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Recent studies show that the magnetic properties of epitaxial thin films of magnetite (Fe_3O_4) deviate strongly from bulk behavior: it is difficult to saturate thin films, ultrathin films may become super paramagnetic, their saturation magnetization drops to zero, and the local magnetic moments are oriented out of plane in zero field. The possible relationship between this anomalous behavior and the occurrence of anti-phase boundaries (APBs) is discussed. Transmission electron microscopy images confirm that APBs are present in our Fe_3O_4 films grown by molecular beam epitaxy on MgO(100). Only APBs with out-of-plane shift vectors are visible. The much higher APB density found in sputtered films suggests that preparation conditions are important. To explain the deviating saturation and the superparamagnetic behavior of thin Fe_3O_4 films at the same time, the magnetic coupling over the APB must be dramatically reduced due to spin disorder along the boundaries.
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I. INTRODUCTION

In the last decade several research groups have reported that the magnetic properties of epitaxial layers of magnetite (Fe_3O_4) are anomalous in several respects. For instance, it has been found that: (a) it is much more difficult to fully saturate epitaxial films than bulk single crystals,[1,2] (b) ultrathin films show superparamagnetic behavior,[3] (c) the saturation magnetization of ultrathin films is considerably reduced with respect to the bulk value,[4] and (d) the local magnetic moments are out of plane in zero field.[1,3,5]

In this article will discuss the extent to which the deviating behavior of thin Fe_3O_4 films is related to an antiphase domain structure, as has been suggested recently.[2,3]

II. ANTIPHASE DOMAINS AND MAGNETISM

Fe_3O_4 grows epitaxially on MgO(100) by virtue of a very close match of the anion sublattices. The cation sublattice of this inverse spinel structure, however, is much more complex. Only half of the octahedral (*B*) sites in the cubic close packed anion sublattice are occupied by equal amounts of Fe^{3+} and Fe^{2+} ions. One eighth of the tetrahedral (*A*) holes are occupied by Fe^{3+} ions. This is accomplished in such a way that the lattice constant a is twice that of the anion sublattice, 8.397 Å. The first step in a layer-by-layer growth mechanism, which is adopted by molecular beam epitaxy (MBE)-grown Fe_3O_4,[7] is the formation of nuclei, followed by growth and eventual coalescence of two-dimensional (2D) islands into a closed layer. Whereas the resulting oxygen sublattice is continuous, the cation sublattice in most cases is not, because the origin of the unit cell of each island randomly starts at eight inequivalent positions. Neighboring islands are related by shift vectors $1/4a\langle 110\rangle$ or combinations thereof. A possible choice of independent shift vectors **R** is $1/4a[0,0,0]$ (no shift), $1/4a[110]$, $1/4a[\bar{1}10]$, $1/4a[\underline{1}00]$, $1/4a[011]$, $1/4a[101]$, $1/4a[0\bar{1}\bar{1}]$, and $1/4a[\underline{1}01]$. All others are related to these by the face-centered symmetry of the cubic unit cell. The first four are in-plane shifts, leaving the rows of *B* sites parallel, the last four are out-of-plane shifts, causing the rows of *B* sites to be perpendicular to each other, as is illustrated in Fig. 1. The boundaries between these shifted domains are so-called antiphase boundaries (APBs) and have been revealed by scanning tunneling microcopy (STM).[7] The first transmission electron microscopy (TEM) pictures of APBs in epitaxial magnetite films, which allow the determination of the APB density, were reported by Margulies *et al.*[2] for a 50 nm thick

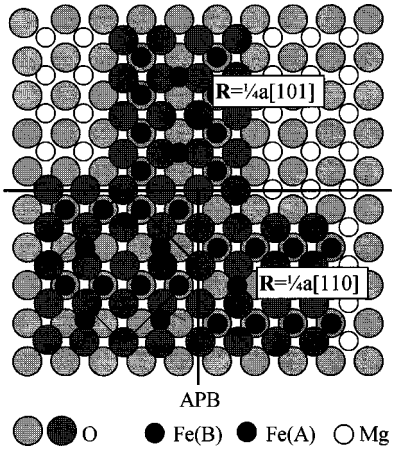

FIG. 1. Two main types of anti-phase domains form, if a layer of spinel, such as magnetite (Fe_3O_4), grows epitaxially on a rock salt substrate such as MgO, i.e., domains which are related to a reference domain by in-plane and out-of-plane shift vectors. An example of each type is shown in the drawing. Only APBs with out-of-plane shift vectors are visible in the TEM picture. A characteristic of the out-of-plane shifted domains is that the rows of octahedrally coordinated cations in atomic layers on the same level are oriented perpendicular to each other.

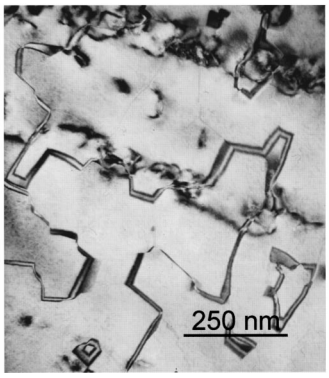

FIG. 2. TEM picture of an Fe_3O_4 layer. The 200 nm film was grown by oxygen-MBE and prepared by ion-beam milling after removal of most of the substrate by abrasion. The fringed dark bands are APBs with out-of-plane shift vectors. The thin black lines are the (forbidden) APBs with in-plane shift vectors.

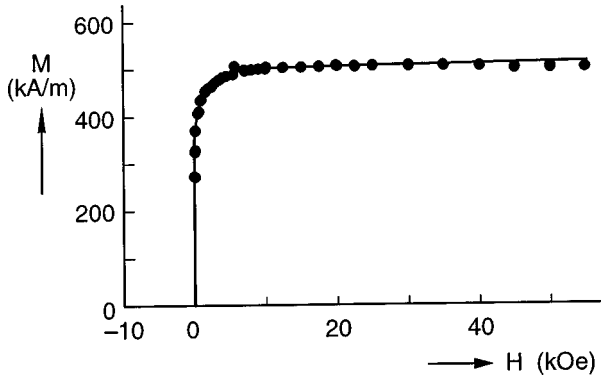

FIG. 3. The fit of Eq. (2) to describe the approach to saturation of the magnetization loop of a 30.5 nm Fe_3O_4 film grown on MgO (100) by MBE. The drawn line corresponds to the fit.

sample grown by sputter deposition at 500 °C, showing on average 27.5 nm wide domains. Figure 2 shows a TEM picture of a 200 nm thick sample grown at Philips Research by oxygen-MBE on MgO(100) at 225 °C and prepared for TEM by ion-beam milling of a thinned sample from the substrate side. The TEM picture was made using a Philips EM400 TEM at 120 kV. The most prominent features of the picture are the dark curved bands, sometimes showing a couple of fringes, which were identified as APBs by tilting experiments. The picture was taken using a number of diffraction beams in the center of reciprocal space. Apart from the (000) beam, spinel-specific {220} beams were also included. The condition for a high contrast of the APB with respect to the ordered domains is that $\mathbf{R}.\mathbf{g} \neq n$, where n is an integer and $\mathbf{g}$ the reciprocal lattice vector of the diffraction beam used to make the picture.[8] For a (220) beam this condition implies that only the APBs for out-of-plane shift vectors can be observed. The dark bands, therefore, are APBs with shift vectors of the type $1/4a[011]$. In addition to the strong contrast features, some narrow faint lines are visible. These lines are most likely related to anti-phase boundaries as well, because they connect kinks in the dark bands. They probably correspond to the ''forbidden'' in-plane APBs. A striking difference between Fig. 2 and the TEM pictures of Margulies *et al.* is the very different APB density. From Fig. 2 a boundary length per unit area of $6.8\times10^{-3}\,\mathrm{nm}^{-1}$ is determined, which corresponds to an average domain size of about 300 nm. Only out-of-plane APBs were considered in order to compare our results with the number determined for sputtered samples, which is an order of magnitude lower (27.5 nm).[2] This large difference is probably connected to the very different preparation conditions, which leads to a very different nucleation density of Fe_3O_4 islands. Our sample was made by oxygen-MBE at 225 °C, whereas Margulies *et al.* used sputter deposition at a very high substrate temperature of 500 °C.

An important consequence of the existence of shifted structural domains is the drastic change of the local magnetic coupling at the APB.[2,3] In bulk magnetite the dominating magnetic coupling is the antiferromagnetic (AF) superexchange interaction between neighboring *A*- and *B*-site cations. The coupling between *B*-site cations is effectively ferromagnetic. At most APBs, however, a new and strong interaction between *B*-site cations becomes important, i.e., a 180° super exchange interaction. Margulies *et al.* argue that the APB may become immobile magnetic domain walls. A magnetic field can only decrease the width of these pinned domain walls, making it very hard to fully saturate the film. The reduction of the magnetization by these domain walls is

$$\Delta M = \rho_w \gamma / H, \tag{1}$$

ρ_w being the APB density and H the external magnetic field. In a simple model[9,10] the domain wall energy per unit area γ can be calculated, assuming an AF coupling across the domain boundary and neglecting magneto-crystalline anisotropy,

$$\Delta M = C\rho_w (AM_s/H)^{1/2} \equiv M_s b H^{-1/2}, \tag{2}$$

where A is the exchange stiffness constant, M_s is the saturation magnetization, and C is a constant. Equation (2) constitutes a direct relation between the APB density and the saturation behavior. If the low density of APBs found in the sample of Fig. 2 is representative for our samples, it follows that saturation should be reached much faster than in the samples of Refs. 1 and 2. Inspection of previously published data[4,11] confirms this conclusion. A fit of Eq. (2) to the magnetization data for the 30.5 nm sample grown by NO_2-assisted MBE of Ref. 11 gives, for instance, a value for b of 4.6 $(\mathrm{Oe})^{1/2}$. This fit is given in Fig. 3. Care should be exercised with the interpretation of this b value, as small changes in the fitted M_s value easily give a 30%–50% variation in b. A similar value of 8.8 $(\mathrm{Oe})^{1/2}$ is reported for a 30 nm sample grown by oxygen MBE.[12] These values are smaller than the values, which can be deduced from the data of Ref. 2 for 500 nm thick samples. However, the difference is not an order of magnitude as expected based on the above model.

Similarly, a variation in the APB density with growth may account for the difference in the M_s value at 4400 kA/m between [111] and [100] oriented Fe_3O_4/CoO bilayers, which in some cases were grown simultaneously.[13,14] For [100] oriented bilayers the observed M_s at 5 K is 476 ± 49 kA/m,[14] whereas this value is only 363 ± 20 kA/m for

simultaneously grown [111] oriented bilayers. A difference in nucleation behavior between growth on a neutral CoO(100) surface and a polar CoO(111) surface and the ensuing difference in APB density seems a natural explanation, as it was verified that stoichiometric Fe_3O_4 was grown.[12,15]

The actual nature of the magnetic coupling over the APB will be undoubtedly much more complicated than suggested by the simple model cited above. Since the boundaries are formed during the coalescence of islands, the APBs will have curved shapes and little preferred orientation, as is evident from Fig. 1. In addition, the cation structure near the boundaries is likely to be rather disordered. A perfect APB, obtained by terminating domains having an ordered spinel structure at a straight boundary, usually will be chemically unstable due to charge pileup. Therefore, one could expect that in general the cations will be redistributed to achieve local charge neutrality. As stated in the beginning of this section, at the APB a new type of magnetic interaction comes into play, i.e., an antiferromagnetic, oxygen mediated 180° super exchange coupling between *B*-site ions. This suggests that the coupling between neighboring domains will be antiferromagnetic as well. However, the local spin arrangement will be largely frustrated due to the above mentioned disorder, and the overall effective coupling between neighboring domains will be strongly reduced. The motional narrowing of the Mössbauer spectra of ultrathin layers (1.8 and 3.5 nm) in fact indicates that the domains are effectively decoupled from one another.[3] Also, samples as thick as 5 nm and magnetized at low *T*, loose their remanent magnetization completely when heated to room temperature. This behavior has been explained by assuming superparamagnetic behavior of the anti-phase domains, i.e., on the time scale of the measurement, the magnetic moments of the individual domains fluctuate rapidly between different orientations. It is likely that the barrier for rotation of the magnetic moments is determined by the residual domain wall coupling. The experimental maximum barrier height for the 1.8 nm film was 0.1 eV, which is a tiny fraction of the maximum possible exchange interaction over the boundary (3 eV per nm of APB[3]). The third anomaly mentioned in the introduction, i.e., the apparent reduction of the saturation magnetization for ultrathin layers, has been modeled by assuming a magnetically inactive interface layer of 0.7 nm.[4] However, by using Mössbauer probe layers enriched with ^{57}Fe, it has been shown that the magnetic structure at the interfaces is very similar to that of the interior of the layer.[3] This result has been confirmed recently.[12] Field-dependent Mössbauer experiments in this study suggest that the random zero-field magnetic moment distribution is only gradually aligned with the applied field. Alternatively, one could explain the magnetically inactive layer by the above mentioned superparamagnetic behavior for ultrathin films. Since in a magnetic field the larger domains can still be magnetized, but the smaller ones cannot, the magnetization is reduced. For extremely thin samples (<5 nm) the blocking temperature has been found to drop even below room temperature, yielding a saturation magnetization which is zero at room temperature.[3]

Finally, from Mössbauer experiments the local magnetic moments in zero field are found to be out of plane,[1,3,5] which is striking, as shape anisotropy is expected to confine the magnetic moments to the plane of the film. It is likely that this phenomenon is related to the APB as well. To reduce magnetostatic interaction, antiferromagnetically coupled neighboring spins at the boundary will prefer to be parallel to the out-of-plane APB. On the other hand, the same pair of antiparallel spins likes to be perpendicular to a local magnetic field. In the absence of an external magnetic field this will be the in-plane anisotropy field. To satisfy both requirements simultaneously, the spins at and close to the boundary will point in out-of-plane directions.

III. CONCLUSIONS

TEM images show that APBs also occur in MBE-grown samples. However, the domain boundary density is much lower than in sputtered films, due to differences in preparation conditions. The slow saturation behavior and the super paramagnetism of ultrathin layers can both be understood, if it is assumed that the magnetic coupling at the APB is disturbed. The coupling strength must be reduced by one to two orders of magnitude in order to explain the low barriers for the fluctuation of the super paramagnetic domains. It is suggested that the APBs are disordered over a finite width, leading to a noncollinear and strongly reduced coupling. Although it seems evident that the APBs are responsible for most of the anomalous behavior of thin Fe_3O_4 films, further investigations are necessary to confirm this relationship and to uncover the real nature of the magnetic structure of the APBs as well as the growth related factors determining the ABP density.

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