Antiparallel state, compensation point, and magnetic phase diagram of Fe_3O_4/Mn_3O_4 superlattices

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(Received 20 March 2000; revised manuscript received 27 October 2000; published 12 February 2001)

The magnetic response of a ferrimagnetic/ferrimagnetic superlattice, $[Fe_3O_4\ (20\ Å)/Mn_3O_4\ (80\ Å)]_{x20}$, is measured as a function of external field (-50–50 kOe) and temperature (5–300 K). A compensation point (T_{cp}) is identified ~33 K at which the remanence changes sign and low-field *M-T* curves show minima, indicating that the net moments of Fe_3O_4 and Mn_3O_4 are antiparallel. At temperatures $>\sim 50$ K, the magnetic response becomes pure Fe_3O_4-like. Detailed *M-H* curves (at $T<50$ K) further exhibit magnetic phase transition at higher external field. As H is above $H^*\sim 10$ kOe, the magnetization is enhanced and then saturates at $H\sim 40$ kOe. These phases are similar to the twisted phases, originating from a competition between Zeeman and exchange energies, previously observed in antiparallel metallic multilayers. A *H-T* magnetic phase diagram of the present superlattice is presented and five phases are included: the Mn_3O_4-aligned, Fe_3O_4-aligned, twisted, ferrimagnetic saturated, and pure Fe_3O_4 phases. *M-H* curves also show asymmetry at temperatures below and above T_{cp}, which is probably related to the anisotropy effect of Mn_3O_4 (tetragonal structure). The fundamental mechanism of the antiparallel coupling between Mn_3O_4 and Fe_3O_4 is also discussed.

DOI: 10.1103/PhysRevB.63.094421 PACS number(s): 75.70.Cn, 75.50.Gg, 81.15.Hi

I. INTRODUCTION

One of the major differences between ferrimagnetic oxides and ferromagnetic metals is that their magnetization has a different temperature-dependent response.[1,2] Due to the competition between the noncompensated antiferromagnetic spins in different crystalline sites, the temperature-dependent magnetization of ferrimagnetic oxides may exhibit different shapes and sometimes may even change sign at certain temperatures (compensation points). Bulk samples such as $Li_{0.5}Fe_{1.25}Cr_{1.25}O_4$ have shown this peculiar reversal behavior and those experimental results have actually become a crucial test for Néel's theory of ferrimagnetism.[3] However, the magnetic configurations in those materials are more complicated than a pure spinel structure and many physical properties (such as compensation point) are difficult to predict. In a recent paper, the magnetic response of a new class of ferrimagnetic/ferrimagnetic superlattice, Fe_3O_4/Mn_3O_4, has shown a similar reversal behavior indicating that the moment of Fe_3O_4 and Mn_3O_4 are antiparallel to each other.[4] Relative to previous studies on ferrimagnetic/antiferromagnetic oxide superlattices,[5–7] the study focused on the direct magnetic coupling between two ferrimagnetic materials. One of the advantages of a superlattice sample is that its well-defined layer structure substantially reduces the complexity of the data analysis. For instance, the magnetic behavior of this superlattice becomes very similar to a pure Fe_3O_4 film as the temperature increases above the T_c of Mn_3O_4 (~43 K), indicating that both Fe_3O_4 and Mn_3O_4 layers still maintain their own magnetic properties. Also the compensation point (~33 K) can be estimated from the relative volume and temperature-dependent characteristics of parent compounds. Therefore, a more detailed study of this system may provide an opportunity to explore fundamental insights such as the magnetic coupling and anisotropy of ferrimagnetic oxides. In this paper, we extend to detailed *M-H* and *M-T* measurements of this ferrimagnetic superlattice and find interestingly that this system also shows various phase transitions at different external fields. These transitions are basically originated from a competition between Zeeman and exchange energies, but due to the layer structure the new phases appear at relatively low external fields. At least five phases are observed and classified in a *H-T* phase diagram. The magnetic coupling strength is then estimated and compared with a metallic system. Finally, the fundamental mechanism of the antiferromagnetic coupling between Fe_3O_4 and Mn_3O_4 is discussed.

II. EXPERIMENT

A series of Fe_3O_4/Mn_3O_4 superlattices were grown on MgO(001) by molecular-beam epitaxy, which is similar to the previous growth of oxide superlattices.[8,9] Briefly, metallic vapor generated from two high-temperature Knudsen cells is oxidized in a plasma oxygen environment and alternatively deposited on the substrate. MgO(001) substrate is chosen mainly because of its high chemical stability and relatively low lattice mismatch with respect to the film to be grown. The deposition rate is ~50 Å/min and the growth temperature is ~300 °C. *In-situ* reflection high-energy electron diffraction (RHEED) and *ex-situ* x-ray diffraction were carried out to analyze the crystalline quality of the films. RHEED patterns taken during the growth indicate that the films are epitaxial in plane. The x-ray diffraction, which analyzes the lattice spacing along the *z* direction, shows that the average lattice constant varies as a function of the relative thickness of the constituent layers and the superlattice structure becomes unstable at some critical thickness. These results are different from low misfit oxide superlattices as studied previously. A detailed discussion of the growth of these large misfit oxide superlattices is given elsewhere.[10] The

magnetic response of Fe_3O_4/Mn_3O_4 superlattices was carried out by a superconducting quantum interference device (SQUID) magnetometer with a temperature range of 5–300 K and a magnetic field up to 50 kOe.[2] Only the results measured with the external field parallel to the film surface are discussed in this communication.

III. RESULTS AND DISCUSSION

The magnetic properties of pure Fe_3O_4 and Mn_3O_4 thin films have been studied first.[10] The results of Fe_3O_4 are similar to a previous report[11] where the saturation magnetization (M_s) is ~450 emu/cm^3 with weak anisotropy. The saturation magnetization of the Mn_3O_4 film is ~150 emu/cm^3 and T_c is ~43 K both of which also consistent with recent reports.[11,12] In addition, Mn_3O_4 has strong anisotropy (due to its tetragonal structure) where the spins prefer to run parallel to the film surface rather than perpendicular to the surface. Notice that because of the difference in T_c and M_s between Fe_3O_4 and Mn_3O_4, the magnetic properties of these superlattices are critically related to the layer sequencing and layer thickness (see below). Figure 1 represents a set of *M-H* curves of $[Fe_3O_4\ (20\ Å)/Mn_3O_4\ (80\ Å)]_{x20}$ measured at different temperatures. A strong temperature dependence of these curves can be clearly seen. The *M-H* curves measured at 55 K and above (not shown) are basically similar to the result of a pure Fe_3O_4 film (because Mn_3O_4 already becomes paramagnetic at those temperatures, see below). The saturation magnetization (M_s) at 55 K is ~130 emu/cm^3. Note that this value is obtained by normalizing the whole volume of the Fe_3O_4/Mn_3O_4 superlattice. If it is only normalized by the volume of Fe_3O_4, the magnetization should be about four times larger, ~650 emu/cm^3, which is somewhat higher than the bulk magnetization of Fe_3O_4 (~500 emu/cm^3). At temperatures less then 55 K, the *M-H* curves change dramatically. First, there seems to be a low-field stage around $H \sim 0$ with reducing remanence and hysteresis as the temperature gets close to T_{cp} ~33 K, and at $T=T_{cp}$, both remanence and coercivity vanish (see the inset at 33 K). Second, these curves open other loops at fields greater than ~10 kOe and smaller than −10 kOe and the magnetization increases substantially beyond these critical external fields. Notice that, however, the *M-H* curves are not quite symmetrical at lower and higher temperatures with respect to T_{cp}. This asymmetry is probably due to the anisotropy effect and will be discussed in more detail (see below). Third, the magnetization saturates at fields greater than ~40 kOe and the saturation magnetization of Fe_3O_4/Mn_3O_4 is ~250 emu/cm^3, which is very close to the expected average value of pure Fe_3O_4 and Mn_3O_4.

Since a theoretical model is not yet available for the present magnetic response, we notice that these results are qualitatively similar to the magnetic response of a Gd/Fe multilayer system. Gd/Fe multilayers are a typical antiparallel system, which has been studied in detail by Camley and coworkers theoretically and by Cherifi *et al.*, experimentally.[13–18] If we use the terminology introduced in the Gd/Fe system, the magnetic response (or the phase diagram) observed from the Fe_3O_4/Mn_3O_4 superlattice can be briefly described as follows: At $T<T_{cp}$ and with relatively low external field, the magnetic state is Mn_3O_4 dominant and parallel to the external field while Fe_3O_4 is antiparallel to the field. At $T>T_{cp}$, it becomes Fe_3O_4 dominant and parallel to the external field while Mn_3O_4 is antiparallel to the field. At $T=T_{cp}$, both moments are equal but opposite to each other, so remanence and coercivity vanish (an antiferromagnetic state). Moreover, if the external field increases beyond a critical value H^*, the aligned magnetic state undergoes a transition to a twisted phase in that Fe_3O_4 and Mn_3O_4 spins form an angle with the external field.[19] The formation of a twisted phase is due to the balance between Zeeman and exchange energies and it is similar to a domain-wall structure or a spin-flop phase in an antiferromagnetic material. The angle between Fe_3O_4 and Mn_3O_4 moments continues to decrease and the total magnetization increases until the total

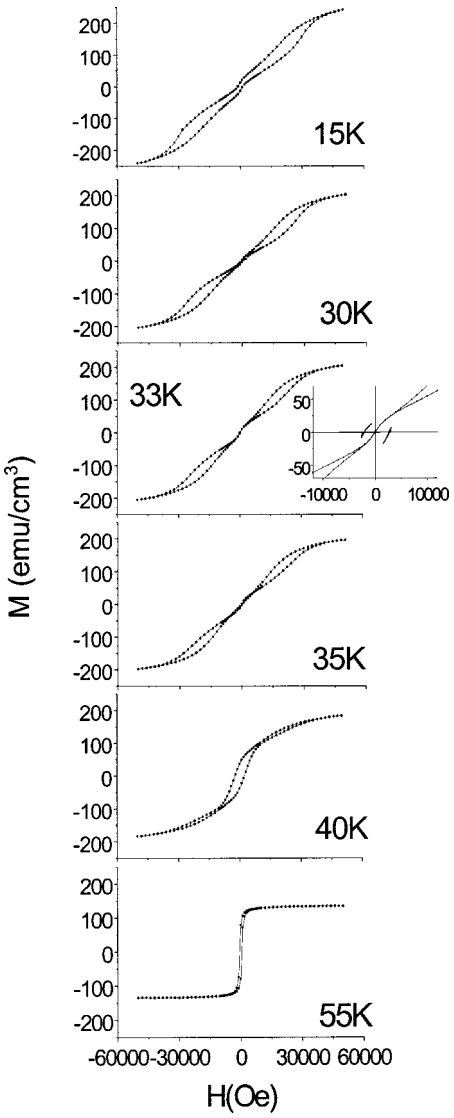

FIG. 1. Magnetic hysteresis curves for a $[Fe_3O_4\,(20\ Å)/Mn_3O_4\,(80\ Å)]_{x20}$ superlattice measured at different temperatures. The applied field is parallel to the film surface. The inset at 33 K clearly shows, with expanded scale, that both remanence and coercivity vanish and H^* at this temperature is ~5 kOe.

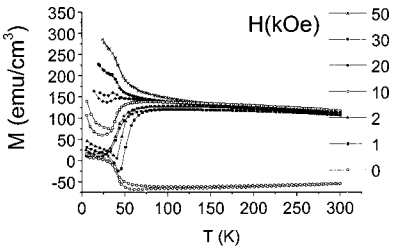

FIG. 2. *M-T* curves for a $[Fe_3O_4(20\,Å)/Mn_3O_4(80\,Å)]_{x20}$ superlattice. The applied field is varied from 0–50 kOe parallel to the film surface and the sample is magnetized with a 50 kOe field at 5 K originally before the measurements are carried out.

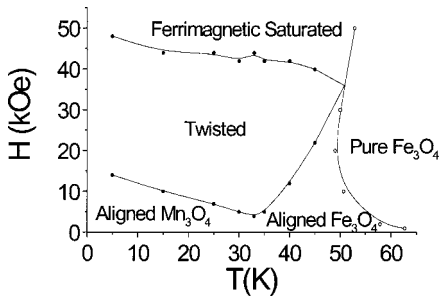

FIG. 3. *H-T* phase diagram of a $[Fe_3O_4(20\,Å)/Mn_3O_4(80\,Å)]_{x20}$ superlattice deduced from experimental *M-H* and *M-T* results.

moment is saturated at a higher field. As mentioned earlier these results are very sensitive to the relative layer thickness of constituent layers. Since the magnetization of Mn_3O_4 is only $\sim\frac{1}{3}$ of Fe_3O_4 and the T_c of Mn_3O_4 is lower, a necessary condition for having a compensation point in Fe_3O_4/Mn_3O_4 superlattices is that Mn_3O_4 has to be three to four times thicker than Fe_3O_4. The present superlattice with Mn_3O_4 (80 Å) and Fe_3O_4 (20 Å) in thickness is a reasonable choice. For Fe_3O_4/Mn_3O_4 superlattices with thicker constituent layers, the magnetic response still shows negative remanence, indicating that antiparallel coupling remains between Fe_3O_4 and Mn_3O_4. However, the interface effect becomes limited (domain-wall structure) and the phase diagram is sensitive to layer thickness.[10] It also needs to be pointed out that although Fe_3O_4/Mn_3O_4 and Gd/Fe exhibit similar magnetic phases, these two systems are fundamentally different. It is known that a ferrimagnetic material itself has opposite but unbalanced spins in *A* and *B* sites. Relative to Gd/Fe, in Fe_3O_4/Mn_3O_4 superlattices it must be the net moments of Fe_3O_4 and of Mn_3O_4 that are antiparallel coupled at a low external field and become twisted at a higher external field.

The antiparallel states and various magnetic phases are further confirmed by temperature-dependent measurements. Figure 2 shows a series of *M-T* curves (5-300-5 K) measured at different external fields. The sample was originally magnetized at $H=50$ kOe and $T=5$ K before all the measurements were carried out. Again, a strong temperature and field dependence of these results are clearly represented. All curves measured at $H<10$ kOe show a minimum $\sim$30 K (except the remanence curve) and they all saturate at $T>60-70$ K with magnetization $\sim$120 emu/cm^3. The remanence curve ($H=0$) changes sign at $T\sim33$ K and becomes nearly constant at $T>60$ K. These reversal behaviors are extremely similar to the original data of $Li_{0.5}Fe_{1.25}Cr_{1.25}O_4$, which strongly indicates that the present system has similar antiparallel states between Fe_3O_4 and Mn_3O_4. However, the high-field results measured at $T<60$ K exhibit different features that have not been observed in bulk samples. For instance, the magnetization tends to increase and gradually saturate at $H>20$ kOe (the paramagnetic background from the substrate becomes comparable to the ferromagnetic response of the ferrimagnetic film at $H>40$ kOe and is difficult to remove completely). These results are consistent with the previous *M-H* curves, which show enhanced magnetization (twisted phase), with a weaker temperature dependence, as the external field is greater than a critical value. Moreover, we notice that there are other unique temperature-dependent features of these data: First, not only the remanence curve changes sign but the curves measured at $H=1$ and 2 kOe also show negative magnetization at certain temperatures. Second, the lower-field ($<$20 kOe) results are different on the warming and cooling curves (thermal hysteresis). The negative magnetization only exists on the warming curve but not on the cooling curve, which indicates that the negative magnetization is due to a metastable state. These metastable states are probably related to the magnetic anisotropy of this superlattice. Because Mn_3O_4 has tetragonal symmetry, it is highly magnetic anisotropic. It seems that it is relatively harder to convert a Mn_3O_4-aligned state to a Fe_3O_4-aligned state than vice versa and a Mn_3O_4 state tends to persist to a higher external field or a higher temperature. Actually this anisotropy-induced asymmetry has been also shown on *M-H* curves (Fig. 1, $T=30$ and 35 K); more detailed discussion about this anisotropy effect will be studied in the future.

After analyzing these *M-H* and *M-T* curves, a phase diagram is obtained in Fig. 3 (full circles are obtained from *M-H* and empty circles from *M-T* measurements). In total, five phases are identified, namely, the Mn_3O_4-aligned, Fe_3O_4-aligned, twisted, ferrimagnetic saturated, and pure Fe_3O_4 phases. Qualitatively, this phase diagram is similar to Gd/Fe results but it has more phases and the compensation point shifts toward a much lower temperature (due to the relatively low T_c of Mn_3O_4). In addition, there are some quantitative differences between these two systems. For instance, the average H^* of Fe_3O_4/Mn_3O_4 ($\sim$10 kOe) is about five times higher than the H^* of the Gd/Fe superlattice ($\sim$2 kOe). This may indicate that the coupling between Fe_3O_4/Mn_3O_4 is much stronger or more complete than in the Gd/Fe system.[20] Moreover, both saturated and pure Fe_3O_4 states are included in the present diagram and thus it provides more information about this system. The magnetic moment in a ferrite oxide is an important parameter because it can be usually estimated with high accuracy (due to its localized electron characteristic). Since the magnetization at high field (ferrimagnetic saturated phase) agrees with the expected average moment of the superlattice, it further supports the previous arguments of the present system. It may be also worth noting that the T_c of Mn_3O_4 is about 10–20 K (dependent on the external field) higher than its bulk value. Similar proximity effect has been seen in other systems[21] but the

present field-dependent feature seems rather unique. Another interesting feature is that four phases including Fe_3O_4-aligned, twisted, ferrimagnetic saturated, and pure Fe_3O_4 phases merge around the coordinate ~(50 K, 37 kOe). Analogous to a triple point seen in a three-state phase diagram, it seems that a multiple phase point may exist in this region.

Finally, we briefly discuss the mechanism of the antiparallel coupling between Fe_3O_4 and Mn_3O_4. Although the magnetic phase diagram of a Fe_3O_4/Mn_3O_4 superlattice is similar to a Gd/Fe multilayer, their coupling mechanisms must be different. In metals, the sign of exchange coupling is basically related to the separation distance between electrons. The major origin of the antiferromagnetic coupling in a Gd/Fe system is probably associated with the atomic size of transition metals and rare-earth elements. However, the electrons in oxides are more localized and the coupling mechanism is originated by superexchange. As mentioned earlier, ferrimagnetic oxides have different spin configurations in *A* and *B* sites. According to Néel's original model the interaction between *A* and *B* sites is the dominant one that forces the spins in *A* and *B* sites to be separately parallel but antiparallel to each other. For a spinel superlattice such as Fe_3O_4/Mn_3O_4, if both layers form complete unit cells, then an *A* site must be followed by a *B* site at the interface and vice versa [schematically shown in Fig. 4(a)]. In that case, the net moments in Fe_3O_4 and Mn_3O_4 should be parallel. However, if they do not form complete cells or even complete layers, mixed ferrites (such as $Fe_{3-x}Mn_xO_4$) may be formed and an antiparallel state for the net moment between Fe_3O_4 and Mn_3O_4 [shown schematically in Fig. 4(b)] becomes possible. But it is hard to make theoretical predictions in those cases. An implication of these arguments is that an antiparallel coupling between two ferrimagnetic layers may not be intrinsic and a parallel coupling between two ferrimagnetic layers may also exist depending on the interface structure. Actually, our recent results have shown that the magnetic response of some Fe_3O_4/Mn_3O_4 superlattices indeed behaves like a parallel-coupled system. In those cases, the magnetic remanence curve stays positive at all temperatures and the magnetization suddenly increases while the temperature cools below the T_c of Mn_3O_4. In principle, x-ray or neutron diffraction can provide the detailed information about the interface sharpness. However, for an oxide superlattice it is by no means trivial.[22] More experimental work needs to be done to understand this basic mechanism.

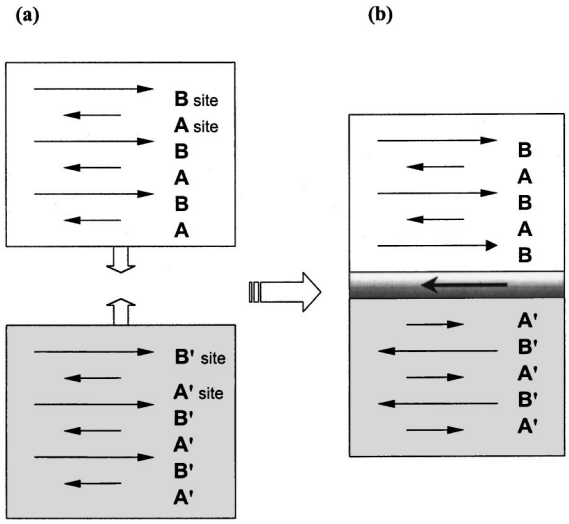

FIG. 4. A schematic illustration of spin configuration along the (001) direction of a ferrimagnetic/ferrimagnetic bilayer. A mixed Mn-Fe-O interface is formed at the interface, which may introduce an antiparallel state of the bilayer system.

IV. CONCLUSIONS

The present study demonstrates that a ferrimagnetic-ferrimagnetic superlattice may give rise to antiferromagnetic coupling at the interface. Its magnetic response shows a rich temperature and external field dependence including a compensation point and various phase transitions. A *H-T* magnetic phase diagram is obtained and five phases are included. Due to their simple layer structure, theoretical calculations may be possible in the future, that will help to understand the magnetic coupling and anisotropy of spinel ferrimagnetic oxides.

ACKNOWLEDGMENT

This work was supported by the National Science Council of the Republic of China through Grant No. NSC 89-2112-M-194-012.

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