlattice, we have also studied the standard thin film samples of Fe_3O_4, Mn_3O_4 and a piece of bulk sample of

ferrimagnetic $MnFe_2O_4$ (manganese ferrite, T_c~570K) as reference. The XMCD result of Fe_3O_4 film (not shown) is consistent with reported data [5]. The XMCD signal in Mn_3O_4 was not observed due to its low T_c. In this paper we report the results based on qualitative analysis of the XMCD measurements.

Experimental

All the superlattice samples in this study were synthesized on MgO (011) substrates by oxygen plasma-assisted MBE the procedure is similar to the previous growth of oxide thin films and superlattices [6]. The thickness of each superlattice is fixed at ~2000Å, including samples of Fe_3O_4 (17Å)/Mn_3O_4 (17Å) with 60 by-layer repeats, (34Å/34Å) with 30 by-layer repeats and (68Å/68Å) with 15 by-layer repeats. Reflection High Energy Electron Diffraction (RHEED) and X-ray diffraction (XRD) were used as *in-stiu* and *ex-situ* characterizations, respectively, to ascertain the crystalline quality of the samples. The reference sample $MnFe_2O_4$ was produced by standard solid state reaction method using Fe_2O_3 and MnO powders as starting materials. The quality of the sample was also confirmed by XRD.

XMCD measurements were performed at the beamline 11-A1 (Dragon beamline) [7] of NSRRC. Total-electron-yield (TEY) mode was used for data collections. The energy resolution was around 0.2 eV for Fe *L*-edge region. Magnetic field along the sample surface of about 1 Tesla was provided by an electromagnet. The electromagnetic current switches between +50A and -50A to produce parallel and anti-parallel magnetic fields for each fixed energy to obtain the μ^+ and μ^- absorption spectra. A negative bias voltage of up to 500V was applied on the samples in order to get reasonable signal strength in TEY mode. The pressure in the chamber of the end station was kept in ultra-high vacuum condition ($<5x10^{-10}$ torr).

Results and discussion

Fig. 1 plots Fe and Mn $L_{2,3}$-edge XAS spectra for the 68Å/68Å sample. The solid line (μ^+) and the circle (μ^-) line are the absorption intensities taken with the projection of the photon spin parallel and antiparallel to the sample magnetization direction, respectively. XMCD, the difference μ^+-μ^-, is plotted below the XAS. The spectrum at Fe L_3-edge has a two-peak structure which is different from the reported XMCD for inverse spinel Fe_3O_4, which composed of two negative peaks and one positive peak [5]. According ref. 4, the negative peaks are contributed from B-site Fe^{2+} and Fe^{3+}, and the positive peak is contributed from A-site Fe^{3+}. [5]. The missing positive feature between the two negative peaks in our superlattice may indicate a modification of the magnetic property in the Fe_3O_4 layer. In other word, the contribution from A-site Fe^{3+}

is not observed in our 68Å/68Å superlattice. The XMCD spectrum at Mn L_3-edge shows prominent positive and negative features indicating the existence of magnetic enisotropy in the Mn_3O_4 layer at room temperature. The shapes of the Fe and Mn XMCD spectra in Fig. 1 show some similarities to that of normal spinel $Mn_{2/3}Zn_{1/3}Fe_2O_4$ ferrite, as reported by Suga *et al.* [8]. The positive and the negative peaks are contributed from 2+ ions in the A-site and the 3+ ions in the B-site, repectively. We have also studied a related ferrite compound, normal spinel $MnFe_2O_4$ for comparison. Fig. 2 plots Fe and Mn $L_{2,3}$-edge XAS and XMCD spectra for the bulk $MnFe_2O_4$ sample, the results are consistent with the reported data [9]. The Fe $L_{2,3}$-edge XAS spectrum in Fig. 2 is very similar to that of the 68Å/68Å superlattic shown in Fig. 1. The XMCD spectrum is also similar to the 68Å/68Å superlattice. On the other hand, comparing the Mn spectra of $MnFe_2O_4$ with that of, it is obvious that XAS are different. The XAS spectral shape of 68Å/68Å superlattice is very similar to that of the Mn_3O_4. However, the XMCD spectra are similar except that the intensity in $MnFe_2O_4$ is much stronger.

Since our measurements were taken in TEY mode, the probing depth depends on the electron mean free path in the materials. The typical probing depth of soft x-ray absorption measurements for most metal oxide at normal incidence is less than 100Å [10]. Our measurements were performed at an incident angle of about 60^o with the sample surface; hence the probing depth is less than 86Å. Considering the top layers of our superlattices are Mn_3O_4, for 68Å/68Å superlattice the Mn spectrum in Fig. 1-(a) characterizes Mn_3O_4 film with little interface effect. On the other hand, The Fe spectrum in Fig. 1-(b) is predominantly interface characterization. The effect of probing depth can be verified by the study of a series of samples, each contains a 40Å Fe_3O_4 films covered with a Mn_3O_4 film of different thickness as shown in Fig. 3. The spectral shape of the Fe L_3-edge XMCD evolves from the Fe_3O_4-like three-peak structure into the interface-affected two-peak structure as the thickness of the Mn_3O_4 increases from 10 to 80Å. The fact that the Fe L_3-edge XMCD of 68Å/68Å superlattice and that of the Mn_3O_4(80Å)/ Fe_3O_4(40Å) both have very similar spectral shape, which is basically the same of the XMCD spectrum of manganes ferrite $MnFe_2O_4$ sample leads us to assume that the interface can be viewed as a layer of $MnFe_2O_4$. This assumption was confirmed by comparing the XAS spectra of a series of $Fe_{3-x}Mn_xO_4$ (x varied from 0 to 3, with an increment of 0.3) thin films, which shows that the spectrum of the thinnest superlattice has the most similarity to that of the film with x value of 1 [11].

Fig. 4 plots Fe and Mn $L_{2,3}$-edge XAS and XMCD spectra for the 17Å/17Å superlattice. For the Fe spectra, XAS is almost identical to that of $MnFe_2O_4$. But Fe

L_3-edge XMCD of 17Å/17Å superlattice shows a small positive intersity between the two negative peaks, indicating some moment contribution from Fe^{3+} at A-site. This observation also indicates that 17Å/17Å superlattice is more Fe_3O_4-like comparing with 68Å/68Å superlattice, which is reasonable due to the more Fe_3O_4 volume in 17Å/17Å superlattice within the probed depth. From Mn spectra, the XAS spectral shape is much more similar to that of $MnFe_2O_4$ and is quite different from that of Mn_3O_4. This is due to the fact that there is less Mn_3O_4 volume and more interfaces within the probed depth in the 17Å/17Å superlattice. Mn L_3-edge XMCD of 17Å/17Å superlattice has similar shape to the other two samples, but the intersity is higher than that of the 68Å/68Å superlattice. This is due to the fact that the Mn moment is stemmed from $MnFe_2O_4$ at the interface, and there are more interfaces in the thinner superlattice. The strength of the Mn L_3-edge XMCD of 34Å/34Å superlattice (not shown) falls between that of the 17Å/17Å and the 68Å/68Å superlattices.

Conclusion

By comparing the spectral shapes of XAS and XMCD of a series of samples, we have demonstrated the existence of a $MnFe_2O_4$ layer at the interface of the Fe_3O_4/Mn_3O_4 superlattices. The XMCD signal strength of Mn increases as the layer thickness decreases implies that these interfacial layers may have enhanced the magnetic moments in the Mn_3O_4 layers. Since Mn_3O_4 has a much lower T_c, a more detailed temperature-dependent XMCD study (currently under way) is necessary to elucidate the effect of the interface magnetic property on the Mn_3O_4 layers.

Acknowledgement

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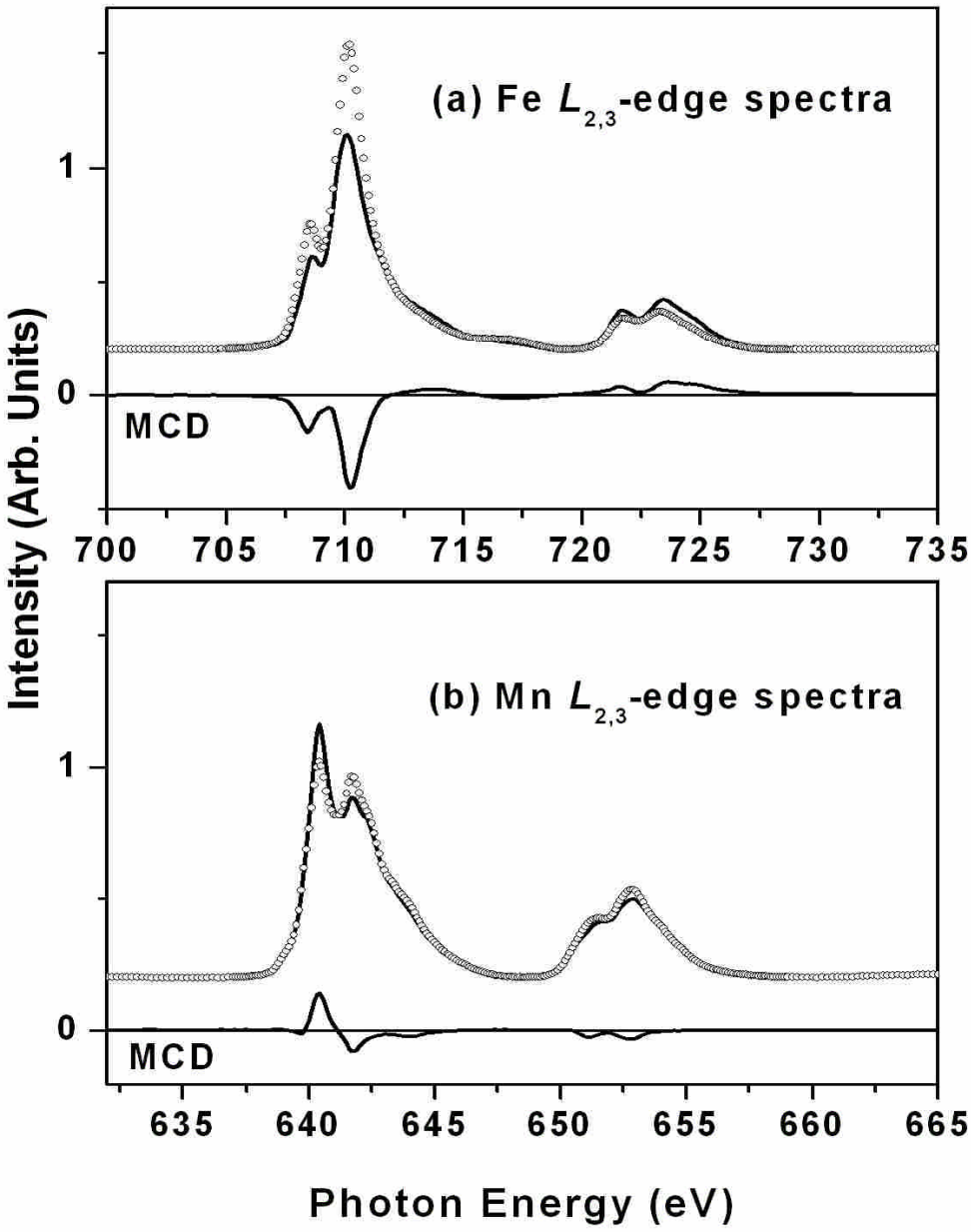
Figure captions:

Fig. 1. Fe (a) and Mn (b) $L_{2,3}$-edge XAS spectra for the 68Å/68Å superlattice. The solid line (μ^+) and the dotted (μ^-) line are the absorption intensities taken with the projection of the photon spin parallel and antiparallel to the sample magnetization direction, respectively. XMCD, the difference μ^+-μ^-, is plotted below the XAS curves.

Fig. 2. Fe (a) and Mn (b) $L_{2,3}$-edge XAS spectra for bulk sample of $MnFe_2O_4$. The solid line (μ^+) and the dotted (μ^-) line are the absorption intensities taken with the projection of the photon spin parallel and antiparallel to the sample magnetization direction, respectively. XMCD, the difference μ^+-μ^-, is plotted below the XAS curves.

Fig. 3. Fe (a) and Mn (b) $L_{2,3}$-edge XAS spectra for the 17Å/17Å superlattice. The solid line (μ^+) and the dotted (μ^-) line are the absorption intensities taken with the projection of the photon spin parallel and antiparallel to the sample magnetization direction, respectively. XMCD, the difference μ^+-μ^-, is plotted below the XAS curves.

Fig. 4. Fe $L_{2,3}$-edge XMCD of superlattice samples of different layer thickness as indicated.


(a) Fe $L_{2,3}$-edge spectra
MCD
(b) Mn $L_{2,3}$-edge spectra
MCD
Intensity (Arb. Units)
Photon Energy (eV)
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700
705
710
715
720
725
730
735
635
640
645
650
655
660
665

Fig. 1.

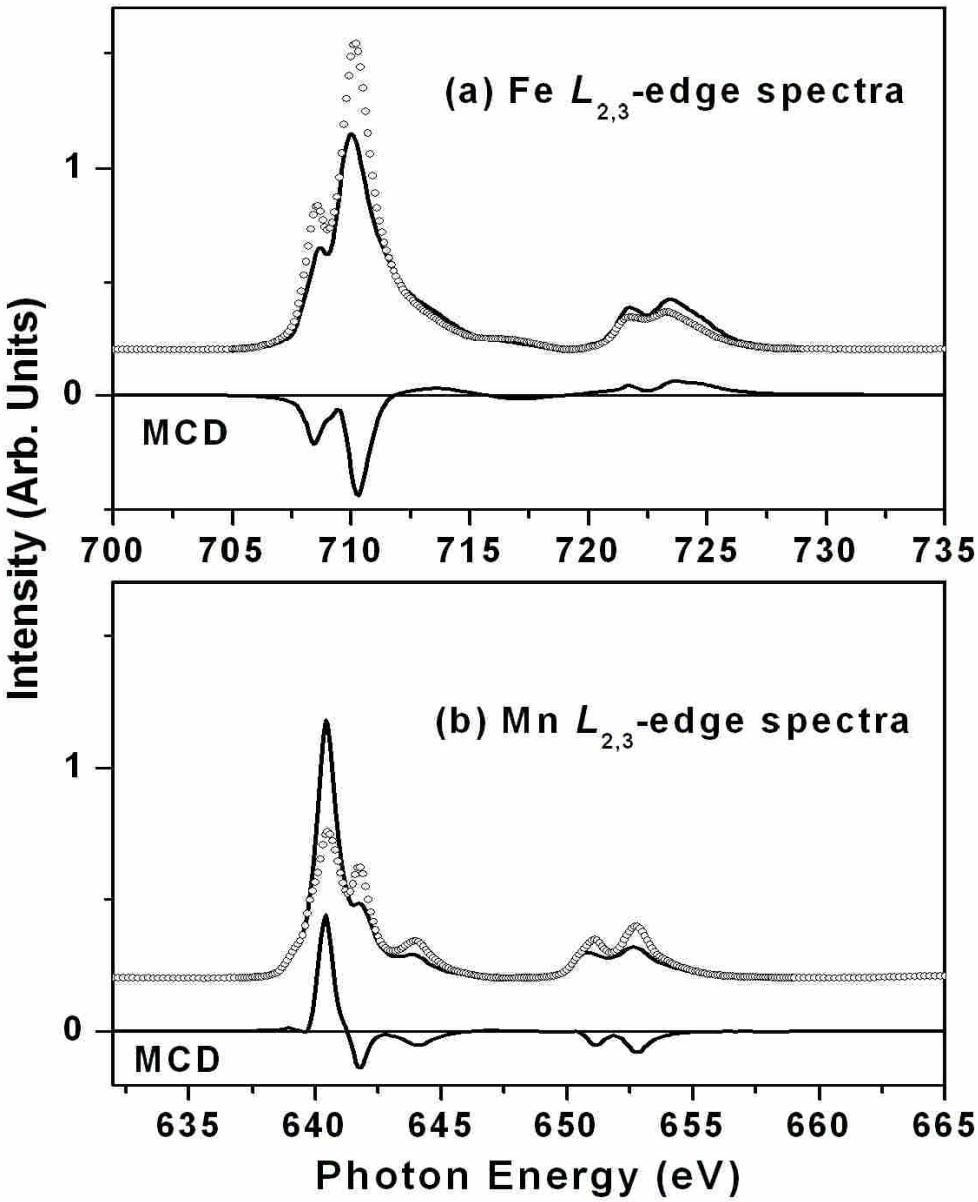
(a) Fe $L_{2,3}$-edge spectra
MCD
(b) Mn $L_{2,3}$-edge spectra
MCD
Intensity (Arb. Units)
Photon Energy (eV)
0
1
700
705
710
715
720
725
730
735
635
640
645
650
655
660
665

Fig. 2.

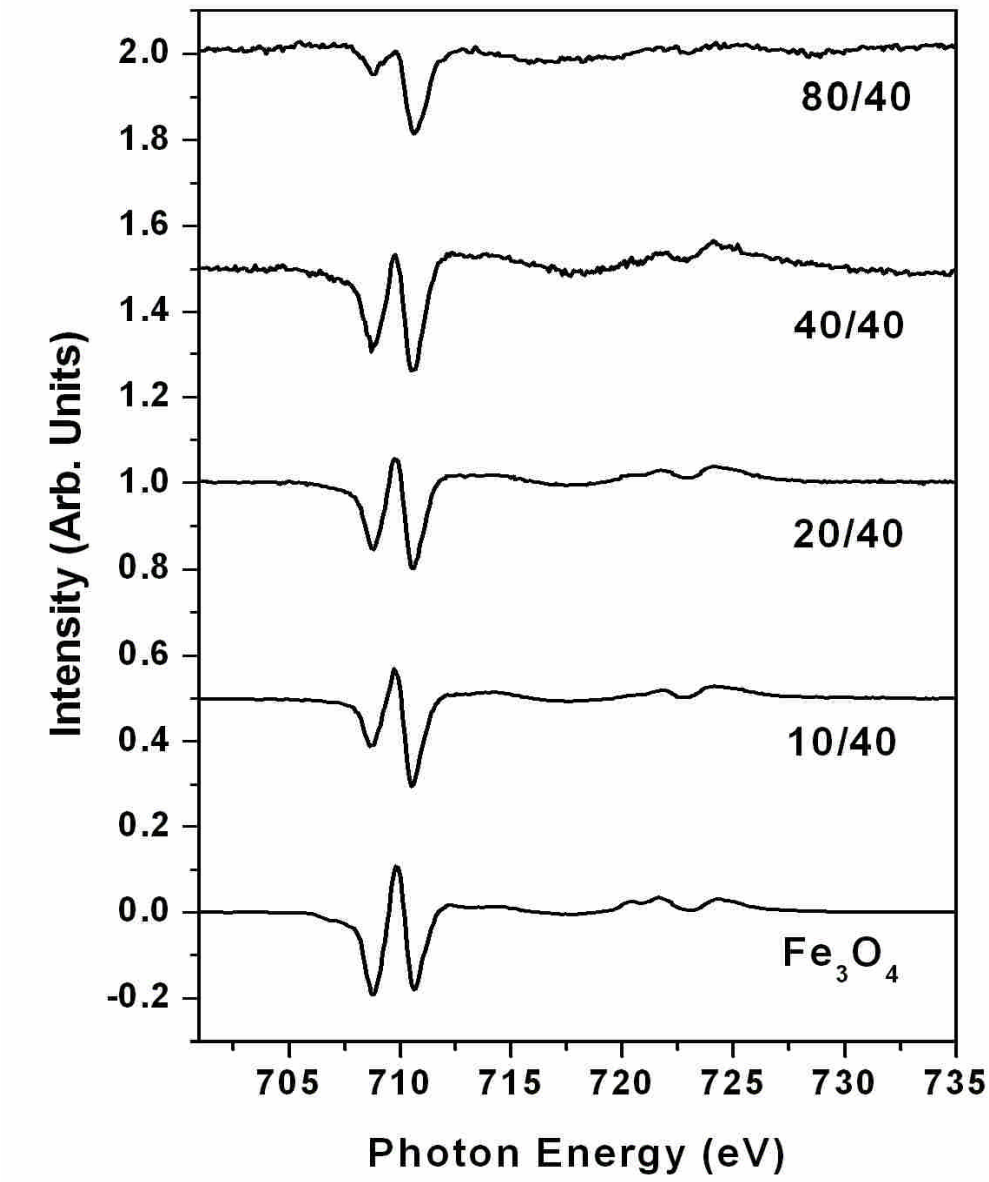
Intensity (Arb. Units)
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
80/40
40/40
20/40
10/40
Fe3O4
705
710
715
720
725
730
735
Photon Energy (eV)

Fig. 3.

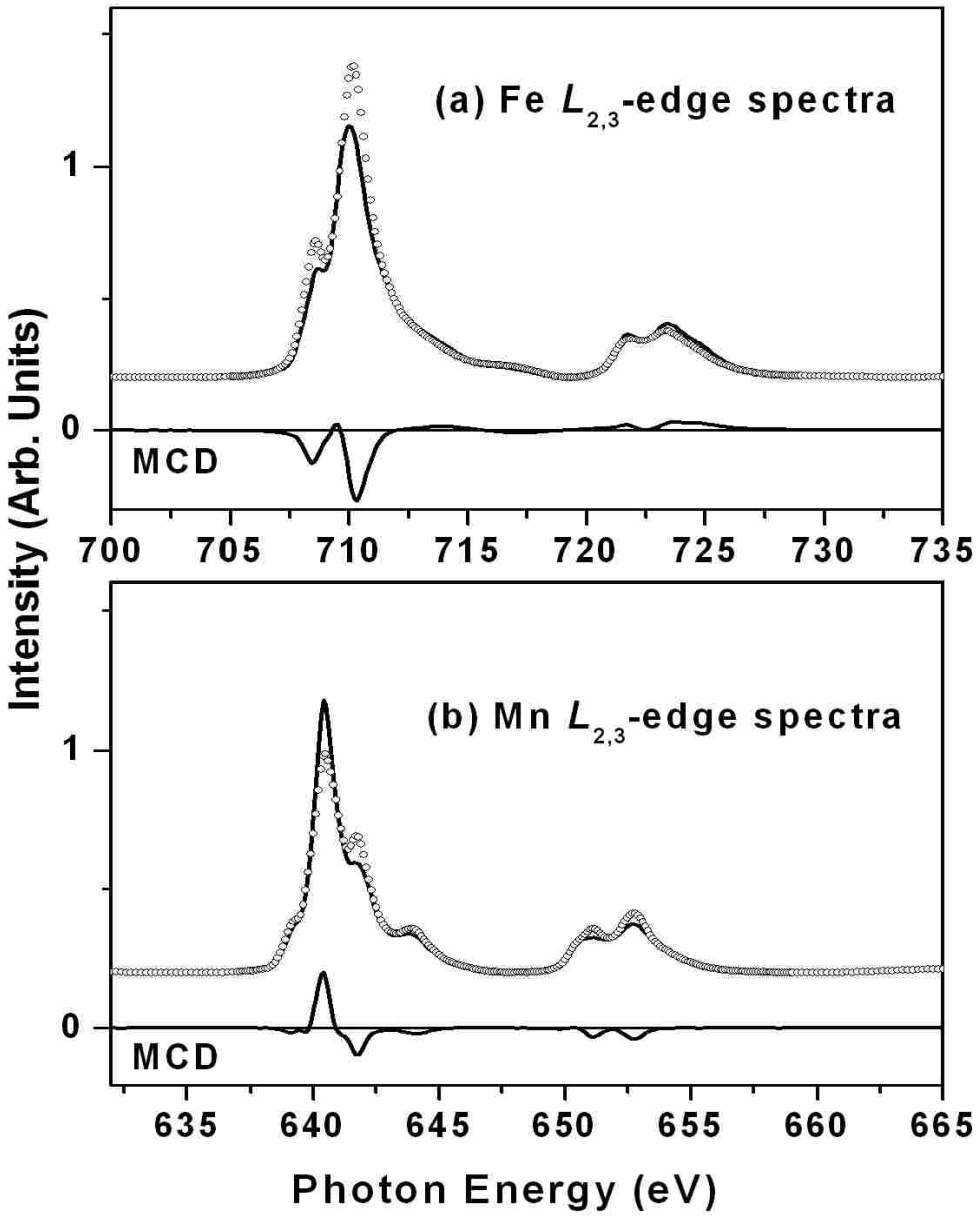
(a) Fe $L_{2,3}$-edge spectra
MCD
(b) Mn $L_{2,3}$-edge spectra
MCD
Intensity (Arb. Units)
Photon Energy (eV)
0
1
700
705
710
715
720
725
730
735
635
640
645
650
655
660
665

Fig. 4.