行政院國家科學委員會專題研究計畫　期中進度報告

金屬氧化物超晶格介面之結構與磁性(2/3)

計畫類別：個別型計畫
計畫編號：NSC92-2112-M-032-019-
執行期間：92 年 08 月 01 日至 93 年 07 月 31 日
執行單位：淡江大學物理系

計畫主持人：張經霖

計畫參與人員：張經霖

報告類型：精簡報告

處理方式：本計畫可公開查詢

中　華　民　國 93 年 5 月 28 日

行政院國家科學委員會補助專題研究計畫 □ 成 果 報 告 ■期中進度報告

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中文摘要

關鍵詞：X-光磁圓雙色性，超晶格，介面，磁性，x-光吸收光譜。

為了解磁性氧化物超晶格之磁偶合，與其界面上形成之混合氧化物層之磁性，我們運用同步輻射光源進行了一系列的吸收光譜實驗。而主要的工作是以X-光磁圓雙色性吸收光譜探討各元素之磁矩，以獲得原子間磁作用的資訊。我們發現不同厚度的Fe_3O_4/Mn_3O_4超晶格樣品中層間磁偶合皆受到介面層的影響。厚的樣品保有其塊材的性質，薄的樣品則表現著混合氧化物層之磁性。所以層間磁偶合會受到後度的影響。我們也量測了一系列的Fe-Mn-O混合氧化物薄膜作為比較以判定界面層磁性的依據。

英文摘要

Keywords： x-ray magnetic dichroism, superlattice, interface, magnetism , x-ray absorption spectroscopy.

In order to understand the magnetic coupling of the magnetic oxide superlattices, and the magnetic properties of the mixed oxide formed at the interfaces. We have performed x-ray magnetic dichroism absorption spectroscopy measurements. A series of Fe_3O_4/Mn_3O_4 superlattices with different layer thickness were studied. We found that the interlayer couplings are always affected by the mixed oxide layer. Thicker samples exhibit their bulk properties, but the thinner samples show similar magnetic property to the mixed oxide. The interlayer coupling is, therefore, thickness dependent. In addition to the Fe_3O_4/Mn_3O_4 superlattices, we have also studied the magnetic properties of a series of mixed Fe-Mn-O thin films to help identify the property of the mixed layers.

I. INTRODUCTION

We report the study of magnetic property of magnetic oxide superlattices using synchrotron radiations. The magnetic interface effect has been explored more deeply after the expertise of thin film synthesis and other modern surface techniques became more mature[1-6]. Various magnetic responses have been observed in recent experiments. Basically, two magnetic materials can be coupled directly or indirectly through other materials; the coupling can be ferromagnetic (parallel) or antiferromagnetic (antiparallel). A simple-minded model of these types of coupling treats the magnetic configuration at the interface as static and only the layer at the interface plays the role. However, more experimental results show that the coupling may be extended into the material and the thickness of the film becomes one of the key parameters to define the magnetic properties. We have utilized x-ray absorption spectroscopy techniques to examine a series of Fe_3O_4/Mn_3O_4 superlattices with various modulation wavelengths.

We found that the interlayer couplings are always affected by the mixed oxide layer. Thicker samples exhibit their bulk properties, but the thinner samples show similar magnetic property to the mixed oxide. The interlayer coupling is, therefore, thickness dependent.

II. EXPERIMENTS

Thin films of Fe_3O_4, Mn_3O_4 and a series of Mn_3O_4/Fe_3O_4 superlattices (17Å/17Å, 34Å/34Å, 68Å/68Å) were grown on MgO(110) by plasma assisted molecular-beam epitaxy (MBE). The base pressure in the disposition chamber is about 5×10^{-9} torr, the oxygen partial pressure is about 5×10^{-5} torr and the substrate temperature is kept at 250 C^o during the growth of metal oxides. A 20 keV reflection high-energy electron diffraction (RHEED), with incident angel 1^o, is used to monitor the quality of the samples *in-situ*. The crystal structures of these samples are characterized by XRD. The details of the growth, structural characterization, and

electro-magnetic properties of pure films and superlattices are given elsewhere [7-9]. The thickness of each superlattice is fixed at ~2000Å, while the thickness of each layer varies from 17Å to 68Å. The thickness of the standard thin films Fe_3O_4 and Mn_3O_4 are ~1200Å.

The soft x-ray absorption spectroscopy (XAS) and x-ray magnetic circular dichroism (XMCD) [10] measurements were performed at room temperature at the Dragon beamline[11] of the National Synchrotron Radiation Research Center in Taiwan. The degree of circular polarization of the incident light was ~80%. The base pressure of the measurement chamber was in the low 10^{-10} torr ranges. The spectra were taken under an applied magnetic field of ~1T along the (110) direction at each photon energy. We used total electron yield (TEY) mode by measuring the sample current of the samples. The incident angle of the of the photon beam is 60^{o} and the energy resolution is about 0.235eV at transition metal $L_{2,3}$-edge.

The Fe_3O_4/MgO standards XMCD data was used for energy calibration and contrast. It was conform to the calculation and experiment by P. Kuiper et al results [12]. The L_3-edge also shows the 3 sharp peaks at absorption spectra of circularly polarized x-ray magnetization component parallel and anti-parallel to the direction of x-ray beam. Those peaks indicated the iron atoms are on difference site and tow difference valences. The Fe_3O_4 is inverse spinel cube structure. Tetrahedral site are occupied by spin down Fe^{3+} d^5 ions and the spin up ions on octahedral site fluctuate between Fe^{+3} and Fe^{2+}.

The Mn_3O_4/MgO has a low T_c (~43K). At room temperature MCD is almost undetectable. More details about magnetic property, ionic and electronic structure of the Mn_3O_4 is in references [13,14]. In order to compared and proved with the interface of superlattices had mixed oxide inside;

we also measured the XAS-MCD of bulk $MnFe_2O_4$. This ferrite is an ionic system where the Mn^{2+} cations occupy predominantly the tetrahedral sites, have a $3d^5$ configuration. Fig-1 show the Fe (a) and Mn (b) 2p for magnetization parallel (I+ sold curve) and anti-parallel (I- dash curve) to the different spectra or MCD. But $MnFe_2O_4$ bulk has very sharp MCD peaks at Mn 2p XAS spectra. Our data Mn and Fe 2p for $MnFe_2O_4$ spectra are similar to that reported [15].

III RESULTS AND DISCUSSION

One of the special properties of oxide superlattices is the formation of a mixed oxide at the interface. We prove the existence $Mn_xFe_{3-x}O_4$ inside at interface. [16] It is most important component of influence in magnetic coupling of those superlattices. In order to compared and proved with the interface of superlattices had mixed oxide inside; we also measured the XAS-MCD of bulk $MnFe_2O_4$.

The probing depth (λ_x) of XAS at normal incident, for most metal oxide is about 100Å[17,18]. Our measurements were taken at incident angle $\theta \sim 60^o$. Therefore, our probing depth is $\lambda_x \cos\theta$ around ~86Å. The top layers of our superlattices are Mn_3O_4. The x-ray beam should pass through the more layers (bilayers, $\Lambda \sim 2.5$) of Mn_3O_4 and Fe_3O_4 in 17Å/17Å. Even 34Å/34Å had 2-3 layers (bilayer, $\Lambda \sim 1$). However, x-ray beam only pass one Mn_3O_4 lays through to Fe_3O_4, the probing include contribution to the one interface of 68Å/68Å superlattice sample. Observation of the $L_{2,3}$-edge XAS of 68Å/68Å sample and the MCD spectrum, show in Fig-2 Fe(a) and Mn(b). We found significant similarity with those of $MnFe_2O_4$. The Fe environment of 68Å/68Å sample is difference form the pure Fe_3O_4. It is more like bulk $MnFe_2O_4$ spectrum. The Fe environment of

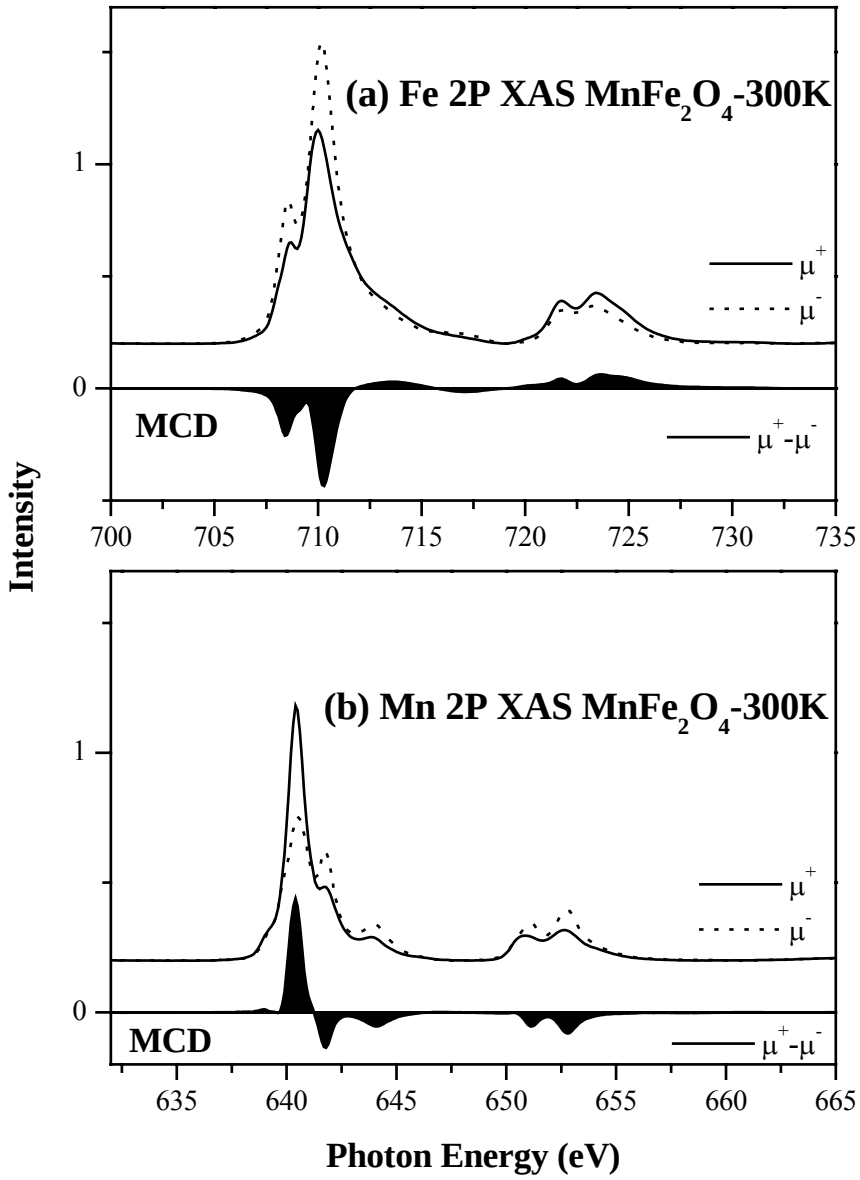

Fig-1. The experimentally observed XAS and MCD (Full black area under curve μ^+-μ^-) of $MnFe_2O_4$ Bulk for Fe 2p XAS (a) and Mn 2p XAS (b). μ^+ represent the XAS for magnetization parallel to photon-spin (Solid line) and μ^- represent that antiparallel.

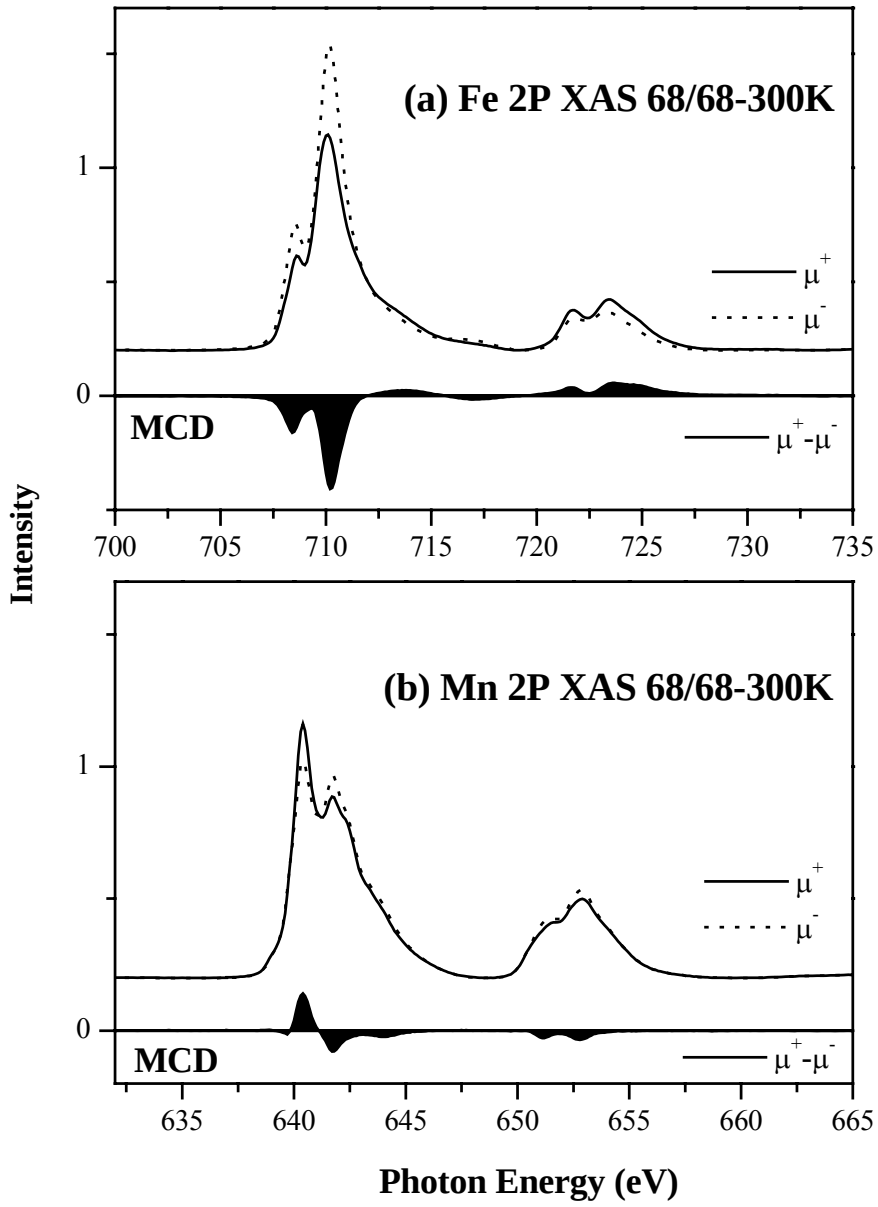

Fig-2 The experimentally observed XAS and MCD (Full black area under curve μ^{+}-μ^{-}) of 68Å/68Å superlattice for Fe 2p XAS (a) and Mn 2p XAS (b). μ^{+} represent the XAS for magnetization parallel to photon-spin (Solid line) and μ^{-} represent that antiparallel.

68Å/68Å superlattice resembles that of the bulk $MnFe_2O_4$ but difference form the Fe_3O_4 according to the XAS and MCD measurement, as follow the Fig-1(a) and Fig-2(a). The Fe_3O_4 have 3 components at Fe MCD L_3-edge spectrum with two negative peaks and one positive peak from B-site Fe^{2+}, Fe^{3+} and A-site Fe^{3+}, respectively [12]. Otherwise, We observed the MCD L_3-edge spectra of the 68Å/68Å superlattice and $MnFe_2O_4$ with a negative double-peak structure. It is obtained from a sum of 70% Fe $L_{2,3}$-edge spectra from $Mn_A[Fe_2]BO_4$ and 30% from $Fe_A[MnFe]_BO_4$ [15].

Form the Mn L-edge MCD measurement in Fig-1(a) and Fig-2(a). We observe the strong similarity of Mn form of MCD spectrum in 68Å/68Å superlattice and $MnFe_2O_4$ but x-ray absorption spectra are difference. The 68Å/68Å superlattice is broader then $MnFe_2O_4$ XAS L_3 spectrum. The absorption is overall average of probing Mn environment. These absorption contributions include more part of Mn_3O_4 and some $MnFe_2O_4$-like interface environment. XAS are difference, MCD similar, due to the fact that. Mn_3O_4 has a low T_c, at room temperature MCD is almost undetectable but $MnFe_2O_4$ has a prominent MCD. In 68Å/68Å superlattice the MCD signal is very similar to that of bulk $MnFe_2O_4$ except that it is much worker in superlattice. The reason is that the amount of $MnFe_2O_4$ is only small fraction at the interface.

In 17Å/17Å superlattice we observe, show in Fig-3 (a) form Fe L-edge MCD data, that contribution from A-site Fe^{3+} is much higher that 68Å/68Å. This is an evidence of the Fe_3O_4 type spectral shape. On the other hand, Mn L-edge data (Fig-3(b)) show a very similar XAS and MCD shape to that of Fe $MnFe_2O_4$. (An indication of the formation of mixed oxide near interface.)

Fig-4 plats Fe L_3-edge MCD of superlattice samples of different thickness as indicated.

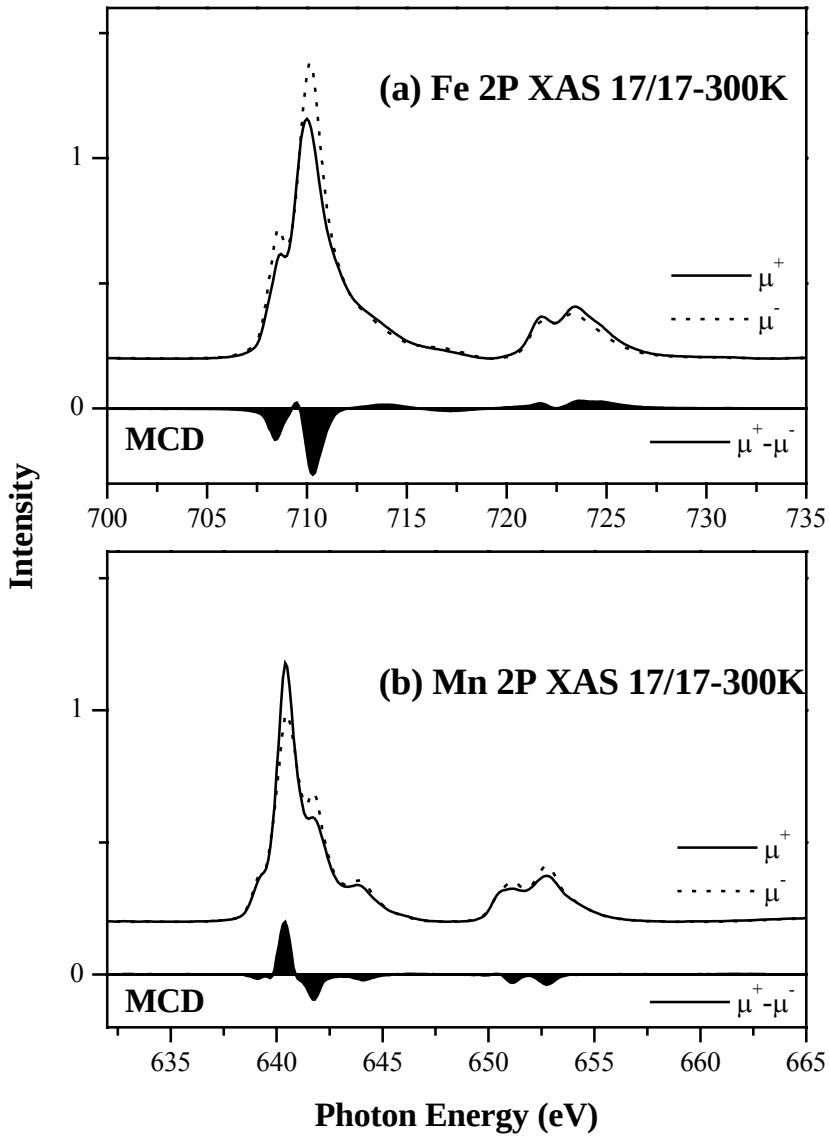

Fig-3 The experimentally observed XAS and MCD (Full black area under curve μ^{+}-μ^{-}) of 17Å/17Å superlattice for Fe 2p XAS (a) and Mn 2p XAS (b). μ^{+} represent the XAS for magnetization parallel to photon-spin (Solid line) and μ^{-} represent that antiparallel.

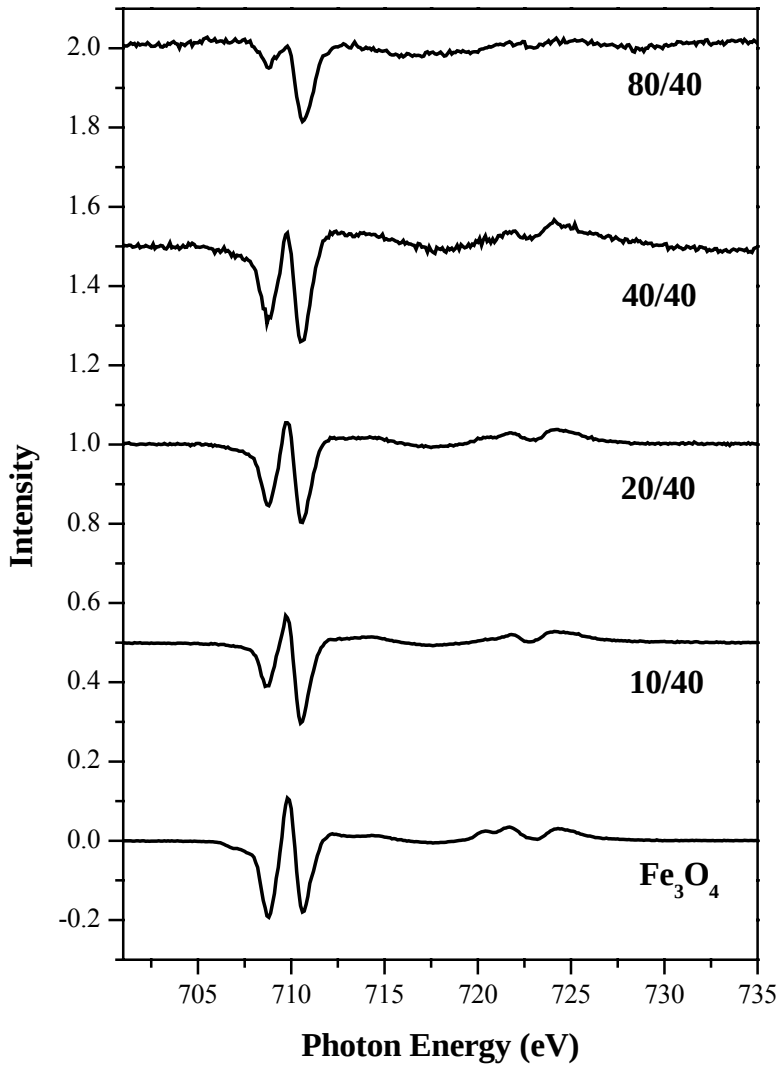

Fig-4 plats Fe L2,3-edge MCD of superlattice samples of different thickness as indicated.

The spectral shape evolves form pure Fe_3O_4 film, which shows 2 downward peaks correspond to the two B-site Fe^{2+} (Low energy) and Fe^{3+} (Higher energy). The upward peak corresponds to the A-site Fe^{3+}. When the thickness of the top layer Mn_3O_4 increases from 10Å to 80Å, we observe basically the same 3-peak structures. However, the intensity of the upward peak decreases, for the 80Å/40Å superlattice what we see is only the region near the interface area. Owing to the limited probing (~80Å).

We discuss the mechanism of the anti-parallel coupling between Fe3O4 and Mn_3O_4. For a spinel superlattice such as Mn_3O_4/Fe_3O_4, if both layers form complete unite cell, then an A site must be followed by B site at the interface. The net moment in Mn_3O_4 and Fe_3O_4 should be parallel. However, in 68Å/68Å this case, we are proved the mixed-ferrite ($MnFe_2O_4$-like) between the Mn_3O_4 and Fe_3O_4, the reason that they do not complete cells or even complete layers. The integral value 68Å/68Å of superlattice MCD L_3-edge spectra of iron is negative and manganese is positive. Those results are consistency with the Superconducting Quantum Interference Device (SQUID) measurement by G. Chern et al [19]. Ferrimagnetic oxides have difference spin configuration in A and B sites such as $MnFe_2O_4$. The most of Mn^{2+} occupied the A site and the magnetic moment direction opposed to B site Fe ion. The Mn_3O_4 layer follows the interface A site Mn^{2+} and anti-parallel state for the magnetic moment was occurred. The interface is mixed-ferrites of influence magnetic coupling in these superlattices.

Otherwise, We consider the net moment of the 17Å/17Å superlattice. The lattices constant of Mn_3O_4 and Fe_3O_4 are around ~8.5Å. There are two unit cells in only one layer of Fe_3O_4 or Mn_3O_4. If we focus on the interface, we should say this sample is $MnFe_2O_4$-like. And the magnetic

behave is the same the bulk $MnFe_2O_4$.

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