Marco Finazzi, Lamberto Duò, and Franco Ciccacci

# 1.1 Introduction

In the last two decades, the availability of experimental techniques endowed with high sensitivity with respect to the magnetic properties of antiferromagnetic (AFM) materials has motivated a large amount of studies dedicated to the investigation of low-dimensional AFM systems consisting of small particles or films deposited onto either nonmagnetic or ferromagnetic (FM) substrates. Similar to the well-known FM materials, such confined AFM systems are in fact characterized by magnetic properties that, because of interface or size effects, can be considerably different from the ones observed in the bulk [1]. Examples range from the stabilization of exotic AFM ordering to the onset of uniaxial anisotropy in low-dimensional AFM samples. Moreover, systems comprising AFM–FM interfaces represent a world of their own, thanks to their rich phenomenology related to interface exchange coupling.

Finite-size effects in both FM and AFM materials reflect deviations from bulk properties associated with the reduction of the sample dimensions. So-called "intrinsic" effects occur in material systems for which one or more sample dimensions, for example, the thickness of a layer or diameter of a particle, is comparable with the intrinsic correlation length scale of the property being considered. Strongly correlated systems such as AFM oxides are characterized by very short correlation lengths, so intrinsic finite-size effects can be observed only in ultrathin films or nanoparticles. In addition, "surface-related" finite-size effects might be caused by the competition between the properties of atoms in the core of a particle or layer and those at the surface, possibly originating from the reduced coordination number. As an example, surface spins often possess higher magnetocrystal anisotropy than the ones in the sample volume because of the reduced symmetry. "Chemical" or "structural" effects may also arise due to phenomena such as surface segregation, relaxation, or reconstruction. Of course, the environment (the material surrounding the particle or the film substrate) can also dramatically alter the properties of interface atoms through hybridization, strain, or chemical interdiffusion, not to mention the crucial role of exchange in determining the magnetism of systems where an AFM material interacts with an FM partner.

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The high degree of correlation between the magnetic, chemical, structural, and morphologic features obviously makes the preparation and the characterization of high-quality samples a crucial point in any study involving low-dimensional systems (see 2). In this respect, AFM transition-metal (TM) monoxides are often regarded as a privileged reference. The reasons for this choice are manifold. First, these oxides can be grown as high-quality thin films on appropriate substrates and are characterized by a high chemical and mechanical stability. Second, their AFM ordering temperature (Néel temperature  $T_N$ ) is relatively high: to cite two relevant cases,  $T_N = 523$  K for bulk NiO and  $T_N = 291$  K for bulk CoO. In the latter case, the proximity of T<sub>N</sub> to room temperature represents an additional advantage in realizing exchange-biased systems, where field cooling from above to below  $T_N$  is required. Another important feature of TM oxides is their insulating nature resulting from strong inter- and intra-atomic electronic correlations. Their magnetic properties arise as a consequence of the short-range superexchange interaction mediated by the oxygen bonds [2]. Because of the absence of itinerant magnetism associated with conduction electrons, the only long-range magnetic interaction is represented by the dipole-dipole interaction, which can be neglected in many cases. Therefore, from the magnetic point of view, TM oxides can be described in the frame of the Heisenberg or Ising formalism as ensembles of well-localized spins with near-neighbor interactions. Finally, we would like to mention that AFM TM oxides are also considered as model systems for the AFM parent compounds of high  $T_c$ cuprates since, in the latter, the interplay between charge and magnetic ordering is described by the Anderson's superexchange theory, which also governs the magnetic properties of AFM insulators such as NiO or CoO.

In this introductory chapter, we present a survey of the peculiar magnetic phenomena observed in low-dimensional systems based on AFM TM oxides, such as surfaces, thin films, interfaces with magnetic or nonmagnetic materials, and multilayers. We also give an overview of the significant physical phenomena that intervene in determining their origin. The chapter is organized as follows: in Section 1.2 we address finite-size effects on the value of the Néel temperature for AFM oxide particles and thin films. Section 1.3 is dedicated to AFM thin-film magnetic anisotropy and how it is influenced by interaction with a nonmagnetic substrate, while interlayer magnetic coupling and micromagnetic structure at AFM–FM interfaces and multilayers are examined in Sections 1.4 and 1.5, respectively. Finally, Section 1.6 concludes the chapter by discussing applications.

#### 1.2

#### Finite-Size Effects on the Magnetic Ordering Temperature

The reduction of the critical magnetic ordering temperature  $T_{order}$  is a typical finite-size effect in both FM ( $T_{order} = T_C$  = Curie temperature) and AFM ( $T_{order} = T_N$ ) low-dimensional systems. It can be seen as a consequence of the sample asymptotically approaching the conditions at which the Mermin–Wagner theorem applies as its size is progressively reduced. This theorem states that, because of fluctuations, continuous symmetry cannot be spontaneously broken (i.e., the

sample cannot develop long-range FM or AFM order) at finite temperature in systems with short-range interactions in dimensions  $d \leq 2$  [3]. Experiments have evidenced drastic reductions in the magnetic transition temperature  $T_N$  for a variety of AFM oxides in low-dimensional geometries such as CuO nanoparticles [4–7], NiO thin films [8, 9], CoO nanoparticles [10] and films [11, 12], and Co<sub>3</sub>O<sub>4</sub> nanoparticles [13-15], nanotubes [16], and nanowires [17].

In a simple mean-field approach, which assumes  $T_{\rm order}$  to be proportional to the exchange energy density of the particle or thin film, the reduction of the magnetic transition temperature is due to the decrease in the total exchange energy associated with the reduced number of neighboring atoms. In this picture, the system environment is not passive and might contribute to defining the total exchange energy, for instance, by inducing surface magnetic anisotropy via a strain field or by modifying the magnitude of the interface moments and the strength of their mutual coupling through hybridization or other interactions (see below). According to the mean-field model, the variation of  $T_{\text{order}}$  with respect to the bulk value  $T_{\text{order}}(\infty)$ is expected to be proportional to the inverse of the particle size or of the film thickness D. However, this prediction is not consistent with the experimental results, and the reduction in the ordering temperature Torder with size is better described in terms of scaling theories [18], according to which the correlation length of the fluctuations of the AFM order parameter diverges logarithmically with the reduced temperature  $(T - T_{order})/T_{order}$  as the temperature T approaches the magnetic ordering transition  $T_{order}$ . For a system with size D much larger than a characteristic length  $\xi$  describing the spatial extent of the spin-spin coupling, this yields a fractional decrease of  $T_{\text{order}}$  that follows a power-law curve [19]:

$$\frac{T_{\text{order}}(\infty) - T_{\text{order}}(D)}{T_{\text{order}}(\infty)} = \left(\frac{\xi + a}{2D}\right)^{\lambda}$$
(1.1)

where  $\lambda$  is the (constant) shift exponent and *a* is the lattice spacing. For  $D \ll \xi$ ,  $T_{\text{order}}$  is expected to vary *linearly* with respect to *D* [19]:

$$T_{\rm order}(D) = T_{\rm order}(\infty) \frac{D-a}{2\xi}$$
(1.2)

The details of the measured dependence of  $T_{\rm order}$  upon D show large differences over the experimentally investigated systems, suggesting that environment effects play a significant role. Moreover, the value of  $\lambda$  is model-dependent: as anticipated above, one obtains  $\lambda = 1$  in mean-field theory [18], while  $\lambda = 1.4$  or 1.6 for a system described by either the three-dimensional Heisenberg [20] or Ising [21] Hamiltonian, respectively. In practice,  $\xi$  and  $\lambda$  are considered as adjustable parameters that have to be fitted to the experimental data:  $\lambda$  has been found to be close to 1.1 for Co<sub>3</sub>O<sub>4</sub> nanoparticles [15], while  $\lambda \approx 1.5$  for CuO thin films [11],  $\xi$  being of the order of a few nanometers in both cases. A more recent model explicitly considers the disordering effect of the lattice thermal vibrations on the spin-spin coherence length at the transition temperature. It predicts a  $T_{\text{order}}$  dependence on D of the form [22]

$$\frac{T_{\text{order}}(D)}{T_{\text{order}}(\infty)} = e^{-\left(\frac{1-\alpha}{D/D_0-1}\right)}$$
(1.3)

In the previous expression,  $D_0 = 2(3 - d)a$  (with d = 0 for particles, d = 1 for nanorods, and d = 2 for thin films), while  $\alpha = \sigma_s^2(D)/\sigma_v^2(D)$ ,  $\sigma_s$  and  $\sigma_v$  corresponding to the root-mean square average amplitude of the oscillations of atoms at the surface (or interface) and in the volume at the transition temperature, respectively. In this model,  $T_N$  is again expected to depend on the total system–environment interface exchange energy.

The models discussed above can be generalized to low-dimensional systems in interaction with *magnetic* environments. In this case, the total exchange energy density of the low-dimensional sample might be even higher than in the bulk because of interface exchange coupling. In this case  $T_N$  might increase as the sample size is reduced, as observed in NiO/CoO and Fe<sub>3</sub>O<sub>4</sub>/CoO multilayers [8, 23]. Similarly, it has been demonstrated that the magnetic coupling of Co nanoparticles embedded in a CoO matrix leads to a marked improvement in the thermal stability of the moments of the FM nanoparticles, with an increase of almost 2 orders of magnitude in the temperature at which superparamagnetism sets in compared to similar particles in a nonmagnetic medium [24]. An intriguing and not yet understood size-related effect is the dependence of the blocking temperature  $T_B$  upon the AFM layer thickness in exchange-biased AFM–FM multilayers.  $T_B$  is defined as the temperature above which the system does not display any bias, and in Fe<sub>3</sub>O<sub>4</sub>/CoO multilayers it is observed to *decrease* by reducing the CoO layer thickness while  $T_N$ , as mentioned above, *increases* [23].

To further highlight the active role even a nonmagnetic substrate might have in determining the value of  $T_N$  in a thin film, we conclude this section by discussing the case of NiO ultrathin films epitaxially deposited on MgO(001) and Ag(001) single-crystal substrates [25]. Stoichiometric and high-quality NiO films were grown by atomic-oxygen-assisted reactive deposition and capped in situ with a protecting MgO film consisting in 25 monolayers (MLs) that avoided NiO film contamination by the residual gas inside the ultrahigh-vacuum chamber and prevented possible oxygen loss during thermal cycling. NiO and MgO have the same rock-salt crystal structure with a lattice constant of 4.2 and 4.1 Å, respectively, corresponding to a tiny lattice misfit of 0.2%. Ag has a face-centered cubic (fcc) structure with a lattice constant equal 4.09 Å and compared to NiO has a lattice misfit of about 3%. Nevertheless, misfit dislocations are avoided by keeping the film thickness below the critical thickness for strain relaxation (about 30 ML for NiO/Ag) [26]. The magnetic properties of the NiO layer have been investigated with X-ray magnetic linear dichroism (see Chapter 3) performed at the Ni  $L_2$  edge. By plotting the dichroic signal ( $L_2$  ratio) as a function of temperature, as done in Figure 1.1, one obtains a direct measure of the long-range order parameter and of the Néel temperature of the material. Figure 1.1 reports results measured for 3-ML- and 30-ML-thick NiO films on Ag(001) and for a 3-ML-thick NiO film on MgO(001). For the 30-ML NiO/Ag film, an ordering temperature  $T_N = 535$  K in thus measured, which is close to the bulk value of 523 K [27]. Apparently, the 30-ML NiO/Ag film is already thick enough to act as the bulk oxide and is not affected any longer by the underlying Ag substrate [28, 29]. Figure 1.1 also suggests that there is no magnetic order in the 3-ML NiO/MgO sample in the measured temperature range, denoting



Figure 1.1 Temperature-dependent Ni linear dichroism signal ( $L_2$  ratio) of (a) 30-ML NiO/Ag(100) and (b) 3-ML NiO/Ag(100) and 3-ML NiO/MgO(100). Reprinted figure with permission from [25]. © 2009, by the American Physical Society.

a strong finite-size-induced reduction of  $T_N$  that can be interpreted as discussed earlier in this section. Conversely, the Néel temperature of the 3-ML NiO/Ag film is  $T_N = 390$  K, at least a factor of 10 higher than in the 3-ML NiO/MgO sample. It is important to notice that the NiO/Ag and NiO/MgO films are essentially identical as far as the NiO part is concerned (same thickness, crystal quality, interface roughness), except for the different value of the lattice mismatch with respect to the substrate. The origin of such a strongly different  $T_N$  value in NiO/MgO and NiO/Ag must thus be external to the NiO film itself and should be looked for in the different types of interactions at the NiO/MgO and NiO/Ag interfaces. To this purpose, we have to consider how the superexchange interactions in the NiO films can be modified by the presence of the substrate. The value of the superexchange coupling constant *J* in a system subjected to charge fluctuations described by the Hubbard energy *U* and the cation–anion charge-transfer energy  $\Delta$  [30] is given by the following expression [31–33]:

$$J = \frac{2t^2}{\Delta^2} \left( \frac{1}{U} + \frac{1}{\Delta} \right) \tag{1.4}$$

with *t* being the anion 2p-cation 3d transfer integral. The value of *J* can be altered in three ways by the interaction with the substrate, resulting in a consequent modification of  $T_N$ .

The first mechanism refers to the prediction that a medium with a high dielectric polarizability should provide an effective screening for various charge excitations in a nearby located material [34]. Such a screening effect on the band gap, the Hubbard energy U, and the charge-transfer energy  $\Delta$  has indeed been experimentally confirmed in C<sub>60</sub>/Ag [35] and MgO/Ag [28, 29, 36]. According to this expectation, the observed higher  $T_N$  value for NiO/Ag compared to NiO/MgO would be associated to the conducting nature of the Ag substrate with respect to the insulating character of MgO, leading, in agreement with Eq. (1.4), to a higher superexchange coupling constant J as a result of the reduction of U and  $\Delta$  by image-charge screening.

A second explanation considers the different strain state induced in the NiO overlayer by the Ag or MgO substrate. By modifying the in-plane interatomic distance, strain influences the overlap between adjacent orbitals and the value of the transfer integral *t*, affecting the value of *J* and hence  $T_N$ . We recall that the application of hydrostatic pressure is known to enhance  $T_N$  in TM oxides [37–40]. However, the theoretical [38] and experimental [39, 40] dependence of *J* and  $T_N$  on the lattice parameter variation is too weak to justify the 10-fold increase of  $T_N$  in NiO/Ag with respect to NiO/MgO as due to the different strain state. Moreover, the strain in an epitaxial layer is nonisotropic and one could expect that the lattice-spacing effect on  $T_N$ will be smaller than the one in an isotropically compressed system, since, in the first case, the change in the interatomic spacing along the surface normal is generally opposite to that in the film plane. Indeed, it has been experimentally shown that for NiO and CoO films on MgO uniaxial strain up to 2% has a negligible effect on  $T_N$  [8].

Finally, interface hybridization might represent a third mechanism according to which the substrate might be capable of influencing  $T_N$ . In this respect, we note that density-functional band-structure calculations on both free-standing and Ag(001)-supported ultrathin NiO films find that the superexchange constant J of a 3-ML-thick film should hardly be affected by a nearby substrate [41, 42]. These arguments leave screening effects as the only possible phenomenon that is able to account for the large value of the Néel temperature in 3-ML NiO/Ag thin films, suggesting at the same time an effective method to counterbalance finite-size-related reduction of critical temperatures in oxide systems.

#### 1.3

#### **AFM Anisotropy**

As mentioned in the previous section, even a nonmagnetic substrate might play an active role in determining the value of  $T_N$  in a thin film. In this section, we discuss how the substrate can also influence the magnetic anisotropy of an AFM overlayer. We limit the discussion to nonmagnetic substrates, leaving AFM–FM coupled layers to the next section.

Well known and long-studied in FM systems, magnetic anisotropy is a phenomenon that has been unveiled only quite recently in AFM thin films. For instance, while the surface magnetic structure of cleaved NiO(001) single crystals is said to be bulk terminated [43], NiO(001) thin layers (less than 20 ML) epitaxially grown on MgO(001) exhibit an out-of plane uniaxial anisotropy [9]. On the other hand, the AFM anisotropy of epitaxial NiO/Ag(001) is found to depend on the NiO thickness: for 30-ML-thick NiO/Ag films, AFM domains with easy axis closer to the surface normal are favored, while 3-ML NiO/Ag are characterized by in-plane AFM anisotropy [44]. CoO films display local moments with magnitude and orientation strongly dependent on the strain induced by the substrate: the magnetic moments in CoO/MnO(001) are oriented out of plane while those in CoO/Ag(001) are in-plane [45]. Hereafter, we discuss the possible sources of AFM magnetic anisotropy.

#### 1.3.1

# Magnetocrystal Anisotropy

While a 3d isolated ion is described by a Hamiltonian that has spherical symmetry, the same ion embedded in a crystal is subjected to the crystal field resulting from the interactions of the electrons belonging to each ion with the surrounding atoms. If this crystal field is strong enough, the orbital degeneracy is completely removed and the ground state is an orbital singlet (the orbital momentum is "quenched") [46]. In these conditions, spin represents the only contribution to the total magnetic moment of the ion, and is, to first approximation, completely decoupled from the lattice. In other words, the system does not develop any magnetic anisotropy. However, if the crystal field is not too large, the spin-orbit interaction, which is proportional to  $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$  ( $\hat{\mathbf{L}}$  = total orbital momentum operator;  $\hat{\mathbf{S}}$  = total spin operator), prevents the quenching of the orbital momentum and couples the spin to the lattice, establishing magnetic anisotropy [46]. In a cubic ionic 3d compound, the crystal field can be considered as a small perturbation (of the order of  $10^4$  K) with respect to the Coulomb interactions between the electrons occupying the d-shell, but is considerably larger than the spin-orbit interaction (about 100 K). Sizable anisotropy can thus emerge only when the symmetry of the lattice and the degeneracy of the ground state are further reduced by a small perturbation. The above-mentioned anisotropy observed in CoO strained films can be explained in this frame (see also Chapter 4): the tetragonal distortion imposed by the substrate further splits the partially occupied  $t_{2g}$  orbitals that constitute the ground state resulting from the application of a cubic crystal-field to the 3d shell. The sign of the splitting depends on the type of tetragonal strain (compressive or extensive) and determines whether the CoO spins will preferentially align in-plane or out of plane [45].

# 1.3.2

# **Dipolar Anisotropy**

Long-range magnetic dipole-dipole interactions have been suggested to play an important role in determining the bulk AFM structure of TM monoxides such as MnO and NiO, where the magnetocrystal anisotropy is expected to vanish [47].

In MnO, this happens because the d-shell electronic configuration of the Mn<sup>2+</sup> ion is 3d<sup>5</sup>, corresponding to an orbital singlet ground state even in the isolated ion. The case of NiO is different: the Ni<sup>2+</sup> 3d fundamental state is characterized by completely filled  $t_{2g}$  orbitals and partially occupied  $e_g$  orbitals. Now,  $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$  does not have matrix elements coupling different  $e_g$  states, implying that the spin–orbit interaction is also negligible for NiO.

The fcc lattice formed by the cations in TM monoxides can be viewed as a combination of four simple cubic lattices. In each sublattice, the moments are forced by the superexchange interaction to align ferromagnetically within {111} planes, while adjacent {111} planes are coupled antiferromagnetically. The superexchange interaction does not couple the magnetic moments of cations in different simple cubic sublattices since these are connected by  $90^{\circ}$  oxygen bonds. The relative orientations of the four lattices with respect to each other and to the crystallographic axes are instead imposed by anisotropic interactions. In MnO and NiO, the larger source of anisotropy is provided by the magnetic dipole interaction, which favors a collinear alignment between the sublattices, resulting in the so-called type-II AFM order. These are characterized by AFM domains (T-domains) in which the moments form FM foils parallel to one of the four equivalent {111} planes of the fcc lattice [47], with the spin aligned in the plane of the foil [47]. This type of AFM ordering is further stabilized by a rhombohedral distortion in the direction perpendicular to the foils caused by magnetostriction. Inside each (111) foil, the spin is driven to align along one of the three equivalent [112] directions (giving three equivalent so-called S-domains) by sources of smaller anisotropy (see Figure 1.2).

The removal of translation symmetry and the possible presence of substrate -induced strain reduce the symmetry of the bulk and cause AFM anisotropy. Since in an AFM material there is no net magnetization, one can apply first-order



Figure 1.2 Collinear arrangement of magnetic cations in MnO and NiO. A domain with (111) ferromagnetic foils and moments parallel or antiparallel to the  $[11\overline{2}]$  direction is shown.

perturbation theory [48] to evaluate the effects of the AFM film finite thickness  $\tau$  and of the tetragonal strain  $\varepsilon = (c/a) - 1$  (*c* and *a* being the out-of-plane and in-plane lattice parameters, respectively). Inclusion of tetragonal strain into a bulk AFM MnO or NiO lattice energetically favors *S*-domains with main spin component *perpendicular* ( $S_{\perp}$ ) to the strain axis for  $\varepsilon < 0$  (compression) and *S*-domains with main spin component *parallel* ( $S_{\parallel}$ ) to the strain axis for  $\varepsilon > 0$  (expansion). In uniformly strained films, this effect coexists with a thickness-dependent perturbation to the total dipolar anisotropy, which stabilizes  $S_{\parallel}$  domains and in-plane anisotropy [48]. At variance with the well-known shape anisotropy of FM thin films, which is proportional to the film volume, this AFM shape anisotropy is proportional to  $\tau^{-1}$  [48]. In the original work [25], the thickness-dependent AFM anisotropy experimentally observed in NiO/Ag(001) films was indeed interpreted as being a consequence of AFM dipolar anisotropy.

# 1.4

# Interlayer Coupling in AFM-FM Bilayers and Multilayers

AFM surfaces are said to be compensated when the surface magnetization of the AFM material is null. In TM monoxides, which are characterized by an AFM order similar to that shown in Figure 1.2, {001} and {011} planes are nominally compensated, while the {111} surfaces are totally uncompensated. The latter, however, exposes the same chemical species and a net electric charge (TM oxides are highly ionic compounds). For this reason, the {111} surfaces are unstable and tend to reconstruct. At compensated AFM-FM interfaces, the exchange interaction is strongly frustrated. Frustration can be partially released by the presence of defects (chemical interdiffusion, atomic steps, missing atoms, dislocations), which make the interface partially uncompensated, at least on a local scale. Defects are instead a source of frustration at nominal totally uncompensated interfaces. There is a general consensus in the scientific community about the importance of considering this interplay between frustration and defects to understand magnetic properties such as exchange bias, interlayer coupling, and micromagnetic structure of AFM-FM bilayers and multilayers. We omit to discuss exchange bias in this introductory chapter, since this argument is extensively treated in this book (see Chapters 5-7). We concentrate instead, in Section 1.4.1, on interlayer coupling, while the micromagnetic structure at AFM-FM interfaces is the subject of Section 1.4.2.

#### 1.4.1

### AFM-FM Interface Coupling

Micromagnetic calculations based on energy minimization show that the ground-state configuration of an ideal magnetically compensated AFM–FM interface corresponds to a perpendicular orientation of the bulk FM moments relative to the AFM magnetic easy axis direction, an arrangement known as *spin-flop state* [49]. This configuration is stable since the magnetic moments both



Figure 1.3 Diagram describing the regions in the parameter space for which the AFM anisotropy axis is either collinear or orthogo-AFM-FM bilayer with the characteristics of NiO/Fe(001). Hex represents the magnitude of the effective exchange field of magnetically active defects at the AFM-FM interface, the American Physical Society. while u is the fraction of interface atomic

sites occupied by such defects: u = 0 for an ideal compensated interface; u = 1 for a totally uncompensated interface. JAFM and m nal to the FM magnetization, obtained for an are the values of the superexchange coupling constant and of the local magnetic moments in the AFM material, respectively. Reprinted figure with permission from [51]. © 2004, by

in the FM and in the AFM layer exhibit a small canting from the  $90^{\circ}$  coupling that vanishes away from the interface but induces a small magnetization in the AFM layer. The spin-flop ground state was also suggested to lead to exchange bias [49], a result that was later confuted by a more accurate model describing the spin dynamics in terms of moment precession rather than energy minimization [50]. The presence of defects can, however, destroy the spin-flop ground state, inducing a collinear coupling between the AFM and FM moments across the interface. The reason why this happens can be captured by a mean-field calculation where the perturbation associated with the defects is simulated by an effective exchange field of magnitude H<sup>ex</sup> acting on the atoms belonging to a compensated AFM-FM interface reproducing the characteristics of the NiO/Fe(001) bilayer [51, 52]. The result is summarized in Figure 1.3, which shows the type of average AFM-FM coupling (collinear rather than perpendicular) between the two layers as a function of  $H^{ex}$  and of the fraction u of magnetically active defects at the interface. Monte Carlo simulations find AFM spins aligning collinearly with the FM moments above  $T_N$ , with a transition from collinear to perpendicular alignment of the FM and AFM spins at a lower temperature in the case of rough interfaces [53]. Besides interface defects, also volume defects such as dislocations inside the AFM material can influence the coupling between the FM magnetization and the AFM anisotropy axis by disrupting the collinear alignment of the spins inside the AFM layer [54].



Increasing NiO thickness

**Figure 1.4** Photoemission electron microscopy images excited by linear X-rays and showing the magnetic contrast obtained at the Fe  $L_{2,3}$  (top) and Ni  $L_2$  (bottom) absorption edges on an NiO/Fe(001) wedged thin film. The field of view shown in each panel straddles a domain wall separating two Fe domains with in-plane magnetization perpendicular to each other. The arrows indicate the direction of the magnetization in the Fe substrate and of the NiO film easy axis. The reported crystallographic directions

refer to the Fe substrate. The NiO thickness increases from the left to the right, with an average value in the left, central, and right panels equal to about 12, 18, and 24 Å, respectively. The NiO thickness variation in each image is about 3 Å. The direction of the NiO easy axis has been rotated by 90° with respect to the one previously reported in [58] (see [59]). Reprinted figure with permission from [58]. © 2006, by the American Physical Society.

Because of the presence of frustration between competitive exchange interactions, the AFM–FM interface coupling in real systems can strongly depend on the interface preparation conditions. Moreover, strain-induced magnetoelastic effects should also be considered (see Chapter 8). For instance, thin FM metal films (Fe, Co) on NiO(001) exhibit perpendicular FM–AFM coupling [55–57], while the coupling is collinear for thin NiO films on Fe(001) [51, 58]. Actually, the original articles [51, 56–58] based on X-ray dichroism indicated the type of coupling to be the opposite of the one reported above. This confusion originated from a misinterpretation of the linear dichroism spectra, which was corrected in later work [59]. The coupling in NiO/Fe(001) is also NiO thickness-dependent: the anisotropy axis is parallel to the Fe substrate magnetization when the NiO thickness is less than about 15 Å, but rapidly becomes perpendicular parallel to the Fe magnetization for a NiO coverage higher than 25 Å, as displayed in Figure 1.4 [58].

A thorough evaluation of exchange and magnetoelastic effects has been conducted for epitaxial NiO thin films on single magnetite (Fe<sub>3</sub>O<sub>4</sub>) crystals [60]. Magnetite is a *ferrimagnetic* material that has a lattice parameter in the (001) plane that is almost exactly twice (mismatch only 0.5%) that of NiO [61]. As a consequence, in an epitaxially grown system, the surface spins of the Fe<sub>3</sub>O<sub>4</sub> interact only, to first approximation, with one of the two uncompensated sublattices of the (001) NiO interface plane. This situation would therefore correspond to an uncompensated NiO/Fe<sub>3</sub>O<sub>4</sub>(001) interface where collinear coupling would be expected

to be energetically favored. Instead, a spin-flop coupling is observed, stabilized by magnetostrictive deformations induced by the magnetite substrate [60]. Collinear coupling was indeed found for the (111) and (110) interfaces, attributed to a strain-induced AFM stacking asymmetry in the NiO. All three interfaces display an uncompensated AFM magnetization, with the largest value observed for the (110) interface, while the (111) and (001) interfaces exhibit only 10% of that value [60].

The interface coupling in CoO/Fe<sub>3</sub>O<sub>4</sub>(001) superlattices (see chapter 7) is also found to be perpendicular [62]. This result, however, has not been explained as being a consequence of magnetoelastic effects, but by rather considering [63] the role of anisotropic exchange, a phenomenon first studied by Dzyaloshinsky and Moriya [64, 65]. By coupling the direction of the spin to the crystal axes, the spin–orbit interaction is responsible for single-ion magnetic anisotropy, as outlined in Section 1.3.1. The same effect also introduces an anisotropic contribution to the isotropic exchange Hamiltonian. This antisymmetric Dzyaloshinsky–Moriya term can be written as  $D(S_1 \times S_2)$ , with  $S_1$  and  $S_2$  being the spin operators of two neighboring magnetic ions, and D a vector that vanishes when the crystal field around each ion has inversion symmetry with respect to the center of their mid-point [46]. Therefore, the Dzyaloshinsky–Moriya anisotropic exchange interaction, which favors a perpendicular coupling, cannot *a priori* be neglected for magnetic ions lying on opposite sides of an interface, where inversion symmetry is broken.

A strong AFM–FM interface coupling might also affect the type of order that is stabilized in the AFM material, as demonstrated in a study conducted on Co/CoO core/shell nanoparticles obtained by oxidation of Co nanospheres. In such a system, Co–CoO interfaces are highly crystalline and oxidation leads to the decompensation of the (100) CoO surface, resulting in a strong core-shell coupling [66]. Polarized-neutron diffraction finds both  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  and (100) AFM modulation, as in bulk CoO [67], corresponding to a stacking of alternate FM foils with the normal parallel to either the [111] direction (type-II AFM order, as in Figure 1.2) or to the [100] direction (type-I AFM order). While in bulk CoO the  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$  neutron diffraction peak prevails [67], oxidation of Co nanoparticles hugely enhances the (100) peak [66].

### 1.4.2

# Coupling between FM Layers Separated by an AFM Oxide Spacer

The insulating nature of TM AFM oxides excludes any intervention of the Ruderman–Kittel–Kasuya–Yosida (RKKY) [68–70] interaction in determining the relative orientation of the magnetization in FM layers in FM–AFM multilayers. The RKKY interaction, in fact, couples the magnetic moments in FM layers through the conduction electrons of a nonmagnetic metal spacer. Instead, when the spacer is an AFM insulator, FM interlayer coupling can be described in terms of Slonczewski's proximity magnetism model [71], which has been developed for uncompensated interfaces and requires strong AFM–FM interfacial coupling, as compared with the domain-wall energy in the AFM material. For perfectly flat interfaces, the expected coupling between the FM layers is either parallel or antiparallel



**Figure 1.5** An artist's impression of the winding spin structures expected to form in the AFM spacer separating two FM slabs according to Sloncewski's proximity magnetism model. The magnetization in the FM layers is indicated by white arrows. Thin gray arrows indicate the spin direction in the AFM planes.

depending on the number of AFM planes. AFM–FM interface roughness results in a lateral modulation of the number of AFM layers, and therefore in a competition between parallel and antiparallel coupling. According to Slonczewski, the perpendicular coupling through an AFM spacer should then be described by an energy term of the form  $C[\theta^2 + (\theta - \pi)^2]$ , where  $\theta$  is the angle between the magnetization of the two FM layers and *C* the AFM-thickness-dependent coupling strength. Therefore, the Slonczewski coupling energy displays a minimum at  $\theta = \pi/2$ , accounting for perpendicular interlayer alignment. The particular expression of the coupling energy term depends on the AFM spins forming winding structures, which are schematically shown in Figure 1.5.

The proximity magnetism model has recently been generalized to the case where the interfacial coupling and AFM domain-wall energy densities are comparable [72]. In this "extended" proximity model, the FM-FM coupling energy can be approximated, to lowest order, by a combination of a biquadratic contribution, proportional to  $\cos^2\theta$ , and a term proportional to  $\sin^2(2\theta)$ . The main difference between Sloncewski's model and its extended version is the behavior of the FM layers at high applied fields, as the magnetizations of the two FM layers become parallel only asymptotically for the Slonczewski coupling term, while in the extended proximity model saturation of the magnetizations of both FM layers in the direction of the applied field is obtained at finite fields. This behavior is related to the existence of local minima at  $\theta = 0$  and  $\theta = \pi$  in the coupling energy term of the extended model. The existence of these additional minima stems from the fact that, for a weak AFM-FM coupling, the AFM spins can rearrange by unwinding the twisted AFM magnetic structure predicted by the proximity model, confining the frustration at one of the AFM-FM interfaces [72]. The presence of the  $\sin^2(2\theta)$  term in the expression of the coupling energy is explained by the inequivalence between  $\pm \pi$  and 0 energy minima, which is a result of the different arrangements of the AFM local moments in different coupling configurations [72].

Perpendicular FM interlayer coupling has indeed been observed in  $Fe_3O_4/NiO/Fe_3O_4(001)$  trilayers [73], which appear to be well described by Slonczewski's

model since, as discussed above, the NiO/Fe<sub>3</sub>O<sub>4</sub>(001) interface is magnetically uncompensated while the magnetocrystal anisotropy in NiO is weak. These two characteristics thus fulfill the conditions of strong interfacial coupling compared to the AFM domain-wall energy density, which is approximately proportional to  $\sqrt{JK}$  [74], *J* and *K* being the exchange coupling constant and the anisotropy constant of the material, respectively. On the other hand, Fe/NiO/Fe(001) trilayers are better described by the extended proximity magnetism model [75]. Despite that Fe<sub>3</sub>O<sub>4</sub> is also formed at the interface obtained by depositing NiO on Fe(001) [76], a different oxide, namely FeO, is expected to form when Fe is deposited on NiO(001) to complete the trilayer [77]. The AFM–FM coupling in the Fe/NiO/Fe trilayer can thus be expected to be much lower than in Fe<sub>3</sub>O<sub>4</sub>/NiO/Fe<sub>3</sub>O<sub>4</sub>, at least at one interface.

Both proximity models predict a perpendicular FM–FM interlayer coupling only when the AFM spacer thickness is below a critical value  $t_c$ , which is expected to be of the same order of magnitude as the width of domain walls ( $\delta_W$ ) in the bulk AFM material. Indeed, a transition between perpendicular to parallel FM–FM coupling in zero applied magnetic field is observed at similar values of  $t_c$  for Fe<sub>3</sub>O<sub>4</sub>/NiO/Fe<sub>3</sub>O<sub>4</sub> ( $t_c \approx 5$  nm) and Fe/NiO/Fe ( $t_c \approx 4$  nm) trilayers. However, the values measured for  $t_c$  are considerably smaller than the experimental value of  $\delta_W$  in bulk NiO single crystals, which has been reported to vary between 134 and 184 nm [78]. Such a large discrepancy is not surprising since proximity models assume a coherent rotation of spins in AFM planes parallel to the interfaces of the multilayer, and do not take into account the three-dimensional structure at the AFM domain walls originating at defects in the AFM volume, such as vacancies and dislocations, or at the interface, such as atomic steps. As discussed in 6, these defects are expected to reduce the coupling energy between the FM layers, with the result that the value of  $t_c$  might be considerably smaller than that of  $\delta_W$  in the bulk AFM material.

# 1.5

# Micromagnetic Structure at AFM-FM Interfaces

It has been shown that in FM films grown on top of an AFM material, the magnetic domains and domain walls tend to be small compared to the case of otherwise similar FM films grown on nonmagnetic substrates. In some cases, domain sizes of the order of a few micrometers have been observed [56, 57, 79–83]. Investigating the origin of the phenomena that contribute to the formation of small magnetic domains is obviously of primary importance in information technology [84]. Chapter 8 will thoroughly address the micromagnetic structure of AFM–AF systems by discussing magnetic-contrast soft X-ray microscopy. In this section, we focus instead on Fe/NiO/Fe trilayers, which display magnetic domains of the Fe overlayer that can be even smaller, with a minimum lateral size of about 20 nm, as shown in Figure 1.6 [85]. The magnetic contrast observed in Figure 1.6b,c is due to domains exhibiting opposite magnetization as a result of the Fe–Fe coupling across the NiO spacer, whose thickness has been chosen so as to obtain a collinear

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Figure 1.6 Spin-polarized low-energy electron microscopy images of magnetic domains in: (a) Fe(001) substrate. In the upper part of the image the spin of the primary electron beam is perpendicular to the domain wall visible in the field of view. In the bottom part the spin is parallel. (b) Fe/NiO/Fe with  $t_{\rm NiO} = 4.5$  nm and  $t_{\rm over} = 1.3$  nm. (c) Same sample area (b) with  $t_{over}$  increased to 6 nm. In (b) and (c), the spin of the primary beam is parallel to the vertical axis of the figure. The field of view in the three images is  $4\times4~\mu\text{m}^2.$  A domain coarsening going from panel (b) to (c) is visible. The direction of the magnetization in domains appearing dark or bright is indicated by the arrows. In panel (a), the  $180^{\circ}$  domain walls are sufficiently wide ( $\delta \approx 240$  nm) to reveal the spin structure of the wall in the upper half of panel (a), obtained by using a  $90^{\circ}$  spin polarization of the primary electron beam of the microscope. Reprinted figure with permission from [85]. © Copyright (2007) by the American Physical Society.

FM–FM coupling. Similar domains are also obtained for thinner NiO layers, corresponding to a perpendicular coupling in zero applied field (see Section 1.4.2).

Before discussing the conditions that allow the stabilization of such small magnetic domains, it is worth mentioning the mechanisms that determine the width  $\delta_W$  of a domain in a bulk material. In fact, a domain cannot be significantly smaller than  $\delta_W$ , otherwise the system would gain energy by simply suppressing it, that is, by allowing the moments inside the domain to reorient in the same direction as the magnetization of the surrounding material. Approximately,  $\delta_W$  is given by the relation [74, 84]

$$\delta_W \approx ab \sqrt{\frac{J}{K}}$$
 (1.5)

where *J* and *K* are the exchange coupling and the magnetocrystal anisotropy constants, respectively, while *a* is the atomic lattice spacing and *b* is a dimensionless parameter, which depends on the details of the spin structure within the wall, for example,  $b \approx 10$  in bulk Fe [86]. A large exchange interaction with respect to the magnetocrystal anisotropy favors thick domain walls, since the local moments would exert a strong torque on those of the neighboring atoms.

Conversely, a large magnetic anisotropy leads to narrow domain walls since the moments of each atom tend to align parallel with the crystallographic directions. Generally, domain walls are quite larger than the lattice spacing since the anisotropy

is much smaller than the exchange energy. For example, in bulk Fe  $K \approx 4 \,\mu\text{eV}$  and  $J \approx 100 \,\text{meV}$  per atom [86–89], corresponding to a  $\delta_W$  value of the order of several hundred nanometers, as observed also in Figure 1.6a. This bulk value for  $\delta_W$  has to be compared with the value  $\delta_W < 20 \,\text{nm}$  (20 nm corresponding to the lateral resolution of the instrument) measured in Figure 1.6b, c on a Fe/NiO/Fe trilayer. Such a large decrease in  $\delta_W$  cannot be traced back to a possible increment in the value of the single-ion anisotropy constant *K* even though the low coordination number and the presence of strain could, in principle, induce a large magnetocrystal anisotropy at surfaces or interfaces ( see section 1.3.1). In fact seems unreasonable that this mechanism could produce the 100-fold raise of *K* that would be required to justify the observed value of  $\delta_W$ . The stabilization of small magnetic domains in the FM overlayer can be instead associated with the AFM–FM interface exchange energy.

One of the first models describing the statistical properties of the magnetic domains at AFM-FM interfaces is due to Malozemoff [90]. In his model, the presence of interface roughness gives rise to a random field acting on the interface spins. The magnetically softer (either AFM or FM) material breaks up into domains whose size is determined by the competition between the exchange interaction and an additional uniaxial in-plane anisotropy. This random field model was the first attempt at including the role of defects to explain why the exchange bias energy density in AFM-FM systems is much smaller than what should be expected from the value of the exchange interaction between AFM and FM atoms across the surface. This model, however, considers a domain structure that resembles a chessboard, where all the domains have a lateral dimension equal to L. This leads to an average interface energy density scaling as 1/L, that is, to an interfacial exchange coupling energy on the domain footprint scaling as L. On inspection of Figure 1.6, it is seen that the domains in the Fe overlayer show instead fractal morphology, with a fractal dimension of about 1.6, very close to the value expected for an Ising system with random fluctuations [85]. The assimilation of the overlayer to an Ising system seems justified by the strong coupling with the second Fe layer, which results, as explained in Section 1.4.2, in a strong uniaxial anisotropy of the overlayer. Models reproducing the fractal structure of the domains [91] show that the exchange coupling energy on a minimum stable domain footprint should instead scale as  $L^2$ . Moreover, the structure of domain walls at AFM-FM interfaces is determined by frustration of the exchange interaction rather than by the balance between exchange and magnetocrystal anisotropy, as explained in 6. The presence of frustration is the driving mechanism that justifies the stabilization of much smaller domains at AFM-FM interfaces than in the bulk of the single constituent materials [92]. By combining all these elements, one realizes that the minimum domain size depends on the balance between the exchange energy eDW contained in a domain wall encircling a circular FM domain of diameter equal to L and the AFM–FM interface exchange energy  $e_{f,af}$ . The domain is stable if  $e_{DW} \propto L$  equals  $e_{f,af} \propto L^2$  [85]. If  $e_{f,af} > e_{DW}$  the domain expands and if  $e_{f,af} < e_{DW}$  the domain shrinks. The scaling laws for  $e_{DW}$  and  $e_{f,af}$  allow determining of the minimum domain size [85]. By explicitly including in the model the dependence of the

### 1.6 Applications 17

exchange energy per unit domain-wall length, one can also reproduce the observed coarsening of the domains, also visible from the comparison of Figure 1.6b,c, which have been obtained on the same sample area after successive Fe depositions [85]. The coarsening is a consequence of  $e_{DW}$  increasing with the Fe thickness (a higher domain wall obviously requires more energy). The higher negative pressure exerted on the domain by its wall has to be compensated by an increase of the domain footprint to provide the necessary AFM-FM exchange energy to prevent the domain from collapsing.

The importance of frustration over anisotropy is further confirmed by magneticcontrast X-ray photoemission microscopy studies on Fe/CoO/Fe(001) trilayers. FM/AFM/FM trilayers in which the AFM material is either NiO or CoO are characterized by interfaces with similar morphology and chemical quality, but NiO and CoO exhibit large differences in the respective values of the magnetocrystal anisotropy: CoO is characterized by  $K = 2 \times 10^5$  erg cm<sup>-3</sup>, while  $K = 3.3 \times 10^2$  erg cm<sup>-3</sup> for NiO [48, 93]. Despite the large difference in the magnetocrystal anisotropy (3 orders of magnitude), the morphology and the minimum domain size in the topmost layer in Fe/NiO/Fe and Fe/CoO/Fe trilayers are very similar [94].

# 1.6 Applications

The most common technological application of AFM materials is in spin valves based on the giant magnetoresistance (GMR) [95, 96] and tunnel magnetoresistance (TMR) [97, 98] effects, which are currently used as reading heads for magnetic storage media or as memory elements in magnetic random-access memories (MRAMs). Such devices consist of two conducting FM materials that exhibit high or low electrical resistance depending on the relative alignment of the magnetic layers. An AFM layer is used to pin the harder FM reference layer by exchange bias, so that the magnetization of only the softer layer in the spin valve is reversed by the application of an external magnetic field. Similarly, the most advanced disk media are antiferromagnetically coupled, making use of interfacial exchange to effectively increase the stability of small magnetic particles whose behavior would otherwise be superparamagnetic.

For most spin-valve sensors, metallic antiferromagnets like NiMn, PtMn, or IrMn were and still are used. Although there were spin-valves using NiO in the early days of the discovery of GMR effect, their use was discontinued for thermal stability reasons. Though the idea of using Co-ferrite as a bias material to replace PtMn in current-in-plane sensors was mooted, this was not implemented. Thus, the number of AFM oxide applications for magnetic recording is limited. Nonetheless, although the AFM pinning layer in a spin-valve does not directly contribute to the magnetoresistance and rather constitutes a parasitic resistance, a considerably enhanced in-plane magnetoresistance as compared to conventional all-metal spin-valves has been observed in Co/Cu/Co and Ni<sub>80</sub>Fe<sub>20</sub>/Cu/Ni<sub>80</sub>Fe<sub>20</sub> spin-valves confined within insulating AFM NiO layers [99, 100]. Such an improvement is

because spin-polarized electrons are reflected back in the FM layer at the NiO/metal interface.

However, as recording densities increase and critical dimensions shrink accordingly, the industry has moved from a current-in-plane to a current-perpendicular-to-plane sensor geometry. Lower sensor cross sections require materials with low resistance-area products like metals to obtain adequate signal-to-noise ratios. For current-in-plane sensors, oxides were useful as they do not shunt the current; however, these sensors have already been abandoned. At present, current-perpendicular-to-plane sensors with conducting antiferromagnets are employed. The same is true also for MRAMs (Stefan Maat, San Jose Research Center - Hitachi Global Storage Technologies, private communication).

#### 1.7

#### Conclusions

AFM oxide materials in low-dimensional geometries, either in nonmagnetic or magnetic environments, display a rich variety of magnetic behaviors. They are very interesting materials to investigate the fundamental physics of finite-size effects expressed by magnetic systems. Despite the limited applications in actual technology, AFM oxides represent very important reference and model systems for studying the interface coupling phenomena that are ultimately exploited in devices such as spin-valves.

This book provides an extensive discussion of the complex and intriguing phenomena observed in such systems, with particular emphasis on the growth and the magnetic characterization through different experimental methods and theoretical modeling approaches.

#### References

- Finazzi, M., Duò, L., and Ciccacci, F. (2009) Magnetic properties of interfaces and multilayers based on thin antiferromagnetic oxide films. *Surf. Sci. Rep*, 64, 139.
- Anderson, P.W. (1950) Antiferromagnetism. Theory of superexchange interaction. *Phys. Rev*, **79**, 350.
- Mermin, N.D. and Wagner, H. (1966) Absence of ferromagnetism or antiferromagnetism in one- or two-dimensional isotropic Heisenberg models. *Phys. Rev. Lett*, 17, 1133.
- Punnoose, A., Magnone, H., Seehra, M.S., and Bonevich, J. (2001) Bulk to nanoscale magnetism and exchange

bias in CuO nanoparticles. *Phys. Rev. B*, **64**, 174420.

- Punnoose, A. and Seehra, M.S. (2002) Hysteresis anomalies and exchange bias in 6.6 nm CuO nanoparticles. *J. Appl. Phys*, **91**, 7766.
- Stewart, S.J., Multigner, M., Marco, J.F., Berry, F.J., Hemando, A., and Gonzalez, J.M. (2004) Thermal dependence of the magnetization of antiferromagnetic copper(II) oxide nanoparticles. *Solid State Commun*, 130, 247.
- Zheng, X.G., Xu, C.N., Nishikubo, K., Nishiyama, K., Higemoto, W., Moon, W.J., Tanaka, E., and Otabe, E.S. (2005) Finite-size effect on Néel temperature

in antiferromagnetic nanoparticles. *Phys. Rev. B*, **72**, 014464.

- Abarra, E.N., Takano, K., Hellman, F., and Berkowitz, A.E. (1996) Thermodynamic measurements of magnetic ordering in antiferromagnetic superlattices. *Phys. Rev. Lett*, **77**, 3451.
- Alders, D., Tjeng, L.H., Voogt, F.C., Hibma, T., Sawatzky, G.A., Chen, C.T., Vogel, J., Sacchi, M., and Iacobucci, S. (1998) Temperature and thickness dependence of magnetic moments in NiO epitaxial films. *Phys. Rev. B*, 57, 11623.
- Sako, S., Ohshima, K., Sakai, M., and Bandow, S. (1996) Magnetic property of CoO ultrafine particle. *Surf. Rev. Lett*, 3, 109.
- Ambrose, T. and Chien, C.L. (1996) Finite-size effects and uncompensated magnetization in thin antiferromagnetic CoO layers. *Phys. Rev. Lett*, 76, 1743.
- Tang, Y.J., Smith, D.J., Zink, B.L., Hellman, F., and Berkowitz, A.E. (2003) Finite size effects on the moment and ordering temperature in antiferromagnetic CoO layers. *Phys. Rev. B*, 67, 054408.
- Gangopadhyay, S., Hadjipanayis, G.C., Sorensen, C.M., and Klabunde, K.J. (1993) Exchange anisotropy in oxide passivated Co fine particles. *J. Appl. Phys*, 73, 6964.
- Resnick, D.A., Gilmore, K., Idzerda, Y.U., Klem, M.T., Allen, M., Douglas, T., Arenholz, E., and Young, M. (2006) Magnetic properties of Co<sub>3</sub>O<sub>4</sub> nanoparticles mineralized in Listeria innocua Dps. J. Appl. Phys, 99, 08Q501.
- He, L., Chen, C., Wang, N., Zhou, W., and Guo, L. (2007) Finite size effect on Néel temperature with Co3O4 nanoparticles. J. Appl. Phys, 102, 103911.
- Wang, R.M., Liu, C.M., Zhang, H.Z., Chen, C.P., Guo, L., Xu, H.B., and Yang, S.H. (2004) Porous nanotubes of Co3O4: synthesis, characterization, and magnetic properties. *Appl. Phys. Lett*, 85, 2080.
- Salabas, E.L., Rumplecker, A., Kleitz, F., Radu, F., and Schuth, F. (2006) Exchange anisotropy in nanocasted Co3O4 nanowires. *Nano. Lett*, 6, 2977.

- Fisher, M.E. and Barber, M.N. (1972) Scaling theory for finite-size effects in the critical region. *Phys. Rev. Lett*, 28, 1516.
- Zhang, R. and Willis, R.F. (2001) Thickness-dependent curie temperatures of ultrathin magnetic films: effect of the range of spin-spin interactions. *Phys. Rev. Lett*, 86, 2665.
- 20. Chen, K., Ferrenberg, A.M., and Landau, D.P. (1993) Static critical behavior of three-dimensional classical Heisenberg models: a high-resolution Monte Carlo study. *Phys. Rev. B*, 48, 3249.
- Ferrenberg, A.M. and Landau, D.P. (1991) Critical behavior of the three-dimensional Ising model: A high-resolution Monte Carlo study. *Phys. Rev. B*, 44, 5081.
- Lang, X.Y., Zheng, W.T., and Jiang, Q. (2006) Size and interface effects on ferromagnetic and antiferromagnetic transition temperatures. *Phys. Rev. B*, 73, 224444.
- van der Zaag, P.J., Ijiri, Y., Borchers, J.A., Feiner, L.F., Wolf, R.M., Gaines, J.M., Erwin, R.W., and Verheijen, M.A. (2000) Difference between blocking and Néel temperatures in the exchange biased Fe<sub>3</sub>O<sub>4</sub>/CoO system. *Phys. Rev. Lett*, 84, 6102.
- Skumryev, V., Stoyanov, S., Zhang, Y., Hadjipanayis, G., Givord, D., and Nogués, J. (2003) Beating the superparamagnetic limit with exchange bias. *Nature*, 423, 850.
- Altieri, S., Finazzi, M., Hsieh, H.H., Haverkort, M.W., Lin, H.-J., Chen, C.T., Frabboni, S., Gazzadi, G.C., Rota, A., Valeri, S., and Tjeng, L.H. (2009) Image charge screening: A new approach to enhance magnetic ordering temperatures in ultrathin correlated oxide films. *Phys. Rev. B*, **79**, 174431.
- 26. Giovanardi, C., di Bona, A., Altieri, S., Luches, P., Liberati, M., Rossi, F., and Valeri, S. (2003) Structure and morphology of ultrathin NiO layers on Ag(001). *Thin Solid Films*, 428, 195.
- Slack, G.A. (1960) Crystallography and domain walls in antiferromagnetic NiO crystals. J. Appl. Phys, 31, 1571.

- Altieri, S., Tjeng, L.H., Voogt, F.C., Hibma, T., and Sawatzky, G.A. (1999) Reduction of Coulomb and charge-transfer energies in oxide films on metals. *Phys. Rev. B*, 59, R2517.
- Altieri, S., Tjeng, L.H., Voogt, F.C., Hibma, T., Rogojanu, O., and Sawatzky, G.A. (2002) Charge fluctuations and image potential at oxide-metal interfaces. *Phys. Rev. B*, 66, 155432.
- Zaanen, J., Sawatzky, G.A., and Allen, J.W. (1985) Band gaps and electronic structure of transition-metal compounds. *Phys. Rev. Lett*, 55, 418.
- Anderson, P.W. (1959) New approach to the theory of superexchange interactions. *Phys. Rev*, 115, 2.
- Zaanen, J. and Sawatzky, G.A. (1987) The electronic structure and superexchange interactions in transition-metal compounds. *Can. J. Phys*, 65, 1262.
- Jefferson, J.H. (1988) Theory of superexchange in antiferromagnetic insulators. J. Phys. C: Solid State Phys, 21, L193.
- Duffy, D.M. and Stoneham, A.M. (1983) Conductivity and 'negative U' for ionic grain boundaries. *J. Phys. C*, 16, 4087.
- 35. Hesper, R., Tjeng, L.H., and Sawatzky, G.A. (1997) Strongly reduced band gap in a correlated insulator in close proximity to a metal. *Europhys. Lett*, 40, 177.
- Altieri, S., Tjeng, L.H., and Sawatzky, G.A. (2001) Ultrathin oxide films on metals: new physics and new chemistry? *Thin Solid Films*, 400, 9.
- Bloch, D. (1966) The 10/3 law for the volume dependence of superexchange. *J. Phys. Chem. Solids*, 27, 881.
- Zhang, W.-B., Hu, Y.-L., Han, K.-L., and Tang, B.-Y. (2006) Pressure dependence of exchange interactions in NiO. *Phys. Rev. B*, 74, 054421.
- 39. Sidorov, V.A. (1998) Differential thermal analysis of magnetic transitions at high pressure: Néel temperature of NiO up to 8 GPa. *Appl. Phys. Lett*, 72, 2174.

- Massey, M.J., Chen, N.H., Allen, J.W., and Merlin, R. (1990) Pressure dependence of two-magnon Raman scattering in NiO. *Phys. Rev. B*, 42, 8776.
- Casassa, S., Ferrari, A.M., Busso, M., and Pisani, C. (2002) Structural, magnetic, and electronic properties of the NiO monolayer epitaxially grown on the (001) Ag surface: an ab initio density functional study. *J. Phys. Chem. B*, 106, 12978.
- Cinquini, F., Giordano, L., Pacchioni, G., Ferrari, A.M., Pisani, C., and Roetti, C. (2006) Electronic structure of NiO/Ag(100) thin films from DFT+U and hybrid functional DFT approaches. *Phys. Rev. B*, 74, 165403.
- Hillebrecht, F.U., Ohldag, H., Weber, N.B., Bethke, C., Mick, U., Weiss, M., and Bahrdt, J. (2001) Magnetic moments at the surface of antiferromagnetic NiO(100). *Phys. Rev. Lett*, 86, 3419.
- Altieri, S., Finazzi, M., Hsieh, H.H., Lin, H.-J., Chen, C.T., Hibma, T., Valeri, S., and Sawatzky, G.A. (2003) Magnetic dichroism and spin structure of antiferromagnetic NiO(001) films. *Phys. Rev. Lett*, **91**, 137201.
- 45. Csiszar, S.I., Haverkort, M.W., Hu, Z., Tanaka, A., Hsieh, H.H., Lin, H.-J., Chen, C.T., Hibma, T., and Tjeng, L.H. (2005) Controlling orbital moment and spin orientation in CoO layers by strain. *Phys. Rev. Lett*, **95**, 187205.
- Yosida, K. (1998) Theory of Magnetism, Series in Solid-State Sciences, Springer.
- Keffer, F. and O'Sullivan, W. (1957) Problem of spin arrangements in MnO and similar antiferromagnets. *Phys. Rev*, 108, 637.
- Finazzi, M. and Altieri, S. (2003) Magnetic dipolar anisotropy in strained antiferromagnetic films. *Phys. Rev. B*, 68, 054420.
- Koon, N.C. (1997) Calculations of exchange bias in thin films with ferromagnetic/antiferromagnetic interfaces. *Phys. Rev. Lett*, 78, 4865.
- Schulthess, T.C. and Butler, W.H. (1998) Consequences of spin-flop coupling in exchange biased films. *Phys. Rev. Lett*, 81, 4516.

- Finazzi, M., Portalupi, M., Brambilla, A., Duò, L., Ghiringhelli, G., Parmigiani, F., Zacchigna, M., Zangrando, M., and Ciccacci, F. (2004) Magnetic anisotropy of NiO epitaxial thin films on Fe(001). *Phys. Rev. B*, 69, 014410.
- Finazzi, M. (2004) Interface coupling in a ferromagnet/antiferromagnet bilayer. *Phys. Rev. B*, 69, 064405.
- Tsai, S.-H., Landau, D.P., and Shulthess, T.C. (2003) Effect of interfacial coupling on the magnetic ordering in ferro-antiferromagnetic bilayers. J. Appl. Phys, 93, 8612.
- Finazzi, M., Biagioni, P., Brambilla, A., Duò, L., and Ciccacci, F. (2005) Disclinations in thin antiferromagnetic films on a ferromagnetic substrate. *Phys. Rev. B*, 72, 024410.
- Matsuyama, H., Haginoya, C., and Koike, K. (2000) Microscopic imaging of Fe magnetic domains exchange coupled with those in a NiO(001) surface. *Phys. Rev. Lett*, **85**, 646.
- 56. Ohldag, H., Scholl, A., Nolting, F., Anders, S., Regan, T.J., Hillebrecht, F.U., and Stöhr, J. (2001) Spin reorientation at the antiferromagnetic NiO(001) surface in response to an adjacent ferromagnet. *Phys. Rev. Lett*, 86, 2878.
- Ohldag, H., Regan, T.J., Stöhr, J., Scholl, A., Nolting, F., Lüning, J., Stamm, C., Anders, S., and White, R.L. (2001) Spectroscopic identification and direct imaging of interfacial magnetic spins. *Phys. Rev. Lett*, 87, 247201.
- 58. Finazzi, M., Brambilla, A., Biagioni, P., Graf, J., Gweon, G.-H., Scholl, A., Lanzara, A., and Duò, L. (2006) Interface coupling transition in a thin epitaxial antiferromagnetic film interacting with a ferromagnetic substrate. *Phys. Rev. Lett*, **97**, 097202.
- Arenholz, E., van der Laan, G., Chopdekar, R.V., and Suzuki, Y. (2007) Angle-dependent Ni<sup>2+</sup> x-ray magnetic linear dichroism: interfacial coupling revisited. *Phys. Rev. Lett*, **98**, 197201.
- Krug, I.P., Hillebrecht, F.U., Haverkort, M.W., Tanaka, A., Tjeng, L.H., Gomonay, H., Fraile-Rodríguez, A., Nolting, F., Cramm, S., and Schneider,

C.M. (2008) Impact of interface orientation on magnetic coupling in highly ordered systems: a case study of the low-indexed Fe<sub>3</sub>O<sub>4</sub>/NiO interfaces. *Phys. Rev. B*, **78**, 064427.

- Borchers, J.A., Erwin, R.W., Berry, S.D., Lind, D.M., Ankner, J.F., Lochner, E., Shaw, K.A., and Hilton, D. (1995) Long-range magnetic order in Fe<sub>3</sub>O<sub>4</sub>/NiO superlattices. *Phys. Rev. B*, 51, 8276.
- Ijiri, Y., Borchers, J.A., Erwin, R.W., Lee, S.-H., van der Zaag, P.J., and Wolf, R.M. (1998) Perpendicular coupling in exchange-biased Fe<sub>3</sub>O<sub>4</sub>/CoO superlattices. *Phys. Rev. Lett*, **80**, 608.
- Ijiri, Y., Schulthess, T.C., Borchers, J.A., van der Zaag, P.J., and Erwin, R.W. (2007) Link between perpendicular coupling and exchange biasing in Fe<sub>3</sub>O<sub>4</sub>/CoO multilayers. *Phys. Rev. Lett*, 99, 147201.
- Dzyaloshinsky, I. (1957) Thermodynamic theory of weak ferromagnetism in antiferromagnetic substances. *Sov. Phys. JETP*, 5, 1259.
- **65.** Moriya, T. (1960) Anisotropic superexchange interaction and weak ferromagnetism. *Phys. Rev*, **120**, 91.
- 66. Inderhees, S.E., Borchers, J.A., Green, K.S., Kim, M.S., Sun, K., Strycker, G.L., and Aronson, M.C. (2008) Manipulating the magnetic structure of Co core/CoO shell nanoparticles: implications for controlling the exchange bias. *Phys. Rev. Lett*, **101**, 117202.
- Tomiyasu, K., Inami, T., and Ikeda, N. (2004) Magnetic structure of CoO studied by neutron and synchrotron x-ray diffraction. *Phys. Rev. B*, **70**, 184411.
- Ruderman, M.A. and Kittel, C. (1954) Indirect exchange coupling of nuclear magnetic moments by conduction electrons. *Phys. Rev*, 96, 99.
- Kasuya, T. (1956) A theory of metallic ferro- and antiferromagnetism on Zener's model. *Prog. Theor. Phys*, 16, 45.
- Yosida, K. (1957) Magnetic properties of Cu-Mn alloys. *Phys. Rev*, **106**, 893.
- Slonczewski, J.C. (1995) Overview of interlayer exchange theory. J. Magn. Magn. Mater, 150, 13.

- Xi, H. and White, R.M. (2000) Coupling between two ferromagnetic layers separated by an antiferromagnetic layer. *Phys. Rev. B*, **62**, 3933.
- van der Heijden, P.A.A., Swüste, C.H.W., de Jonge, W.J.M., Gaines, J.M., van Eemeren, J.T.W.M., and Schep, K.M. (1999) Evidence for roughness driven 90° coupling in Fe<sub>3</sub>O<sub>4</sub>yNiOyFe<sub>3</sub>O<sub>4</sub> trilayers. *Phys. Rev. Lett*, 82, 1020.
- Hubert, A. and Schäfer, R. (1998) Magnetic Domains: The Analysis Of Magnetic Microstructures, Springer, Berlin.
- Brambilla, A., Biagioni, P., Portalupi, M., Zani, M., Finazzi, M., Duò, L., Vavassori, P., Bertacco, R., and Ciccacci, F. (2005) Magnetization reversal properties of Fe/NiO/Fe(001) trilayers. *Phys. Rev. B*, 72, 174402.
- 76. Finazzi, M., Brambilla, A., Duò, L., Ghiringhelli, G., Portalupi, M., Ciccacci, F., Zacchigna, M., and Zangrando, M. (2004) Chemical effects at the buried NiO/Fe(100) interface. *Phys. Rev. B*, 70, 235420.
- 77. Regan, T.J., Ohldag, H., Stamm, C., Nolting, F., Lüning, J., Stöhr, J., and White, R.L. (2001) Chemical effects at metal/oxide interfaces studied by x-ray-absorption spectroscopy. *Phys. Rev. B*, 64, 214422.
- Weber, N.B., Ohldag, H., Gomonaj, H., and Hillebrecht, F.U. (2003) Magnetostrictive domain walls in antiferromagnetic NiO. *Phys. Rev. Lett*, 91, 237205.
- Nolting, F., Scholl, A., Stöhr, J., Seo, J.W., Fompeyrine, J., Siegwart, H., Locquet, J.-P., Anders, S., Lüning, J., Fullerton, E.E., Toney, M.F., Scheinfein, M.R., and Padmore, H.A. (2000) Direct observation of the alignment of ferromagnetic spins by antiferromagnetic spins. *Nature*, 405, 767.
- Scholl, A., Nolting, F., Seo, J.W., Ohldag, H., Stöhr, J., Raoux, S., Locquet, J.-P., and Fompeyrine, J. (2004) Domain-size-dependent exchange bias in Co/LaFeO<sub>3</sub>. *Appl. Phys. Lett*, 85, 4085.
- 81. Welp, U., Velthuis, S.G.E., Felcher, G.P., Gredig, T., and Dahlberg, E.D.

(2003) Domain formation in exchange biased Co/CoO bilayers. J. Appl. Phys, **93**, 7726.

- 82. Blomqvist, P., Krishnan, K.M., and Ohldag, H. (2005) Direct imaging of asymmetric magnetization reversal in exchange-biased Fe/MnPd bilayers by x-ray photoemission electron microscopy. *Phys. Rev. Lett*, **94**, 107203.
- 83. Chopra, H.D., Yang, D.X., Chen, P.J., Brown, H.J., Swartzendruber, L.J., and Egelhoff, W.F. Jr. (2000) Nature of magnetization reversal in exchange-coupled polycrystalline NiO-Co bilayers. *Phys. Rev. B*, 61, 15312.
- Dennis, C.L., Borges, R.P., Buda, L.D., Ebels, U., Gregg, J.F., Hehn, M., Jouguelet, E., Ounadjela, K., Petej, I., Preibeanu, I.L., and Thornton, M.J. (2002) The defining length scales of mesomagnetism: a review. J. Phys.: Condens. Matter, 14, R1175.
- Rougemaille, N., Portalupi, M., Brambilla, A., Biagioni, P., Lanzara, A., Finazzi, M., Schmid, A.K., and Duò, L. (2007) Exchange-induced frustration in Fe/NiO multilayers. *Phys. Rev. B*, 76, 214425.
- Lilley, B.A. (1950) Energies and widths of domain boundaries in ferromagnetics. *Phil. Mag*, 41, 792.
- Stoner, E.C. (1950) Ferromagnetism: magnetization curves. *Rep. Prog. Phys*, 13, 83.
- Kittel, C. (1949) Physical theory of ferromagnetic domains. *Rev. Mod. Phys*, 21, 541.
- Stearns, M.B. (1986) in 3d, 4d, and 5d Elements, Alloys and Compounds, Landolt-Börnstein, New Series, Group III, Vol. 19, Pt. a(ed. H.P.J.Wijn), Springer, Berlin, p. 34.
- Malozemoff, A.P. (1987) Random-field model of exchange anisotropy at rough ferromagnetic-antiferromagnetic interfaces. *Phys. Rev. B*, 35, 3679.
- Esser, J., Nowak, U., and Usadel, K.D. (1997) Exact ground-state properties of disordered Ising systems. *Phys. Rev. B*, 55, 5866.
- **92.** Morosov, A.I. and Sigov, A.S. (2004) New type of domain walls: domain

walls caused by frustrations in multilayer magnetic nanostructures. *Phys. Solid State*, **46**, 395.

- Carey, M.J., Berkowitz, A.E., Borchers, J.A., and Erwin, R.W. (1993) Strong interlayer coupling in CoO/NiO antiferromagnetic superlattices. *Phys. Rev. B*, 47, 9952.
- Brambilla, A., Sessi, P., Cantoni, M., Finazzi, M., Rougemaille, N., Belkhou, R., Vavassori, P., Duò, L., and Ciccacci, F. (2009) Frustration-driven micromagnetic structure in Fe/CoO/Fe thin film layered systems. *Phys. Rev. B*, **79**, 172401.
- 95. Grünberg, P., Schreiber, R., Pang, Y., Brodsky, M.B., and Sowers, H. (1986) Layered magnetic structures: evidence for antiferromagnetic coupling of Fe layers across Cr interlayers. *Phys. Rev. Lett*, 57, 2442.
- Baibich, M.N., Broto, J.M., Fert, A., Nguyen Van Dau, F., Petroff, F., Eitenne, P., Creuzet, G., Friederich, A., and Chazelas, J. (1988) Giant mag-

netoresistance of (001)Fe/(001)Cr magnetic superlattices. *Phys. Rev. Lett*, **61**, 2472.

- 97. Miyazaki, T. and Tezuka, N. (1995) Giant magnetic tunneling effect in Fe/Al<sub>2</sub>O<sub>3</sub>/Fe junction. J. Magn. Magn. Mater, 139, L231.
- 98. Moodera, J.S., Kinder, L.R., Wong, T.M., and Meservey, R. (1995) Large magnetoresistance at room temperature in ferromagnetic thin film tunnel junctions. *Phys. Rev. Lett*, 74, 3273.
- 99. Swagten, H.J.M., Strijkers, G.J., Bloemen, P.J.H., Willekens, M.M.H., and de Jonge, W.J.M. (1996) Enhanced giant magnetoresistance in spin-valves sandwiched between insulating NiO. *Phys. Rev. B*, **53**, 9108.
- 100. Veloso, A., Freitas, P.P., Wei, P., Barradas, N.P., Soares, J.C., Almeida, B., and Sousa, J.B. (2000) Magnetoresistance enhancement in specular, bottom-pinned, Mn83Ir17 spin valves with nano-oxide layers. *Appl. Phys. Lett*, 77, 1020.