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Magnetic Properties of Ni/NiO Nanowires Deposited onto CNT/Pt Nanocomposites**

By Verónica Salgueiriño-Maceira,^{*} Miguel A. Correa-Duarte,^{*} Manuel Bañobre-López, Marek Grzelczak, Michael Farle, Luis M. Liz-Marzán, and José Rivas

Several nanometer-scale technological applications rely on the promising scenario of highly anisotropic magnetic materials. Bearing this in mind, we have studied the structure, magnetic properties, and interfacial exchange anisotropy effects of unique wires of Ni/NiO synthesized using carbon nanotubes as substrates. Structural analyses of these nanocomposites in correlation with magnetic measurements show that the crystalline NiO outer shells cause an enhanced exchange bias, providing an extra source of anisotropy that leads to their magnetization stability. These Ni/NiO nanowires, with a spin-glass-like behavior and with their magnetic moments in a blocked state over a wide temperature range that includes room temperature, should therefore inspire further study concerning the applicability of anisotropic structures.

1. Introduction

The physical properties of 1D structures of magnetic materials on the nanometer scale are presently the subject of intensive research, but in spite of this considerable attention only few cases have been reported.^[1–4] These building blocks, as in the case of spherical nanoparticles, are at the border between the solid and molecular states, displaying novel effects. For complex magnetic materials that comprise ferromagnetic and antiferromagnetic components, a careful characterization in terms of crystalline structure, magnetization, axial and unidirectional magnetic anisotropy, superparamagnetism, and the exchange-bias effect is required. Several methods have been exploited for the synthesis of these magnetic colloids while controlling the magnetic anisotropy:

Dr. M. A. Correa-Duarte, M. Grzelczak, Prof. L. M. Liz-Marzán Departamento de Química Física Universidade de Vigo 36310 Vigo (Spain) E-mail: macorrea@uvigo.es

Prof. M. Farle Fachbereich Physik and Center for Nanointegration (CeNIDE) Universität Duisburg-Essen 47048 Duisburg (Germany) relatively simple variations in surfactant composition to selectively control the growth rates of different faces;^[1] similar procedures to those concerning semiconductor materials;^[5,6] assembling previously synthesized magnetic nanoparticles as chains or necklaces;^[2–4,7–12] exploiting electrostatic interactions between the surface charge of magnetic nanoparticles and previously modified carbon nanotubes (CNTs);^[13] and depositing the magnetic material on the surface of CNTs in a step-by-step procedure, leading to homogeneous outer shells. To investigate the possibility of obtaining nanowires with a very narrow size distribution and without chemical bonding at the surface we have chosen this fourth option. We recently demonstrated that the direct reduction of nickel salt onto the surface of CNTs in the presence of Pt nanoparticles leads to very homogeneous nanowires of Ni/NiO.^[14] The present work describes the magnetic properties of these nanometer-sized Ni/ NiO wires supported on CNT/Pt nanocomposites in detail.

The overall magnetic behavior of these nanowires, comprising magnetic nanocrystals of Ni and NiO, is a result of the properties of the individual constituents (dependent on intrinsic parameters like the size, shape, and structure), the morphology they have acquired (anisotropic nanowires), and their interparticle interactions, with negligible magnetic contribution from the CNTs. Some characteristics of a collective super spin-glass state, which can be considered as a counterpart of a conventional spin-glass, are reported, and are a consequence of random orientations of the easy axes of the nanocrystals in every wire and the long-range character of the dipolar interactions. In the absence of an external magnetic field the magnetic moment of these nanocrystals, which constitute the composites, would be in a blocked state unless thermal activation were able to overcome the anisotropy energy barrier and induce flipping of the moment between easy directions (superparamagnetism).^[15] However, these assemblies of nanocrystals, forming wires and containing an interface



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^[*] Dr. V. Salgueiriño-Maceira, M. Bañobre-López, Prof. José Rivas Departamento de Química-Física e Física Aplicada Universidade de Santiago de Compostela 15782 Santiago de Compostela (Spain) E-mail: vsalgue@usc.es

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between a ferromagnet (FM; Ni) and an antiferromagnet (AFM; NiO), exhibit an additional unidirectional anisotropy owing to magnetic coupling at the FM/AFM interface (exchange bias), which leads to magnetization stability.^[16,17]

Exchange biasing has important technological applications, such as in giant-magnetoresistance-based spin valves that are used in hard-drive read heads and other spintronics applications.^[18,19] In nanometer-scale systems, the key factor in this magnetic interaction would be controlling the volume, shape, crystallinity, and structure of both the FM and AFM materials.^[20-27] Ni/NiO nanowires therefore offer an attractive approach to control exchange coupling, anisotropic morphology, and spin-glasslike behaviour. Significant technological impacts based on this type of nanometer-sized assembly can thus be expected.

2. Results and Discussion

The experimental procedure for the synthesis of the Ni/ NiO-coated CNTs comprised several stages.^[14] Firstly, CNTs were functionalized through wrapping with a positively charged polyelectrolyte; poly(allylamine hydrochloride) (PAH). This polyelectrolyte is the "glue" or linker by which negatively charged Pt nanoparticles can be connected to the surface of the CNTs. The so-called polymer-wrapping technique^[28] represents a noncovalent functionalization which, as opposed to defect-side and covalent-side wall functionalization, prevents disruption of the intrinsic nanotube sp²-structure conjugation, thereby preserving the electronic structure of the CNTs. The second stage involves attachment of the Pt nanoparticles,^[29] which provides the catalytic activity necessary for the further deposition of a very uniform and homogenous layer of Ni, without surfactants or other stabilizers in water solution. This fact represents a relevant issue, since the use of surfactants or other stabilizers usually induces a perturbation of the magnetic properties.^[30,31]

Figure 1 shows representative transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images of the samples that reflect the homogenous coating of individual



Figure 1. a,b) Representative TEM images of the CNT@Pt structures coated with a uniform outer layer of Ni/NiO. c) HRTEM image reflecting the polycrystalline nature of the Ni/NiO layer deposited onto the CNT@Pt nanocomposites.

CNTs and reveal the multidomain and crystalline nature of the Ni/NiO layers on the final composite. Likewise, the dark-field image in Figure 2b shows the polycrystalline character of the coating. By Fourier transform analysis, the following intershell and interplanar distances were determined: multiwalled nanotubes (MWNTs) 3.36 Å, Pt 2.19 Å, and Ni 2.03 Å and 1.72 Å, corroborating the envisaged structure of the CNT@Pt/Ni/NiO nanocomposites.^[14] CNT@Pt/Ni nanocomposites were exposed to an oxygen-rich environment during the magnetic-material-deposition process (aqueous solution) promoting the formation of the chemically stable NiO outer layer around each Ni nanocrystal.^[14,32] This surface-passivation process provides the samples with an additional surface stabilization and simultaneously protects the inner, metallic Ni from further oxidation.

We report hereafter the main results obtained for the magnetic properties of CNT@Pt/Ni/NiO nanocomposites, measured in the solid state as powders. The hysteresis loops, measured at 25, 100, 200, and 300 K are plotted in Figure 3. The large values of the coercive field (Fig. 3b), even at room temperature, indicate that the magnetic moments are in a blocked state in the homogeneous Ni/NiO shell around every CNT. Each nanowire can be considered as a heterogeneous magnetic system consisting of FM Ni nanocrystals surrounded by AFM NiO shells, homogeneously coating the CNT/Pt nanotubes. The ferromagnetic component is confirmed by hysteresis (present at 300 K and lower temperatures), with coercivities $(H_{\rm C})$ and remanent magnetizations. The AFM NiO was identified by X-ray photoemission spectroscopy (XPS) and scanning transmission electron microscopy (STEM) analysis.^[14] The oxygen-rich environment of the nanocomposites (in aqueous solution), which causes the formation of the stable NiO outer shells, favors the appearance of interfacial FM/AFM exchange anisotropy. Indeed, when the system is cooled under an applied magnetic field of magnitude $H_{\rm FC} = 5$ kOe (1 Oe = $10^{3}/4\pi$ A m⁻¹), the hysteresis loops of the nanocomposites are shifted with respect to the field axis (Fig. 4), confirming the presence of unidirectional anisotropy due to the exchange coupling at the interface of the FM/AFM materials.^[16,17,33] Figure 4 shows hysteresis curves collected at 5 K

> (zero-field-cooled (ZFC) and field-cooled (FC) (5 kOe)) displaying this shift along the direction of the cooling field with coercivities $H_{\rm C} = |H_{\rm C1} - H_{\rm C2}|/2 = 370$ Oe (ZFC) and $H_{\rm C} = 560$ Oe (FC) and exchange-bias field $H_{\rm E} = -(H_{\rm C1} + H_{\rm C2})/2 = 225$ Oe (in the FC curve). The relatively large value of the exchange-bias field, $H_{\rm E}$, indicates a unidirectional exchange anisotropy resulting from the exchange interaction between the uncompensated surface spins of NiO and metallic Ni in the Ni/NiO-coated CNT@Pt nanocomposites. This shift of the hysteresis loop can be established either by cooling the FM/AFM material in a magnetic saturation field below the Néel temperature of the AFM





Figure 2. TEM images of the same area of the Ni/NiO-coated CNT@Pt nanocomposites under a) bright and b) dark field.

(5 kOe in this case) or by depositing both materials in an external magnetic field. $^{[34]}$

Exchange bias at FM/AFM interfaces is also characterized by a coercivity enhancement, revealing the induced unidirectional anisotropy. The coercive field $H_{\rm C}=90$ Oe of the Ni/ NiO-coated CNT/Pt nanocomposites at 300 K is larger than



Figure 3. a) Hysteresis loops at 25, 100, 200, and 300 K of the Ni/NiO-coated CNTs/Pt nanocomposites. b) Temperature dependence of the coercivity (H_C) .



Figure 4. a) Magnetic hysteresis loops at T = 5 K (zero-field cooled (ZFC) and field cooled (FC) (5 kOe)). b) Magnified view at smaller fields.

typical values reported for bulk Ni. This can be explained by taking into account an influence of the interface anisotropy that, through exchange coupling, can modify the magnetism of the Ni/NiO nanocrystals. Roy and co-workers^[20] have anticipated that the NiO shell (in Ni/NiO core/shell nanoparticles) can act as a pinning layer, pinning the core spins near the interface of the Ni inner shell and the NiO outer shell via exchange interactions. This prevents the core spins from rotating freely and follows the applied field, thereby leading to the observed large coercivities. In fact, the loop shifted along the magnetization axis indicates that after the field-cooling process a fraction of the uncompensated moments is pinned because of a very high local anisotropy and cannot reverse at the available magnetic field strength.^[25]

Summarizing this part, Ni/NiO-coated CNTs/Pt nanocomposites were found to exhibit features characteristic of an exchange-biased system. The magnetic behavior of the ferromagnetic component in the nanocomposites is markedly affected by the outer shell of NiO, as can be seen from the open hysteresis loops (Fig. 3a). The unidirectional anisotropy



Figure 5. Field-cooled (FC; 5 kOe) and zero-field-cooled (ZFC) magnetization measurements of Ni/NiO-coated CNT/Pt nanocomposites.

increases the total anisotropy K so that the thermal energy at room temperature is overcome and the magnetic moments of the composites remain magnetically stable in the time window of the measurement.

Magnetization versus temperature measurements at two different magnetic fields (H = 100 and 1000 Oe) for the Ni/ NiO-coated CNTs/Pt are included in Figure 5. The ZFC and FC magnetization curves split below T = 300 K and T = 100 K, respectively, at the applied magnetic fields, and in both cases the ZFC magnetization curve exhibits a peak at around T =40 K. This temperature indicates a collective freezing of the magnetic moments (blocking temperature $T_{\rm B}$). The irreversibility shown is strongly dependent on the magnitude of the applied magnetic field and can be presumably associated with slow relaxation processes for an assembly of interacting nanocrystals. This behavior can be attributed to a random distribution of strong magnetic dipole-dipole interactions and surface anisotropy effects between the Ni cores and the NiO shells in the nanocrystals. The fact that the temperature at which the irreversibility takes place decreases with increasing magnetic field^[35] can be explained if the effects of the anisotropy field and the dipole-dipole interaction are overcome by the applied magnetic field.^[36]

Indeed, one of the most challenging questions in nanoparticulate systems concerns the collective dynamics at low temperatures. In a dilute system, the magnetic dipole–dipole interaction between the particles is negligible compared to the anisotropy energy of an individual nanoparticle. The dynamics follow the predictions of the Néel-Brown model^[37,38] and the system is considered as purely superparamagnetic. However, in a concentrated system the dipole–dipole interaction can be of the order of the particle anisotropy energy and strongly affect the low-temperature dynamics. 3D random distributions and random orientations of the anisotropy axes of such nanoparticles in an insulating matrix with a high enough packing density will create a competition of different spin alignments.^[39] Despite sophisticated experimental work^[40–44] and Monte Carlo simulations^[45-47] supporting collective dynamics at low temperature, there are also contradictory results in favor of superparamagnetism behavior and noncollective blocking. If a low-temperature collective super-spin-glass state is formed, typical properties of an ordinary atomic spin-glass should be observed in this phase. The collective behavior of the Ni/NiO nanowires is not exclusive of conventional spin-glasses, and indeed has been reported in systems of concentrated magnetic particles^[48] and other nanostructured magnetic materials,^[39] where dipolar interactions introduce a collective state and magnetic relaxation dependence. In order to label the nanowires collective behavior as spin-glass-like, we report memory effects by means of a ZFC magnetization experiment with a 2 h stop during cooling at zero field.^[49] Figure 6 illustrates the memory effect of the ZFC magnetization after this "stop-and-wait" protocol, performed below the blocking temperature. The sample was zero-field cooled down to 5 K twice, after a waiting time of $t_w = 2$ h at 20 K ($T_w < T_B = 40$ K) in the second case. The stop-and-wait magnetization data (solid symbols) lie significantly above the conventional ZFC magnetization at temperatures lower than 20 K (the temperature at which the stop-and-wait experiment took place). This difference below T_w indicates that the magnetic-moment configuration spontaneously rearranges towards equilibrium as their correlation length increases. This implies that the correlation between the nanocrystal moments develops in a similar way to the correlation between the spins in spin-glasses. Therefore, when interpreting the dynamic behavior of these interacting Ni/NiO nanocrystals in the nanowires, the effects of the spin-glass-like correlations may have to be taken into account. The dynamic magnetic properties observed in the Ni/NiO-coated CNTs/Pt nanocomposites seem to favor the spin-glass hypothesis explaining the observed collectivity and glassiness.



Figure 6. ZFC magnetization curves, measured with and without a waiting time ($t_w = 2$ h), showing the memory effect.

3. Conclusions

We have reported a detailed magnetic characterization of Ni/NiO-coated CNT/Pt nanocomposites. The results reveal a nanometer-scale system with blocked-state behavior, even at room temperature, which is a consequence of the properties of the individual constituents (Ni/NiO nanocrystals), the morphology they have acquired (anisotropic nanowires), and the complex magnetic interactions between them (collective spin-glass-like behavior). These nanocrystal assemblies containing an interface between a ferromagnet (FM; Ni) and an antiferromagnet (AFM; NiO) exhibit an additional unidirectional anisotropy when cooled in a magnetic field owing to magnetic coupling at the FM/ AFM interface; it is this extra source of anisotropy that leads to magnetization stability. Significant technological impacts can therefore be expected for this system.

4. Experimental

Ni/NiO-coated CNTs/Pt nanocomposites were produced by a step-wise reduction of NiCl2 using hydrazine following a procedure reported elsewhere^[14]. After fabrication, the nanocomposites were dried, allowing evaporation of the solvent. TEM images were collected using a JEOL JEM 1010 transmission electron microscope operating at an acceleration voltage of 100 kV. HRTEM images were obtained using a JEOL JEM 2010F transmission electron microscope operating at an acceleration voltage of 200 kV. Magnetic measurements were collected using a commercial Quantum Design superconducting quantum interference device (SQUID) magnetometer with applied magnetic fields H up to 10 kOe in the temperature range 5 $K \le T \le 300$ K. The exchange bias was checked by measuring hysteresis loops at 5 K in both ZFC and FC conditions. The temperature dependence of the magnetization was measured by warming up the sample under two different applied magnetic fields (H=100 and1000 Oe) in both zero-field-cooled (ZFC) and field-cooled (FC) conditions. After each measurement at the given conditions, the sample was demagnetized by warming up to 300 K. Magnetic memory experiments were carried out, cooling the sample in zero field from 300 to 5 K and waiting at T=20 K (temperature below the blocking temperature, $T_{\rm B} = 40$ K) for 2 h. Thereafter, the magnetization as a function of the temperature was recorded under an applied magnetic field of 1000 Oe in the temperature range of 5 K < T < 50 K.

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- [1] V. F. Puntes, K. M. Krishnan, A. P. Alivisatos, Science 2001, 291, 2115.
- F. Dumestre, B. Chaudret, C. Amiens, M.-C. Fromen, M.-J. Casanove, P. Renaud, P. Zurcher, *Angew. Chem. Int. Ed.* 2002, *41*, 4286.
- [3] F. Dumestre, B. Chaudret, C. Amiens, M. Respaud, P. Fejes, P. Renaud, P. Zurcher, Angew. Chem. Int. Ed. 2003, 42, 5213.
- [4] C. Goubault, F. Leal-Calderon, J.-L. Viovy, J. Bibette, *Langmuir* 2005, 21, 3725.
- [5] Z. Zhang, Z. Tang, N. A. Kotov, S. C. Glotzer, *Nano Lett.* 2007, 7, 1670.
- [6] Z. Tang, Y. Wang, S. Shanbhang, M. Giersig, N. A. Kotov, J. Am. Chem. Soc. 2006, 128, 6730.

- [7] V. Salgueiriño-Maceira, M. A. Correa-Duarte, A. Hucht, M. Farle, J. Magn. Magn. Mater. 2006, 303, 163.
- [8] S. Scanna, A. P. Philipse, Langmuir 2006, 22, 10209.
- [9] F. Martínez Pedrero, M. Tirado Miranda, A. Schmitt, J. Callejas Fernández, J. Chem. Phys. 2006, 125, 084706.
- [10] B. D. Korth, P. Keng, I. Shim, S. E. Bowles, C. Tang, T. Kowalewski, K. W. Nebesny, J. Pyun, J. Am. Chem. Soc. 2006, 128, 6562.
- [11] M. Klokkenburg, R. P. A. Dullens, W. K. Kegel, B. H. Erné, A. Philipse, *Phys. Rev. Lett.* **2006**, *96*, 037203.
- [12] E. M. Claesson, A. P. Philipse, Langmuir 2005, 21, 9412.
- [13] M. A. Correa-Duarte, M. Grzelczak, V. Salgueirino-Maceira, M. Giersig, L. M. Liz-Marzán, M. Farle, K. Sierazdki, R. Diaz, J. Phys. Chem. B 2005, 109, 19060.
- [14] M. Grzelczak, M. A. Correa-Duarte, V. Salgueirino-Maceira, B. Rodríguez-González, J. Rivas, L. M. Liz-Marzán, Angew. Chem. Int. Ed. 2007, 46, 7026.
- [15] J. L. Dormann, D. Fiorani, E. Tronc, Magnetic Relaxation in Fineparticle Systems. In *Advances in Chemical Physics*, Vol. 98, (Eds: I. Prigogine, S. A. Rice), John Wiley & Sons, New York 1997.
- [16] W. H. Meiklejohn, C. P. Bean, Phys. Rev. 1956, 102, 1413.
- [17] A. E. Berkowitz, K. Takano, J. Magn. Magn. Mater. 1999, 200, 552.
- [18] T. Seto, H. Akinaga, F. Takano, K. Koga, T. Orii, M. Hirasawa, J. Phys. Chem. B 2005, 109, 13403.
- [19] V. Skumryev, S. Stoyanov, Y. Zhang, G. Hadjipanayis, D. Givord, J. Nogués, *Nature* 2003, 423, 850.
- [20] A. Roy, V. Srinivas, S. Ram, J. A. De Toro, J. M. Riveiro, J. Appl. Phys. 2004, 96, 6782.
- [21] S. A. Makhlouf, F. T. Parker, F. E. Spada, A. E. Berkowitz, J. Appl. Phys. 1997, 81, 5561.
- [22] J. B. Tracy, D. N. Weiss, D. P. Dinega, M. G. Bawendi, *Phys. Rev. B* 2005, 72, 064404-1.
- [23] R. H. Kodama, S. A. Makhlouf, A. E. Berkowitz, *Phys. Rev. Lett.* 1997, 79, 1393.
- [24] M. Fraune, U. Rüdiger, G. Güntherodt, S. Cardoso, P. Freitas, Appl. Phys. Lett. 2000, 77, 3815.
- [25] A. Tomou, D. Gournis, I. Panagiotopoulos, Y. Huang, G. C. Hadjipanayis, B. J. Kooi, J. Appl. Phys. 2006, 99, 123915.
- [26] M. Spasova, U. Wiedwald, M. Farle, T. Radetic, U. Dahmen, M. Hilgendorff, M. Giersig, J. Magn. Magn. Mater. 2004, 272–276, 1508.
- [27] V. Salgueiriño-Maceira, M. Spasova, M. Farle, Adv. Funct. Mater. 2005, 15, 1036.
- [28] M. J. O'Connell, P. Boul, L. M. Ericson, C. Huffman, Y. Wang, E. Haroz, C. Kuper, J. Tour, K. D. Ausman, R. E. Smalley, *Chem. Phys. Lett.* 2001, 342, 265.
- [29] N. A. Kotov, T. Haraszti, L. Turi, G. Zavala, R. E. Geer, I. Dekany, J. H. Fendler, J. Am. Chem. Soc. 1997, 119, 6821.
- [30] D. A. Leeuwen, J. M. Van Ruitenbeek, L. J. de Jongh, A. Ceriotti, G. Pacchioni, O. D. Harberlen, N. Rosch, *Phys. Rev. Lett.* **1994**, 73, 1432.
- [31] M. Respaud, J. M. Broto, H. Rakoto, A. R. Fert, L. Thomas, B. Barbara, M. Verelst, E. Snoeck, P. Lecante, A. Mosset, J. Osuna, T. Ould Ely, C. Amiens, B. Chaudret, *Phys. Rev. B* 1998, *57*, 2925.
- [32] A. Roy, V. Srinivas, S. Ram, J. A. de Toro, U. Mizutani, *Phys. Rev. B* 2005, 71, 184443.
- [33] W. H. Meiklejohn, J. Appl. Phys. 1962, 33, 1328.
- [34] M. Fraune, U. Rüdiger, G. Güntherodt, S. Cardoso, P. Freitas, Appl. Phys. Lett. 2000, 77, 3815.
- [35] C. Antoniak, J. Lindner, V. Salgueiriño-Maceira, M. Farle, *Phys. Status Solidi A* 2006, 203, 2968.
- [36] P. Zhang, F. Zuo, F. K. Urban, III, A. Khabari, P. Griffiths, A. Hosseini-Tehrani, J. Magn. Magn. Mater. 2001, 225, 337.
- [37] X.-C. Sun, X.-L. Dong, Mater. Res. Bull. 2002, 37, 991.
- [38] L. Néel, Annales Geophysique 1949, 5, 99.



[39] W. F. Brown, Jr., Phys Rev. 1963, 130, 1677.

- [40] S. Sahoo, O. Petracic, W. Kleemann, P. Nordblad, S. Cardoso, P. P. Freitas, *Phys. Rev. B* 2003, 67, 214422.
- [41] J. L. Dormann, D. Fiorani, R. Cherkaoui, E. Tronc, F. Lucari, F. D'Orazio, L. Spinu, M. Nogués, H. Kachkachi, J. P. Jolivet, J. Magn. Magn. Mater. 1999, 203, 23.
- [42] C. Djurberg, P. Svedlindh, P. Nordblad, M. F. Hansen, F. Bodker, S. Morup, Phys. Rev. Lett. 1997, 79, 5154.
- [43] T. Johsson, P. Svedlindh, M. F. Hansen, Phys. Rev. Lett. 1998, 81, 3976.
- [44] W. Kleeman, O. Petracic, Ch. Binek, G. N. Kakazei, Y. G. Pogorelov, J. B. Sousa, S. Cardoso, P. P. Freitas, *Phys. Rev. B* 2001, 63, 134423.
- [45] J. García-Otero, M. Porto, J. Rivas, A. Bunde, Phys. Rev. Lett. 2000, 84, 167.
- [46] M. Ulrich, J. García-Otero, J. Rivas, A. Bunde, Phys. Rev. B 2003, 67, 024416.
- [47] J. O. Andersson, C. Djurberg, T. Jonsson, P. Svedlindh, P. Nordblad, *Phys. Rev. B* 1997, 56, 13983.
- [48] T. Jonson, J. Mattsson, C. Djurberg, F. A. Khan, P. Nordblad, P. Svedlindh, Phys. Rev. Lett. 1995, 75, 4138.
- [49] F. Rivadulla, M. A. López-Quintela, J. Rivas, Phys. Rev. Lett. 2004, 93, 167206.