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In-plane magnetization of an ultrathin film of $Fe_3O_4(111)$ grown epitaxially on Pt(111)

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The magnetic properties of an eight-monolayer $Fe_3O_4(111)$ film grown epitaxially on Pt(111) have been studied by the magneto-optic Kerr effect (MOKE) and conversion electron Mössbauer spectroscopy. The MOKE results indicate that a saturation of the magnetization is achieved with a field of about 500 Oe. In zero field the magnetization remains saturated. Apart from a paramagnetic contribution of 11%, which is interpreted as originating from the interface layer, the Mössbauer spectrum is identical to that of bulk Fe_3O_4. Furthermore, the data indicate that all the magnetic moments are in the plane of the film. [S0163-1829(98)50642-X]

Understanding of ultrathin ferromagnetic structures has increased rapidly in recent years. Interest in these systems derives from the unique fundamental properties, for instance two-dimensional magnetism, as well as the potential for new applications, particularly in information storage devices. The majority of research has focused on the properties of ferromagnetic metal overlayers on nonmagnetic substrates. More recently, however, thin iron oxide films have emerged as promising candidates for high-density magnetic recording media due to their superior chemical and magnetic stabilities.

The scientific and technological importance of spinel iron oxides has motivated numerous investigations of their structural and magnetic properties.[1–13] Epitaxial Fe_3O_4 films have been grown on various substrates including MgO(100),[1–8] MgO(110),[6,7] α-$Al_2O_3(0001)$,[7,9–11] $MgAl_2O_4$,[5,7] and $SrTiO_3$.[5] Unfortunately, most of these films have exhibited anomalous or undesired magnetic properties. The anomalous behavior includes unsaturated magnetization at applied fields as large as 70 kOe (Ref. 7) as well as out-of-plane magnetic moments. These properties have been associated with structural defects.[4] Recently, it has been reported that well ordered ultrathin epitaxial $Fe_3O_4(111)$ films can be grown on Pt(111).[14–17] In this paper we focus on measurements of the magnetic properties of such a film using the magneto-optic Kerr effect (MOKE) and conversion electron Mössbauer spectroscopy (CEMS).

The well-known phenomenon of rapid electron hopping in Fe_3O_4, which creates ''$Fe^{2.5+}$'' ions above the Verwey transition temperature of about 120 K, controls the intrinsic electrical properties. The magnetic properties, on the other hand, are known to depend critically on the structural order as well as the stoichiometry. For an ultrathin film it should be possible to control these parameters as well as obtaining reduced dimensionality. This allows for the development of films with unique properties, which may potentially be tailored to specific applications. Here we present evidence of a complete in-plane ferrimagnetic alignment of magnetic moments in a metal oxide ultrathin film.

A film of $^{57}Fe_3O_4$ was grown on a clean and ordered Pt(111) surface. The substrate was cleaned by cycles of 1 keV Ar^+ sputtering and annealing in oxygen at a pressure of 2×10^{-6} mbar and a temperature of 840 K with subsequent annealing in UHV at 870 K. A clean and ordered 1×1 Pt surface was evidenced by low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) measurements. The iron evaporation rate was calibrated by means of Fe/Pt AES peak ratios obtained after evaporating at room temperature without oxidizing. Iron oxide films were grown by first depositing a monolayer (ML) of high-purity ^{57}Fe and then oxidizing at a pressure of 1×10^{-6} mbar and a temperature of 840 K. It was found that higher oxidation temperatures resulted in island growth after the first 1–2 layers, consistent with earlier reports.[18] This Fe deposition/840 K oxidation procedure was repeated a further seven times to form a continuous film. We will in the following refer to the resulting overlayer as an 8-ML oxide film by analogy with earlier studies.[14,15] At this thickness, a sharp hexagonal LEED pattern was observed which had a 2×2 periodicity with respect to the substrate. An example is reproduced in Fig. 1. This, along with AES peak ratios, is consistent with the formation of an epitaxial film of $Fe_3O_4(111)$.[14–17] The sample could be magnetized by passing a current through *in situ* magnetizing coils. The magnetic field generated by the coil was calculated, as well as measured using a Hall probe, both methods yielding the same result.

The MOKE measurements were performed in the longitudinal mode with the magnetic field along the [110] direction *in situ* at room temperature by ramping the current through the coils while monitoring the rotation of linearly polarized light admitted through a vacuum window, reflected at the $^{57}Fe_3O_4$ film, and analyzed through another window. The incident light was modulated by means of a linear polarizer and a photo-elastic modulator. The reflected light was then analyzed by means of a linear polarizer, a photodiode, and lock-in techniques. MOKE measurements were also performed following the CEMS measurements to confirm that

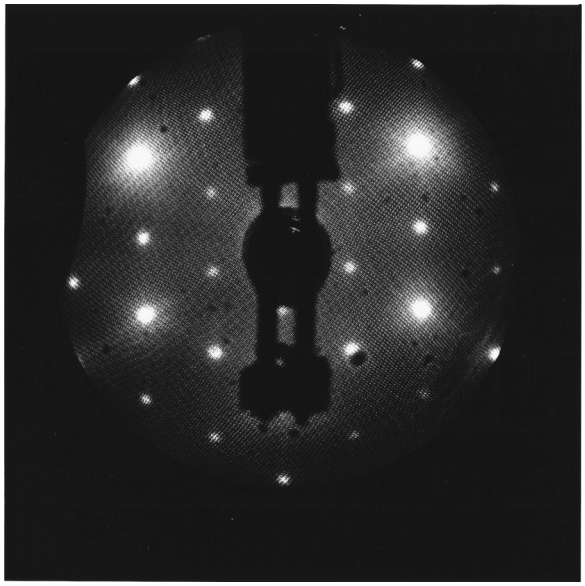

FIG. 1. LEED pattern of the 8-ML Fe_3O_4(111) film taken at 91 eV. The horizontal direction is parallel to [110].

the magnetic hysteresis loop had not been altered during the course of the CEMS measurements.

The CEMS measurements of the film were performed *ex situ* without capping the surface. Tests were carried out to investigate any effect of atmospheric contamination. Changes to neither the structure and cleanliness nor the magnetic hysteresis loops could be detected with LEED, AES, or MOKE after exposure of the film to atmosphere. The CEMS spectrum was recorded at 293 K in a geometry where the sample surface normal was parallel to the gamma ray beam within a He/CH_4 flow proportional counter. This conventional spectrometer incorporated a 30 mCi ^{57}Co in Rh source and a double ramp vibration wave form so that the folded spectrum appeared on a flat background. The spectrometer was calibrated using a 25 μm foil of iron and isomer shift values are quoted relative to Fe at 293 K.

A MOKE hysteresis loop of the 8-ML Fe_3O_4 film recorded *in situ* in the longitudinal geometry is shown in Fig. 2. It can be seen that the magnetization is more or less saturated at an applied field of about 500 Oe. The application of short magnetizing pulses of about 1500 Oe did not increase the magnetization over that observed at 500 Oe. At zero applied field the magnetization remains saturated. The coercive field is about 200 Oe.

The CEMS spectrum is shown in Fig. 3. It is seen to be well fitted by three magnetic sextet components and a nonmagnetic singlet. The hyperfine parameters of the fitted components are listed in Table I. The magnetic components exhibit hyperfine fields and isomer shifts which are within the range of values reported for bulk Fe_3O_4 at room temperature.[19,20] By reference to the interpretation of bulk Fe_3O_4 data,[19,20] component *A* in Fig. 3 and Table I, is identified with Fe^{3+} ions in the tetrahedral sites and B_1 and B_2 with inequivalent $Fe^{2.5+}$ ions[19,20] on octahedral sites. The values of $R=4$ (intensity of lines 2 and 5)/(intensity of lines 3 and 4) for each magnetic sextet component define the spin direction as completely in plane. These findings are in contrast with the results from Fe_3O_4 films grown on MgO,[7]

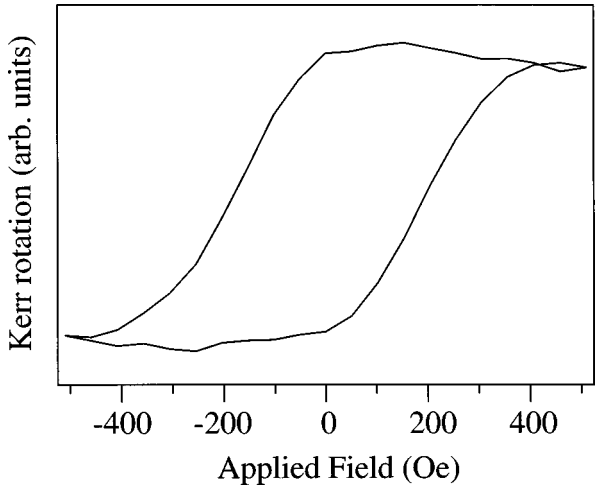

FIG. 2. MOKE hysteresis loop recorded in the longitudinal geometry at 293 K from an 8-ML epitaxial film of Fe_3O_4(111) on Pt(111).

where a maximum *R* value ($2p$ in Ref. 7) of 3.2 is reported and hence the spins are partly out of plane. Moreover, the relative occupancy of the *A* and *B* sites is $(0.75\pm0.10):1$ in our ultrathin film whereas it is 1:2 in the thicker films formed in Ref. 7 and in bulk Fe_3O_4.[19,20] The discrepancy can be explained by the fact that the *A* and *B* sites are situated in separate layers along the [111] direction of the Fe_3O_4 lattice.[15] Because of the limited number of Fe layers in the ultrathin film it is possible to have a larger fraction of *A* sites than in the infinite lattice.

The nonmagnetic singlet component *C* is not seen in bulk Fe_3O_4, suggesting that it may arise from Fe atoms at the Fe_3O_4/Pt interface. The value of isomer shift for this component agrees with the value of 0.355 mm/s observed for Fe in a Pt matrix.[21] The 11% relative area of this component is consistent with a structure where the first iron layer is paramagnetic at room temperature. While we cannot exclude other origins of the paramagnetic singlet, such as segregation of Fe into the Pt substrate or dissolved Fe in the Fe_3O_4 film, our observations are in line with earlier studies which concluded that the first monolayer of iron oxide grown on Pt(111) has the FeO stoichiometry.[14,18] Since the Néel temperature of the bulk antiferromagnet FeO is 198 K, we inter-

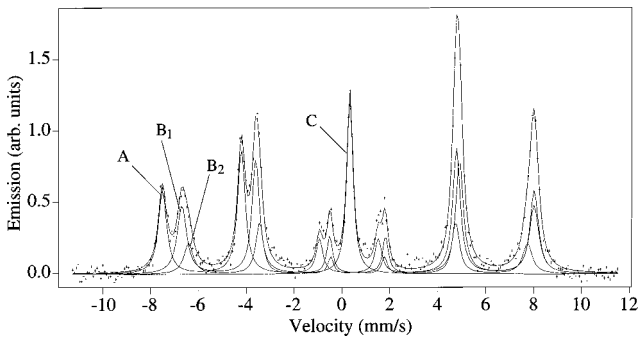

FIG. 3. Mössbauer spectrum recorded at 293 K from 8-ML Fe_3O_4(111) on Pt(111). The spectrum is fitted with three magnetic sextet components and one nonmagnetic singlet. The *y*-axis zero refers to the fitted background level. Hyperfine parameters of the fitted components are listed in Table I and are discussed in the text.

TABLE I. Hyperfine parameters of the fitted components for the Mössbauer spectrum shown in Fig. 2. Errors shown in brackets relate to the least significant digit of the value. The significance of the values is discussed in the text.

Component	Isomer shifts (mm/s)	Quadropole shifts (mm/s)	Linewidth (mm/s)	Hyperfine field (kG)	R	Area (%)
A	0.28 (1)	−0.03 (1)	0.38 (1)	480 (1)	4.0	38 (2)
B_1	0.66 (2)	0.01 (1)	0.38 (1)	455 (2)	4.0	35 (2)
B_2	0.66 (2)	0.01 (1)	0.38 (1)	438 (2)	4.0	16 (2)
C	0.34 (1)	-	0.31 (1)	-	-	11 (1)

pret our observations of a paramagnetic singlet at room temperature as due to a paramagnetic FeO interface layer with subsequent layers behaving as bulk Fe_3O_4.

In summary, we have produced a well ordered ultrathin film of Fe_3O_4 which exhibits the first evidence of a spontaneous and complete in-plane ferrimagnetic alignment of magnetic moments in a metal oxide ultrathin film. In addition, the magnitude of the magnetic moments agree with those observed in bulk Fe_3O_4,[19,20] as evidenced by CEMS spectra. Furthermore, we have detected a paramagnetic contribution of 11% to the intensity in the CEMS spectra. We interpret this as originating from an FeO interface layer between the film and the substrate. Saturation of the magnetization of the Fe_3O_4 film was, as detected by MOKE, achieved with a field of about 500 Oe. The magnetization remained saturated in remanence. This work suggests that ultrathin iron oxide films with identical magnetic properties to bulk samples without defects can be produced. Such films might find applications in high-density magnetic recording.

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