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We report on the finite size effects in the Verwey transition of stress-free magnetite (Fe_3O_4) thin films. A limit thickness of 20 nm is evidenced, above which the transition temperature T_V is constant and close to 120 K (bulk value) and below which no genuine transition is observed. Field Cooled and Zero Field Cooled measurements evidence irreversibilities for all thicknesses. This irreversible behavior abruptly disappears around T_V for the thicker films, when the magnetic anisotropy vanishes. These behaviors are interpreted in terms of assemblies of interacting magnetic Fe_3O_4 clusters, which are smaller than the antiphase domains present in the films.

The Verwey transition has been the subject of a huge research effort for almost a century[1, 2]. The phenomenon is observed in various compounds like Fe_3O_4 [3], Eu_3S_4 [4] and Ti_4O_7 [5]. Though it was first evidenced through anomalies concerning magnetite (Fe_3O_4) specific heat[6] and magnetization [7], the feature mostly associated to the transition is the sharp drop in resistivity observed when heating the sample above the transition temperature T_V ($\simeq$ 120 K for Fe_3O_4). The phenomenon is extremely sensitive to the pressure applied to the sample [8, 9] and to very small variations of stoichiometry [10]. In a pioneering work, Verwey carved the concept of charge ordering [3] in order to explain this peculiar metal-insulator transition observed in materials in which electronic correlations, electron-phonon coupling and kinetic energy of the carriers are of the same order of magnitude [1].

The Verwey transition has given a great impulse to studies of its prototypical material Fe_3O_4, which were mostly carried out on bulk single crystals (for recent reviews, see refs. [1] and [2]). However, growth and study of Fe_3O_4 thin films has recently gained momentum given its potential interest for spintronics [11, 12] triggered by the prediction of the total spin polarization (half-metallicity) of the compound[13]. Exploring this potential use requires that Fe_3O_4 thin films be part of multilayers later patterned into devices like spin valves and magnetic tunnel junctions [14]. Studies on the Verwey transition through transport and magnetism measurements then provide a simple, non destructive way of studying Fe_3O_4 independently of the other parts of the device and of checking that it has not been affected during the whole process.

From a more fundamental point of view, the study of the Verwey transition of nanometric objects can also unravel finite size effects. However, the studies published so far on the Verwey transition of Fe_3O_4 thin films were carried out on stressed samples given the small lattice mismatch with the substrate (MgO [15, 16, 17, 18, 19, 20, 21, 22], $MgAl_2O_4$ [18, 22, 23] or $ZnFe_2O_4$[23]). Epitaxy thus create an interplay between strain and film thickness h, the films adopting the lattice parameter of the substrate up to a substrate-dependant critical thickness and relaxing continuously afterward. The continuous decrease of T_V with decreasing thickness below $h \simeq 200$ nm has thus been ascribed to epitaxial stress [17]. Relaxed films are then required in order to study the influence of the film thickness on the Verwey transition. Besides, a superparamgnetic behavior has been reported [24, 25] for very thin films ($h \leq 5$ nm), which has been ascribed to the presence of antiphase boundaries (APBs) in the samples. These defects are indeed observed regardless of the substrate used [15], the mean antiphase domain (APD) size, typically a few tens of nm, evolving [26, 27] as $h^{1/2}$. A second finite lengthscale comes into play when dealing with Fe_3O_4 epitaxial thin films. The aim of this paper is to unravel finite size effects in the Verwey transition of Fe_3O_4 thin films by studying well characterized, stress-free samples, focusing on the low thickness ($h < 50$ nm) regime.

Fe_3O_4 (111) thin films were grown onto α-Al_2O_3 (0001) substrates in a Molecular Beam Epitaxy setup dedicated to oxide thin films elaboration by co-deposition of atomic oxygen and metal, which is described in details elsewhere [28, 29]. Deposition rates are evaluated *in situ* using a quartz balance and also *ex situ* by X-ray reflectivity ; the precision on the thickness of the Fe_3O_4 layers is about 5%. X-ray photoelectron spectra at the Fe 2*p* photoemission line recorded *in situ* for each film were typical of stoichiometric Fe_3O_4. Punctual X-ray magnetic circular dichroism measurement [12] also showed no sign of deviation from perfect magnetite for the studied film.

Full relaxation of the films is expected even for very thin films given the large lattice mismatch (and hence the small critical thickness) between Fe_3O_4 and α-Al_2O_3 (8 %) . This relaxation has been evidenced by real-time RHEED (Reflection High Energy Electron Diffraction)[28], even though a dilation is observed during the first growth stages . The latter phenomenon is purely dynamic, since transmission electron micrographs show no sign of a gradient of lattice parameter after the end of sample growth, and all the films presented in this paper are fully relaxed indeed. The growth is 2D as evidenced by the RHEED patterns recorded during depo-

sition, even though a few films showed additional spots aside from the streaks characteristic of 2D growth (unless otherwise stated, the RHEED patterns of the samples considered in the following exhibited only well defined streaks). The mean antiphase domain size does evolve as $h^{1/2}$ and is about 25 nm for a 15-nm thick film[27].

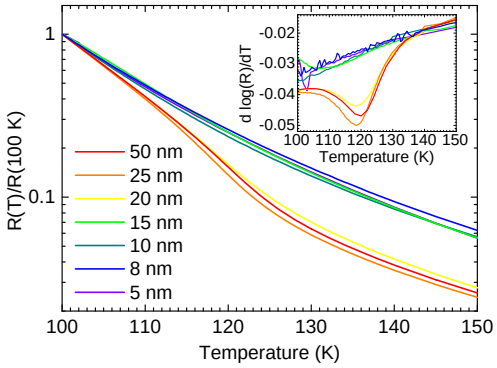

FIG. 1: (color online) Transport measurements on Fe_3O_4 thin films. Resistivities have been normalized with respect to ρ(100K) for the sake of clarity. The inset shows the logarithmic derivative of the resistivity, which shows the second order Verwey transition as a minimum for films thicker than 20 nm

Two- and four-probe transport measurements were carried out within a Quantum Design physical properties measurements system, using either the device electronics or some external apparatus designed for high resistance measurements (up to 10 GΩ). Measurements were performed during sample warming at a very slow rate (less than 0.1 K/min in the transition region) in order to ensure a complete thermalization of the sample. $R(T)$ measurements reported here were realized under zero magnetic field though we checked that the results are not affected by the application of constant fields up to 70 kOe.

Resistivity vs temperature measurements for seven samples are displayed in figure 1. As already reported for stressed Fe_3O_4 thin films [21, 22], the Verwey transition is second order for the Fe_3O_4 films grown on α-Al_2O_3, and not first order as in the case of single crystals. The Verwey temperature T_V is thus defined as the minimum of the logarithmic derivative of the resistance. In sharp contrast to the continuous variation of T_V reported for strained samples, the films for which RHEED patterns indicated purely 2D growth fall into two categories as a function of film thickness: those with $h \geq 20$ nm exhibit a clear, rather sharp Verwey transition at a temperature close to 120 K, whereas those with $h < 20$ nm do not show any sign of transition. The few thick films of lesser crystalline quality (for which RHEED patterns show spots aside from streaks) exhibit either a reduced T_V or no transition at all.

Field-Cooled (FC), together with and Zero-Field-

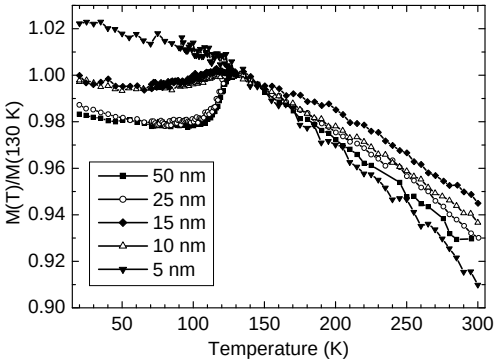

FIG. 2: Field-cooled magnetization of selected Fe_3O_4 thin films. Magnetizations have been normalized with respect to M_{FC} (130K) for the sake of clarity. The Verwey transition appears as a drop of magnetization, readily seen for the 25 nm and 50 nm-thick films. Although no genuine transition exist for the 10-nm thick film, the M_{FC} curve shows a maximum at $T \simeq 125$ K.

Cooled (ZFC) measurements were realized with a superconducting quantum interference device (SQUID) magnetometer. The ZFC curve was acquired first, after AC-demagnetization of the sample at room temperature. M_{FC} corresponds to the reversible part of the magnetization and FC measurements are thus the genuine test of the Verwey transition (M_{ZFC} and its comparison with M_{FC} will be discussed later in this paper). Figure 2 displays some representative examples of FC measurements. The transition appears as a sharp variation of the FC magnetization of the 50- and 25 nm-thick films at 119 K, T_V being defined as the temperature for which the slope of $M_{FC}(T)$ is maximum. The thinnest films ($h < 10$ nm) show no signs of transition. However, FC measurements also evidence an intermediate class of films (10 nm$\leq h \leq$ 15 nm) which do not exhibit a proper transition, but show a broad maximum of M_{FC} at $T \simeq 120$ K. As for transport measurements, T_V is independent of film thickness and close to the bulk value above a treshold thickness. Moreover, both measurements give consistent values of this treshold thickness above which a genuine Verwey transition is observed.

Coercivity was measured as a function of temperature with a vibrating sample magnetometer. A 10 kOe field was applied during cooling to avoid twinning while cooling through T_V [30]. No shift in the hysteresis loops was observed, contrary to what has been reported for Fe_3O_4 (100) films grown on MgO[31]. For all but the thinner films ($h \leq 5$ nm), the coercive field H_c also presents anomalies in the vicinity of 120 K, namely a local minimum followed in the case of the thicker films by a sharp increase when cooling the sample below $T \simeq 120K$, as evidenced by figure 3. This phenomenon is to be linked with the peculiar behavior of Fe_3O_4 anisotropy in this temperature range. Indeed, Fe_3O_4 exhibits an *isotropy point*, *i.e.* a tempera-

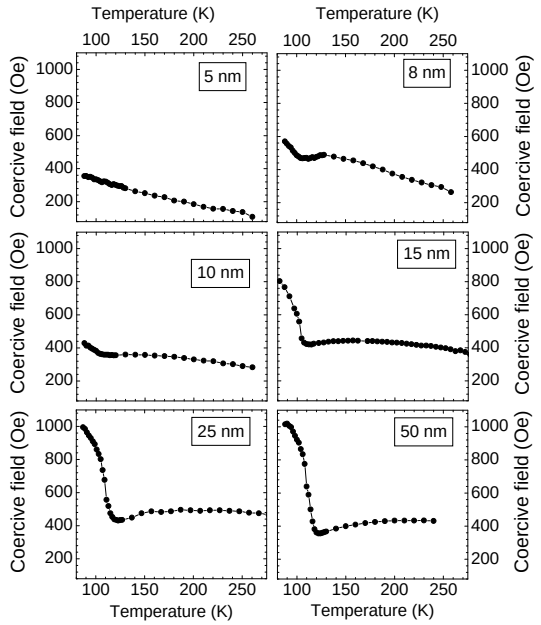

FIG. 3: Coercivity vs temperature curves for various film thicknesses

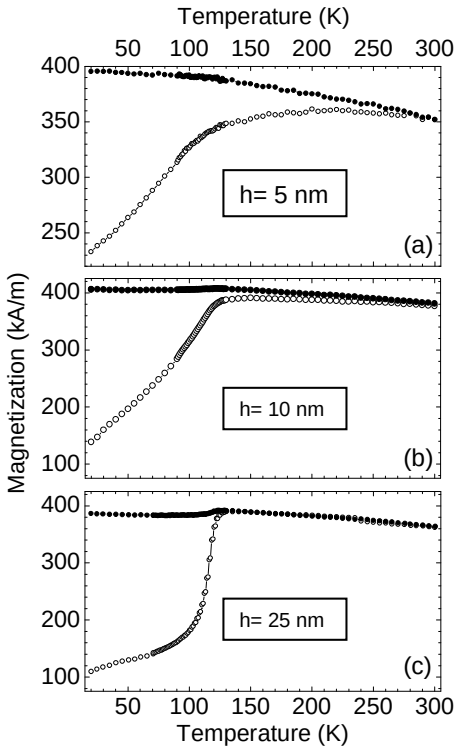

FIG. 4: Field Cooled ($-\bullet-$) and Zero Field Cooled ($-\circ-$) magnetization of selected samples

ture noted T_K (a few K above T_V) for which the magnetic anisotropy vanishes[32]. T_K can also be deduced from the $H_c(T)$ curves, since it corresponds to the coercivity minimum [22]. Fig. 3 shows that all but the thinnest film exhibit a local minimum of H_c, and T_K is indeed found slightly higher than T_V when the Verwey transition does occur ($h \geq 20$ nm), and still above 110 K for samples of intermediate thickness (8 nm $\leq h \leq$ 15 nm).

We now focus on the ZFC measurements, of which relevant examples are displayed in figure 4. A strong separation of the ZFC and FC curves at low temperature is observed for all samples, and is the signature of a frozen magnetic state. In the thinnest samples, the magnetic irreversibilities extend up to at least room temperature (since no control of the oxygen partial pressure was available in the magnetometer, no heating beyond 300 K was attempted to avoid the irreversible transformation of Fe_3O_4 into α-Fe_2O_3). Irreversibilities are observed in the ZFC/FC curves of the thinnest samples for a measurement field of 1kOe which is higher than the coercive field obtained from hysteresis loops (see Fig. 3), suggesting that the zero-field cooled state (established after demagnetization of the sample) is more strongly frozen than the state obtained by decreasing the field from the saturation value. It is likely that the demagnetized zero-field cooled state consists in a microstructure of numerous and strongly pinned magnetic domains.

All samples exhibit a slow increase of the ZFC curve below 100 K (see Fig. 4) which is characteristic of the progressive magnetic unblocking observed in frozen superparamagnetic systems in response to a temperature increase [33] , and the FC curve shows a superparamagnetic-like decrease when heating above 120 K. However, the 25 nm film shows a spectacular rise up of the ZFC magnetization in the 110 K region, where an abrupt decrease of the coercive field is correlatively observed (Fig 3) close to the Verwey transition, slightly below T_K at which anisotropy cancels out. The frozen magnetic domains are suddenly free to relax in this temperature range, as would happen for frozen magnetic nanoparticles whose anisotropy barriers decrease [33]. This phenomenon is only observed for thicker films (h ¿ 20 nm), where the Verwey transition and the coercivity fall off are well marked. The temperature dependence of the ZFC magnetization of the thinner films (which do not exhibit these features) is comparable with that of a frozen superparamagnet in which some large magnetic grains remain blocked at room temperature.

The slope of the high temperature region (150-300 K) of the FC curves can be analyzed in terms of a superparamagnetic Curie-Weiss behavior, in order to roughly estimate the size of the fluctuating magnetic Fe_3O_4 clusters which are involved in the freezing process at lower temperatures. Given the extremely small amount of matter comprised in the samples, and hence the weakness of the signal, no direct measurement of the initial susceptibility could be performed, and we approximate it with the M/H ratio obtained from the FC measurements under

H=1 kOe. We write:

$$\frac{H}{M} \simeq \frac{1}{\chi} = \frac{3k_B(T-\theta)}{\mu_0 N n m_0^2} \quad (1)$$

where N is the density of iron atoms of moment m_0 in Fe_3O_4 , n the number of iron moments strongly coupled in a superparamagnetic Fe_3O_4 cluster, and θ the Curie temperature which corresponds to the inter-cluster interaction energy. For the 7 samples analyzed, we obtain $\theta \simeq -700$ K, and n slowly increasing from 3000 to 5000 when the film thickness varies from 5 to 50 nm. Since the two fitting parameters n and θ depend only weakly on the film thickness, there is no obvious relation between these magnetic entities and the antiphase domains which are observed in Fe_3O_4 epitaxial thin films. The antiphase domains are indeed 1-2 orders of magnitude larger, and their in-plane size has been shown to vary as $h^{1/2}$ [26, 27], (their volume thus varies as h^2). The magnetic Fe_3O_4 clusters which give rise to the observed superparamagnetic behavior should be thought of as a microstructure of the domains or of their boundaries, the exact nature of which remains unclear.

In summary, we report on the Verwey transition on stress-free Fe_3O_4 thin films epitaxially grown onto α-Al_2O_3 as a function of the film thickness h. A limiting thickness is evidenced: the films exhibit a clear Verwey transition at a temperature T_V close to 120 K (which is also the transition temperature of bulk samples) for $h \geq 20$ nm, whereas there is no hint of transition when h is below 10 nm. FC/ZFC measurements show an irreversible behavior for all the films, the sharp variation of the ZFC curve for $h \geq 20$ nm being linked to the variation of the anisotropy, evidenced by the anomalous behavior of the coercivity. These results are interpreted in terms of interacting magnetic Fe_3O_4 clusters smaller than antiphase domains, their size and interactions hardly depending on film thickness.

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