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1995 J. Phys.: Condens. Matter 7 1121

(http://iopscience.iop.org/0953-8984/7/6/013)

J. Phys.: Condens. Matter 7 (1995) 1121–1128. Printed in the UK

Polarization of Pd atoms in Ni/Pd magnetic multilayers

T Yang†, B X Liu†, F Pan‡, J Luo‡ and K Tao‡

† Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, People's Republic of China

‡ Institute of Materials Science, Tsinghua University, Beijing 100084, People's Republic of China

Received 22 August 1994, in final form 18 October 1994

Abstract. Ni/Pd multilayered films with various Ni and Pd layer thicknesses were prepared by electron gun evaporation. These films were all polycrystals with (111) preferential orientation. Also, both experimental analysis and computer simulation results indicated the existence of a diffusion layer at the Ni–Pd interfaces. The nominal magnetic moment per Ni atom measured for these multilayered films varied with change in the Ni layer thickness. For a thinner Ni layer, the magnetic moment was smaller than that of bulk Ni, while it was larger for the thicker Ni layer. This variation is attributed to the opposite effects of two factors, namely the favourable effect of Pd atom polarization versus the magnetic degradation mainly due to the decrease in the Curie temperature with decreasing Ni layer thickness. The effect of Pd atoms polarized by their neighbouring Ni atoms was also verified by the results of thermal annealing the multilayers.

1. Introduction

As a promising artificial synthetic material, nanometre multilayered films have displayed many novel physical properties, which hardly arise in ordinary thin films or bulk materials and have vital importance in both fundamental research and application. In the appearance of these properties, the interface plays a very important role. For example, in some multilayered films, the magnetic moment per atom decreased with decreasing thickness of magnetic layer owing to several physical factors including the interfacial effect [1–3]. Also, magnetic and non-magnetic atoms can interact with each other through the interface. It has already been revealed that the non-magnetic element Pd could be polarized by its neighbouring ferromagnetic elements [4, 5]. This polarization effect has been observed in Pd/Fe [6, 7] and Pd/Co [8–10] multilayered films and was explained by theoretical calculations [11, 12]. Ni/Pd multilayered films has also been studied previously by several workers [13, 14]. However, the results were quite different. Flevaris and Krishnan [13] studied the magnetization density modification by the modulation period and observed much higher moments for a short period compared with that of bulk Ni in Ni_mPd_m multilayers [13]. Different results were also reported, namely that on decreasing the Ni layer thickness the magnetization of Ni was first a little lower and then slightly higher than that in bulk Ni [14]. We report, in this paper, the structural characteristics and magnetic properties of Ni/Pd multilayered films with various thicknesses of Ni and Pd layers and discuss the effects of polarization of Pd atoms as well as the change in the Curie temperature of the Ni layers.

0953-8984/95/061121+08$19.50

2. Experimental procedure

Multilayered films were prepared by alternatively depositing Ni and Pd both with a purity of 99.99% onto glass substrates in an electron gun evaporation system with a background vacuum level of 10^{-7} Torr, The deposition rate was monitored and controlled to be 0.5–1.5 Å s^{-1} with a quartz oscillator. The inductively coupled plasma (ICP) method was employed to determine the absolute content of both Ni and Pd masses in the multilayers and the measurement error was within 5%. The periodicity of the multilayers was determined by standard θ–2θ x-ray diffraction with Cu Kα radiation at small angles, while the crystalline structures were identified by x-ray diffraction at large angles. The individual layer thicknesses of Ni and Pd, however, were deduced from their masses obtained by the ICP method. The magnetic properties were measured with a vibrating-sample magnetometer (VSM) at room temperature. The VSM was calibrated by a standard nickel ball of 0.0646 g mass. To eliminate the interference of the glass substrate, the hysteresis loop of the glass substrate and the sample holder of the VSM was firstly measured and the maximum moment was about one to two orders lower than those of the Ni/Pd multilayers. The hysteresis loops of the Ni/Pd multilayers were then measured, and the magnetic moment of the substrate and the sample holder was subtracted automatically by computer. Six of the same Ni/Pd multilayers were used together in one measurement to reduce the measured error and the final error of the magnetic moment was about 1%. Magnetic fields up to 15 kOe were applied both parallel and perpendicular to the film plane. By taking the above precautions in the experiments, the error of the calculated magnetic moment per Ni atom was around 6%. Some multilayers were vacuum annealed at 350 °C for 1 h to study the change in the magnetic properties.

3. Results and discussion

3.1. X-ray characterization

Figure 1 is a small-angle x-ray diffraction pattern of Ni(6.5 Å)/Pd(39 Å) multilayers. It can be seen that up to the third-order diffraction peak appears clearly; from this the periodic structure of the multilayers is confirmed. Similar results were also obtained for the other multilayered films. The periodicities of all the multilayers determined by small-angle x-ray diffraction were found to be always slightly thicker than those obtained from the ICP method. In fact, the deposited multilayers frequently contained some porous regions, which was the reason why the ICP results were somewhat smaller than those given by diffraction analysis. Since the individual layer thickness of the metals could not be obtained by diffraction analysis, we used the thicknesses determined by the ICP method in the following discussion to denote the multilayers.

The large-angle x-ray diffraction analysis revealed that all the Ni/Pd multilayers studied were polycrystalline structures with (111) preferential orientation and the diffraction patterns were characteristic of a modulated structure. Figure 2(a) is a large-angle diffraction pattern of the $(Ni(23 Å)/Pd(25 Å))_{25}$ multilayers obtained by step scanning, in which four peaks appear: one is the central Bragg peak, corresponding to the average lattice, and the other three are the satellite peaks. The background from the glass substrate has been removed.

To understand further the structural feature of the Ni/Pd multilayers, for the $(Ni(23 Å)/Pf(25 Å))_{25}$ multilayers, computer simulation was performed based on the x-ray diffraction theory. Since Ni and Pd are easily miscible within the entire composition range, a statistical model of the superlattice structure was employed according to Gladyszewski

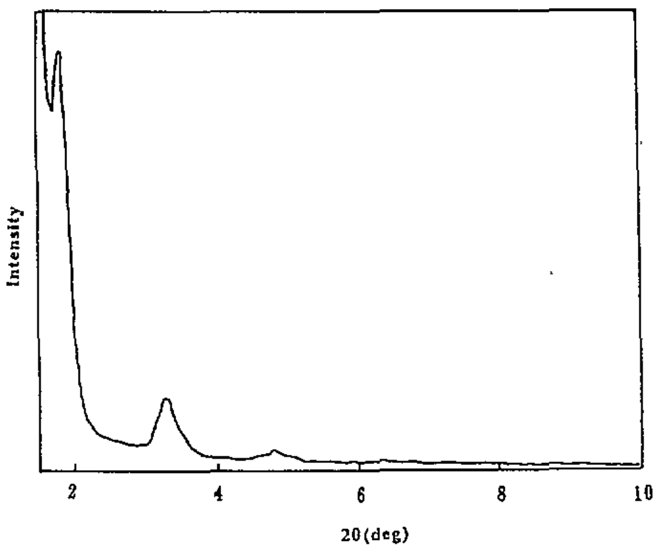

Figure 1. A small-angle x-ray diffraction pattern for Ni(6.5 Å)/Pd(39 Å) multilayered films. (The layer thicknesses of Ni and Pd were obtained by the ICP method.)

[15], in which interdiffusion at interfaces was reasonably assumed and the concentration profile in the interface region was expressed by

$$C(x) = \frac{1}{2} \pm \frac{1}{2}\Phi\left(\frac{x-i}{\sqrt{2}\sigma}\right)$$

where $\Phi(x)$ is the error function, $x = i$ stands for the layer at the interface ($C(i) = 0.5$), and σ is a simulation parameter, which corresponds to the thickness of the interdiffused region at the interfaces. By adjusting the simulation parameters, a best fit to the observed spectrum was obtained and is displayed in figure 2(*b*). In this simulated spectrum, σ was taken to be 3.2, corresponding to an interdiffused layer 3.2 atomic layers thick. Obviously, the simulated spectrum agrees well with the observed spectrum. On the other hand, when a very sharp interface is assumed by taking σ to be zero, a large discrepancy was found between the observed and simulated spectra as shown in figure 2(*c*). It was thus concluded that an interdiffused layer was indeed formed at Ni–Pd interfaces in the deposited Ni/Pd multilayers.

3.2. *Magnetic properties*

Magnetic hysteresis loops were measured with the VSM at room temperature with magnetic fields applied both parallel and normal to the film plane. For multilayered films with a fixed Pd layer thickness, no perpendicular magnetic anisotropy was observed for a Ni layer thickness greater than $d_{Ni} = 6.5$ Å, for which the ferromagentism is hardly discernible in the hysteresis loop. For some multilayered films with thicker Ni layers, the in-plane direction was obviously the easy direction of magnetization. On decreasing the Ni layer thickness, the parallel and perpendicular hysteresis loops became close to each other; yet the change occurred very slowly. It seemed that the interfacial anisotropy favouring perpendicular magnetization in these multilayers was very small; this was probably related to the formation

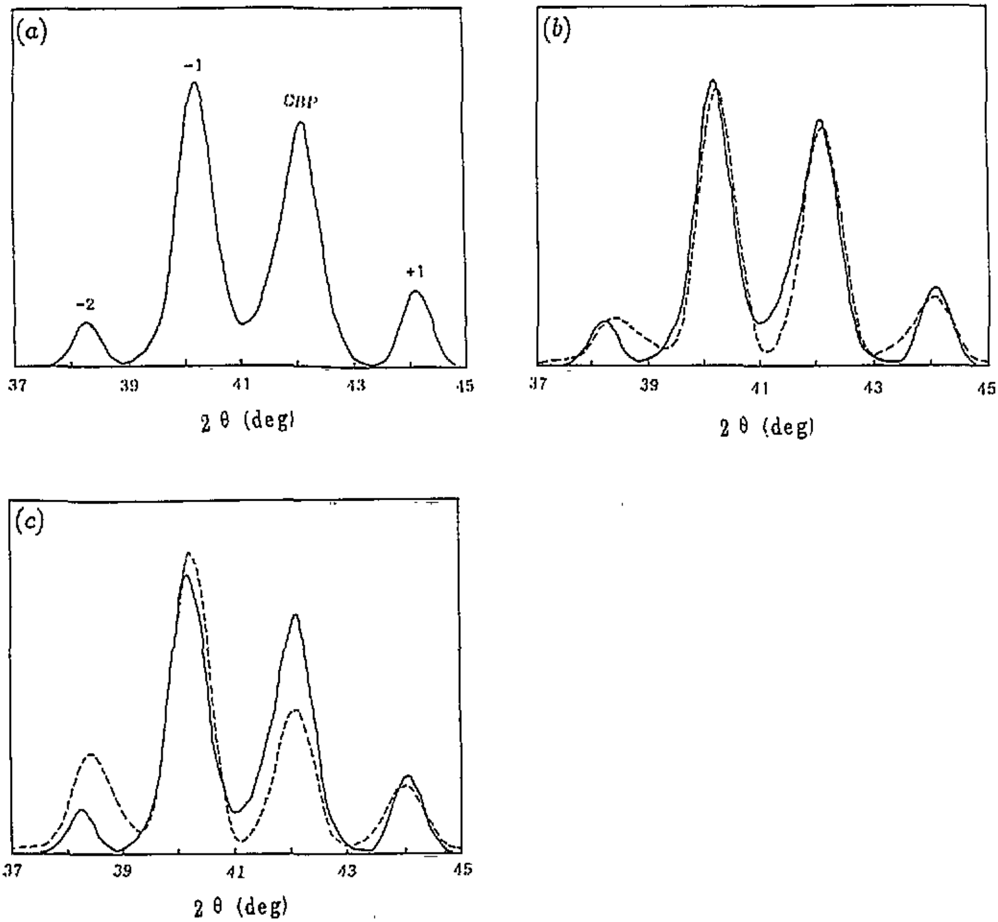

Figure 2. Experimental (——) and simulated (- - -) large-angle x-ray diffraction patterns of (Ni(23 Å)/Pd(25 Å))$_{25}$ multilayers. In (*a*), CBP is the central Bragg peak. For the simulated patterns an interdiffused region 3.2 atomic layers thick is assumed in (*b*), while a sharp interface is assumed in (*c*).

of the diffused layers at the interfaces, reducing the interfacial anisotropy energy arising from the lowered symmetry proposed by Néel [16].

Figure 3(*a*) depicts the measured nominal magnetic moment μ per Ni atom as a function of Ni layer thickness d_{Ni}, while the Pd layer thickness was fixed at 39 Å. It can be seen that for the thinner Ni layers the nominal magnetic moments per Ni atom were smaller than that of bulk and that for the thicker Ni layers, e.g. Ni(56 Å)/Pd(39 Å) and Ni(61 Å)/Pd(39 Å): the nominal magnetic moment per Ni atom was a little greater than that of the bulk Ni, which certainly needs further study. On the other hand, the variation in the Pd layer thickness had little influence on the nominal atomic magnetic moment of Ni, as is illustrated in figure 3(*b*).

It should be pointed out that the present results are different from those previously reported ones [13, 14], in which the magnetization of Ni in Ni/Pd multilayers with a very thin Ni layer was larger than that of bulk Ni. The decrease in the atomic magnetic moment of ferromagnetic elements on reducing the magnetic layer thickness has been frequently observed in magnetic multilayered films and one possible factor was due to the lowered Curie temperature when the ferromagnetic layer was very thin [17]. In our case of Ni/Pd

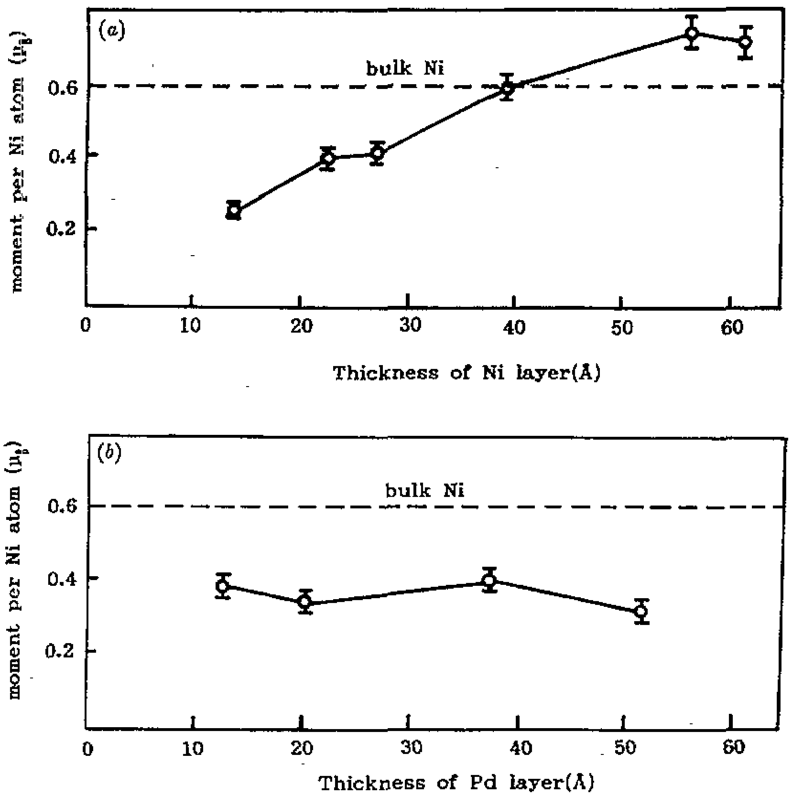

Figure 3. Dependence of measured magnetic moment per Ni atom in Ni/Pd multilayered films on (*a*) Ni layer thickness (with a Pd layer thickness of 39 Å) and (*b*) Pd layer thickness (with a Ni layer thickness of 19 Å).

multilayered films, however, there is another factor contributing positively to the nominal magnetic moment per Ni atom, namely the polarization of Pd atoms by neighbouring Ni atoms proved previously in many experiments [4–10] and theoretical calculations [11, 12]. It is well known that the Curie temperature of magnetic multilayered films decreases with decreasing magnetic layer thickness [18]. In particular when the ferromagnetic layer was very thin, the Curie temperature dropped rapidly; this has been observed in some other Ni-based multilayers such as Ni/Re [19] and Ni/Ag [20]. As mentioned above, the ferromagnetism of the Ni/Pd multilayers is hardly discernible when the Ni layer is as thin as 6.5 Å, implying that the Curie temperature is close to room temperature. It was thought that, when the Ni layer was very thin, although Pd atoms at interfaces were polarized and possessed some extra magnetic moment, yet they could not compensate the decrease caused by the lowered Curie temperature; the nominal magnetic moment per Ni atom was still smaller than that in bulk Ni. When the Ni layer became thicker, the increment in magnetic moment due to Pd atom polarization exceeded the less strong effect of lowering the Curie temperature for thicker Ni layers. Also, the lattice deformation due to the misfit between Ni and Pd at interfaces and the porosity might also affect the magnetization behaviours. In our case, the interdiffused layers buffered the misfit effect slightly.

3.3. Effects of annealing

Annealing was carried out in a vacuum furnace with a vacuum level of 3×10^{-6} Torr for the Ni(27 Å)/Pd(39 Å) multilayered sample for 1 h. Figure 4 shows two small-angle diffraction patterns of the sample before and after annealing. It can be seen that only one modulation peak remains after annealing while three peaks are shown before annealing. Apparently, thermal annealing caused the composition profile farther away from the rectangular distribution, as more Pd atoms had mixed with Ni atoms in the annealed multilayers. The magnetic hysteresis loops before and after annealing are presented in figure 5, showing clearly the increase in the saturation magnetization upon annealing. Qualitatively speaking, this increase, we believe, was from more polarized Pd atoms in the annealed films. The annealing result can, in turn, serve as evidence of the polarization of Pd atoms on mixing with Ni atoms.

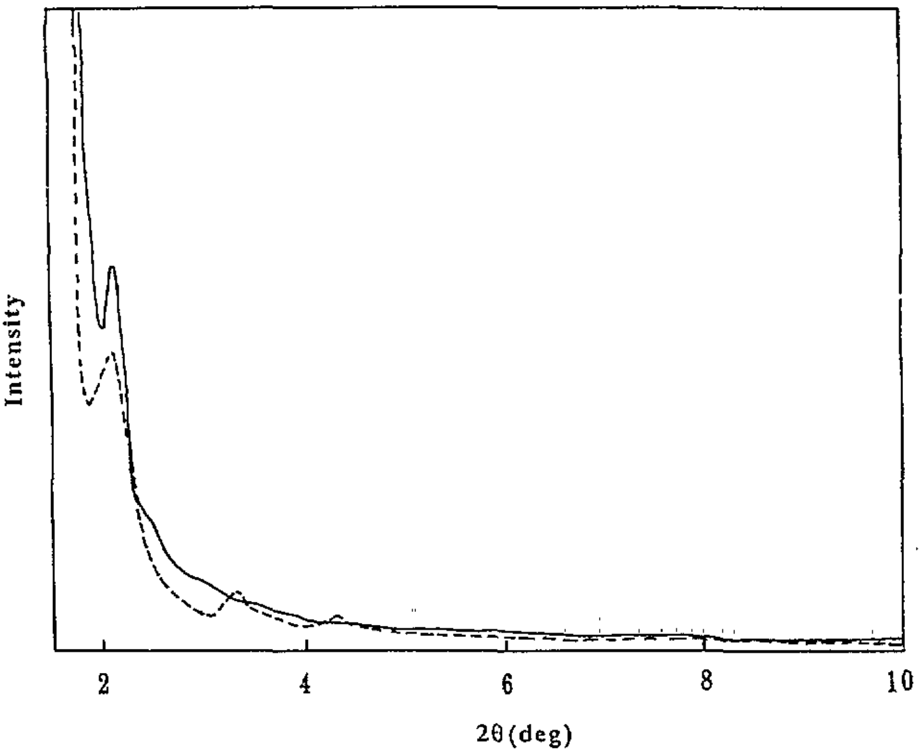

Figure 4. Small-angle x-ray diffraction patterns for Ni(27 Å)/Pd(39 Å) multilayered films before (- - -) and after (——) annealing at 350 °C for 1 h.

It is worthwhile mentioning that it was slightly easier for the as-deposited multilayered film and slightly more difficult for the annealed film to magnetize perpendicular to than parallel to the film plane. This suggested that the intermixing at interfaces decreased the interfacial anisotropy, favouring perpendicular magnetization.

4. Conclusion

In conclusion, interesting magnetic properties were observed in the vapour-deposited Ni/Pd multilayered films with various Ni and Pd layer thicknesses. Two major factors were

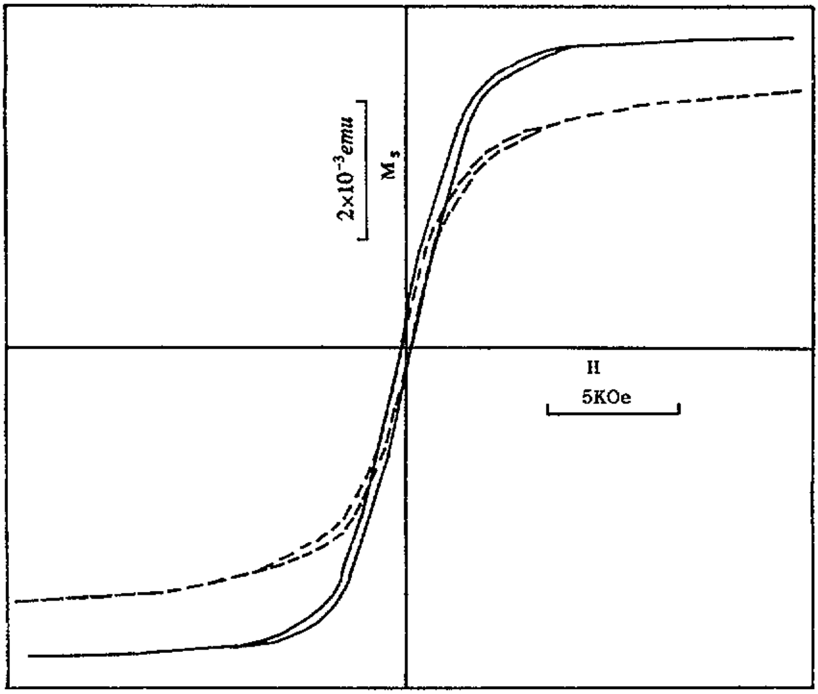

Figure 5. Magnetic hysteresis loops for Ni(27 Å)/Pd(39 Å) multilayered films before (- - -) and after (——) annealing at 350 °C for 1 h.

responsible for these: the polarization of Pd atoms through mixing with Ni, which raised the nominal magnetic moment per Ni atom, and the lowered Curie temperature, which reduced the moment in the Ni/Pd multilayers. Consequently, the observed nominal magnetic properties were a balance between these two factors.

Acknowledgments

This work was supported in part by the National Natural Science Foundation of China. The authors are grateful to the researchers at the TEM Laboratory, the VSM Laboratory and the Chemical Analysis Centre of Peking University, and at the Institute of Materials Science of Tsinghua University for their kind help.

References

[1] Rodmacq B and dos Santos C A 1992 *J. Magn. Magn. Mater.* **109** 298
[2] Chidress J R, Chien C L and Jankowski A F 1992 *Phys. Rev.* B **45** 2855
[3] Porte M, Lassri H, Krishnan R, Kaabouchi A F, Maaza M and Sella C 1993 *Appl. Surf. Sci.* **66** 131
[4] Bozorth R M, Wolff P A, Davis D D, Compton V B and Wernick J H 1961 *Phys. Rev.* **122** 1157
[5] Nieuwenhuys G J 1975 *Adv. Phys.* **24** 515
[6] Pan F, Yang T, Zhang J and Liu B X 1993 *J. Phys.: Condens. Matter* **5** L507
[7] Zhai H R, Wang H, Lu M, Zhang H Y, Zhou S M, Liu Y H, Zhang L and Mei L M 1992 *J. Magn. Magn. Mater.* **104–7** 1825

[8] Yang T, Pan F and Liu B X 1994 *Phys. Status Solidi* a **142** 443
[9] Sato N 1991 *J. Appl. Phys.* 70 6065
[10] den Broeder F J A, Donkersloot H C, Draaisma H J G and de Jonge W J M 1987 *J. Appl. Phys.* **61** 4317
[11] Wu Ruqian, Li Chun and Freeman A J 1991 *J. Magn. Magn. Mater.* **99** 71
[12] Oswald A, Zeller R and Dederichs P H 1986 *Phys. Rev. Lett.* **56** 1419
[13] Flevaris N K and Krishnan R 1992 *J. Magn. Magn. Mater.* **104–7** 1760
[14] Smardz L 1990 *J. Magn. Magn. Mater.* **83** 119
[15] Gladyszewski G 1989 *Thin Solid Films* **170** 99
[16] Néel L 1954 *J. Physique Radium.* **15** 225
[17] Sato N 1988 *J. Appl. Phys.* **63** 3476
[18] Gradmann U 1974 *J. Appl. Phys.* **3** 16
[19] Bergholz R and Gradmann U 1984 *J. Magn. Magn. Mater.* **45** 389
[20] Rodmacq B and Dos Santos C A 1992 *J. Magn. Magn. Mater.* **104–7** 1739