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LETTER TO THE EDITOR

Fe/Pd nano-multilayers prepared by vapour deposition, and their magnetic anomaly

F Pan†‡, T Yang†, J Zhang† and B X Liu†§

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

‡ International Centre for Materials Physics, Academia Sinica, Shengyang 110015, People's Republic of China

§ Centre of Condensed Matter and Radiation Physics, CCAST (World Laboratory), Beijing 100080, People's Republic of China

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Abstract. Electron-beam vapour deposition was employed to prepare Fe/Pd nano-multilayers with various thicknesses and periodicities. It was found that the magnetic moment per Fe atom in Fe/Pd multilayers was considerably enhanced when the Fe layer thickness was less than 6.5 nm, up to $3.27\mu_B$ at an Fe layer thickness of 1.6 nm, and that there was an increasing tendency towards perpendicular magnetization as the thickness of the Fe layer decreased. The magnetic enhancement may be attributed to the formation of a non-equilibrium Fe-enriched phase with FCC structure at the Fe/Pd interfaces.

Multilayered films consisting of ferromagnetic and non-magnetic layers on a nanometre scale with artificial periodicity have received considerable attention in recent years because these films may exhibit anomalous magnetic properties, namely a change in magnetization as the magnetic layer thickness is reduced and the appearance in some cases of a uniaxial interfacial anisotropy etc [1–5]. In our recent studies [6–8], electron-beam vapour deposition (e-gun) was employed to prepare Fe/noble-metal (Cu, Ag and Au) multilayers, and the magnetic moment per Fe atom was significantly enhanced with decreasing Fe layer thickness, while the thickness of noble metal remained fixed. In these films, the maximum magnetic enhancement was found to decrease from Fe/Cu to Fe/Ag(Au) with increasing difference of the covalent radius of the constituent metals (0 for Fe/Cu and 0.017 nm for Fe/Ag(Au)). It is therefore of interest to study the magnetic behaviour in other Fe/FCC-metal systems. Pd is of FCC structure and the difference in the covalent radii between Fe and Pd is about 0.011 nm, which is between that of Fe/Cu and Fe/Ag(Au). To our knowledge, Fe/Pd multilayers and superlattices have been studied by several authors [9–12]; however, they were all prepared by methods other than the e-gun technique. In this paper, we report the magnetic properties of Fe/Pd nano-multilayers prepared by the e-gun technique and discuss the possible mechanism of the magnetic-moment enhancement.

The Fe/Pd multilayered films were prepared by alternately depositing pure Fe (99.99%) and Pd (99.99%) at rates of 0.1–0.2 nm s^{-1} onto NaCl single-crystal and glass substrates of thickness 0.1 mm in an e-gun evaporation system with a vacuum of 5×10^{-7} Torr. The thickness of the Pd layer was fixed at 6.5 nm, while the Fe layer thickness varied from 1.2 to 6.5 nm monitored by an *in situ* quartz oscillator. The total thickness of the films was approximately 130 nm. The samples were analysed by transmission electron microscopy

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(TEM), selected area electron diffraction (SAD) and x-ray diffraction to identify the structure of the films. Rutherford backscattering (RBS) and small-angle x-ray diffraction were also employed to measure the thickness and the periodicity of the samples. The magnetic properties were measured with a vibrating sample magnetometer (VSM) in a magnetic field of 4 kOe at room temperature. The size of the VSM samples was 5 mm × 5 mm. To reduce the measuring error, four identical specimens were combined in one measurement to obtain the hysteresis loops. Since the content of the Fe in the samples is crucial in calculating the magnetic moment per Fe atom, after measuring the magnetic properties, the alloy films were dissolved in 5 ml aqua regia (HNO_3:HCl = 1.3) and PLASMA-SPEC-I inductive coupled plasma (ICP) atomic emission spectrum was employed to determine the Fe content in the multilayers. An average magnetic moment per Fe atom was then calculated.

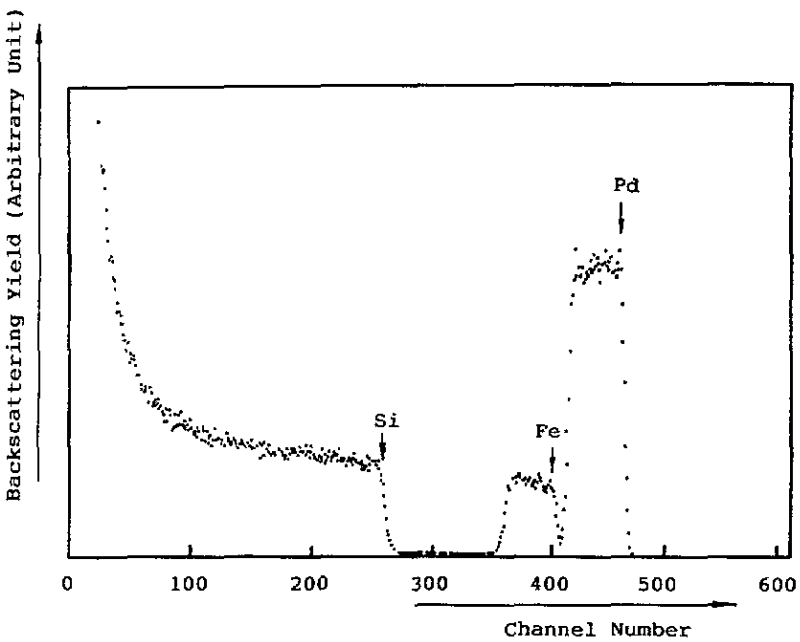

Figure 1. RBS spectrum of an [Fe(3 nm)/Pd(6.5 nm)]$_{14}$ multilayer.

RBS and small-angle x-ray diffraction analysis results indicated that the composition, thickness and periodicity of all the samples agreed with the nominal values. For example, figure 1 shows an RBS spectrum of an [Fe(3 nm)/Pd(6.5 nm)]$_{14}$ (the subscript is the number of Fe/Pd bilayers) sample on an Si substrate. The incident $^4He^+$ ion beam was at 2.1 MeV and the backscattering angle was 165°. From the spectrum, one can learn that the peaks corresponding to the high and low channels are the peaks of Pd and of Fe, respectively. Although the detector used at these energies has insufficient energy resolution (about 10 nm) to allow the individual layers to be resolved, the Pd peak at its left edge and the highest channel of the Fe peak can still be distinguished. Thus, by calculating the area and width of Pd and Fe peaks, it can be found that the total thickness of [Fe(3 nm)/Pd(6.5 nm)]$_{14}$ is 133 nm and that the average thickness of the Fe and Pd layers is 3 nm and 6.5 nm, respectively, confirming the deposited metal thicknesses.

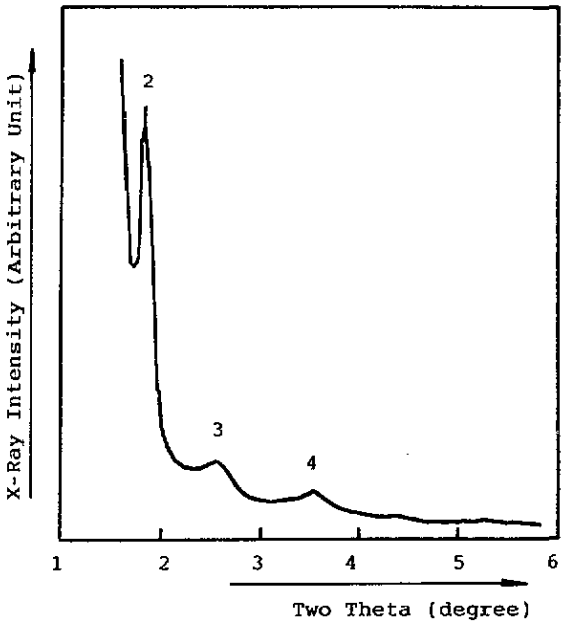

Figure 2. Small-angle x-ray diffraction pattern of an $[Fe(3\ nm)/Pd(6.5\ nm)]_{14}$ multilayer.

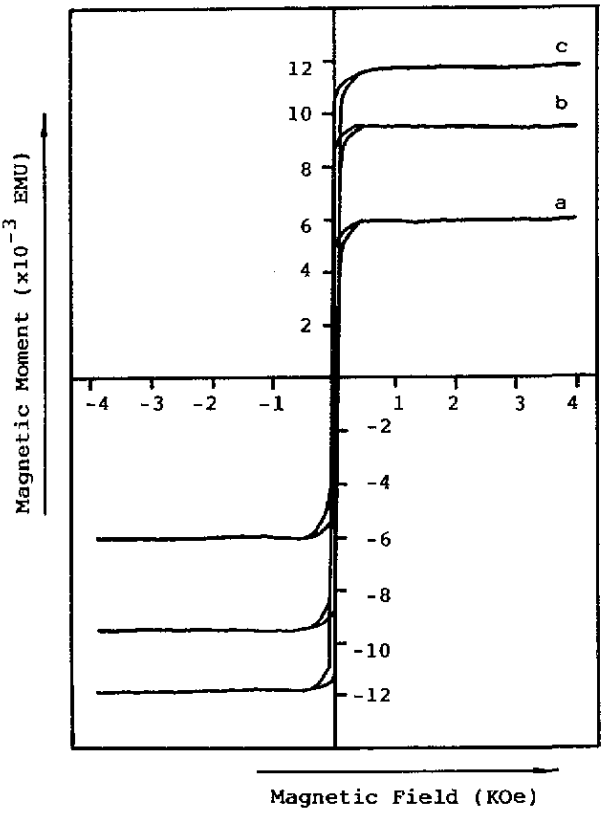

Figure 3. The hysteresis loops of Fe/Pd multilayers: curve a, Fe(1.6 nm)/Pd(6.5 nm); curve b, Fe(3 nm)/Pd(6.5 nm) and curve c, Fe(6.5 nm)/Pd(6.5 nm).

Figure 2 shows a small-angle x-ray diffraction pattern for an [Fe(3 nm)/Pd(6.5 nm)]$_{14}$ multilayer taken with Cu Kα radiation. From this figure, the second-, third- and fourth-order diffraction peaks of the Fe/Pd bilayer can be observed. According to these data, the periodicity of the multilayers is about 9.8 nm, which also agrees with the RBS and ICP results.

Table 1. The magnetic moment per Fe atom in different Fe/Pd multilayers.

Sample	σ_s ($\times 10^{-3}$ emu)	Weight of Fe (μg)	σ (μ_B)
Fe(1.2 nm)/Pd(6.5 nm)	5.137	18.25	2.77
Fe(1.6 nm)/Pd(6.5 nm)	5.995	18.05	3.27
Fe(3.0 nm)/Pd(6.5 nm)	9.457	30.60	3.04
Fe(4.3 nm)/Pd(6.5 nm)	10.950	39.10	2.77
Fe(6.5 nm)/Pd(6.5 nm)	11.800	40.80	2.85

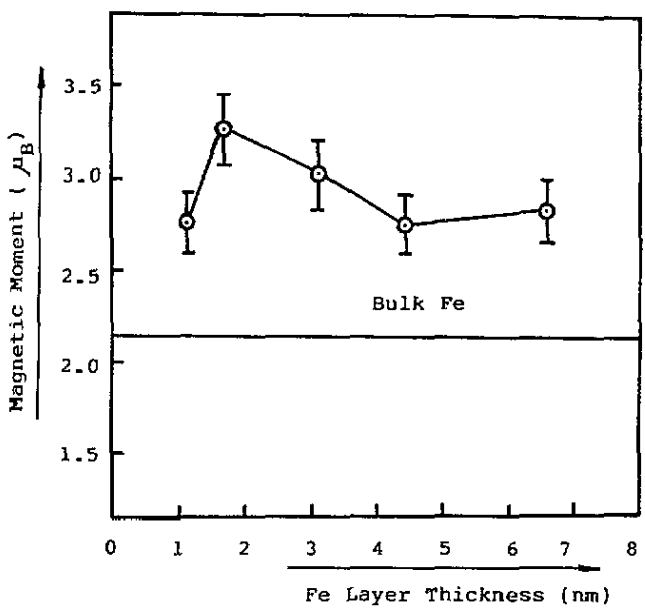

Figure 4. Magnetic moment of Fe/Pd multilayers as a function of the thickness of the Fe layer; the Pd layer thickness was kept at 6.5 nm.

The magnetic properties of Fe/Pd multilayers were measured by a VSM with a resolution of 2×10^{-6} emu. The results indicated that all the Fe/Pd multilayers had an in-plane easy axis of magnetization. The hysteresis loop of the substrate and holder was measured first. The largest magnetic moment of the substrate and holder was about 4×10^{-4} emu, which was about 1–2 orders of magnitude lower than that of the Fe/Pd multilayers. Then the hysteresis loops of Fe/Pd multilayers were measured, and the magnetization of the substrate and holder was subtracted automatically by the computer during the measurement of the Fe/Pd multilayered films. Figure 3 shows the hysteresis loops of three Fe/Pd multilayers in

a magnetic field of 4 kOe, which was parallel to the film plane. Table 1 and figure 4 show the magnetic moment per Fe atom in Fe/Pd multilayered films. Apparently, the interference of the magnetic moment of the substrate and holder has a negligible effect on the measured values of the Fe/Pd multilayers and the precision of the measured magnetic moment is to within less than 1%. Taking into account an error of 5% in the ICP measurement, the total measured error was about 6%. It can be observed from figure 4 than when the Pd layer was fixed at 6.5 nm, the magnetic moment per Fe atom in all the Fe/Pd multilayers was obviously higher than that of bulk Fe ($2.15\mu_B$), and the enhancement of the magnetic moment increased with decreasing Fe layer thickness, reaching a maximum value of $3.27\mu_B$, i.e. about 1.5 times that of the bulk Fe, at an Fe layer thickness of 1.6 nm, then it dipped slightly with decreasing Fe layer thickness.

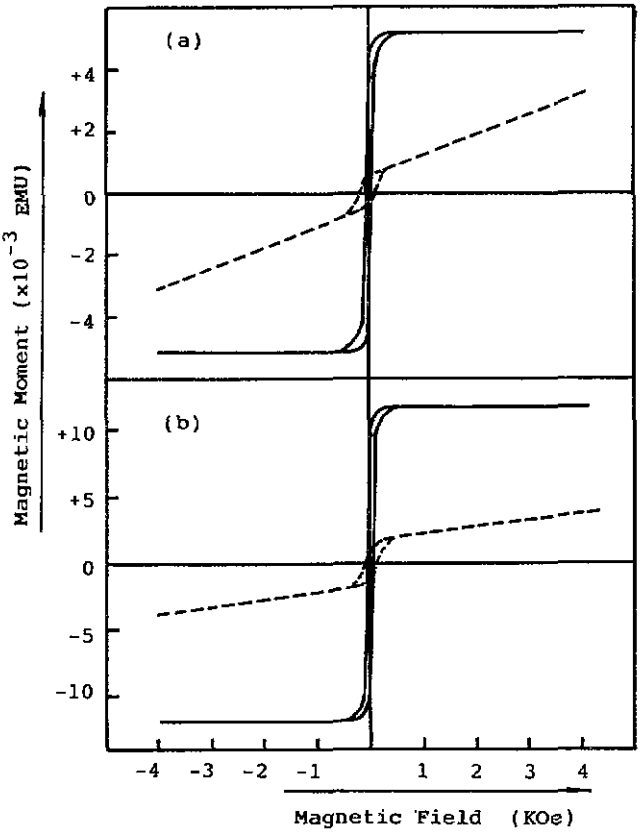

Figure 5. The hysteresis loops measured in a magnetizing field parallel (full curves) and perpendicular (broken curves) to the film plane for (a) Fe(1.2 nm)/Pd(6.5 nm) and (b) Fe(6.5 nm)/Pd(6.5 nm) multilayers.

Figure 5 shows two hysteresis loops of twe Fe/Pd multilayers measured with the magnetic field parallel and perpendicular to the film plane. From the figure, the saturation field, for the perpendicular case, depended on the thickness of the Fe layer when the Pd layer was fixed at 6.5 nm. Saturating the Fe(1.2 nm)/Pd(6.5 nm) multilayers was much easier than saturating the Fe(6.5 nm)/Pd(6.5 nm) ones. This revealed that as the Fe layer thickness decreased, there was an increasing tendency for perpendicular magnetization in the Fe/Pd multilayers, which was similar to those observed in Fe/noble-metal multilayers [7, 12, 13].

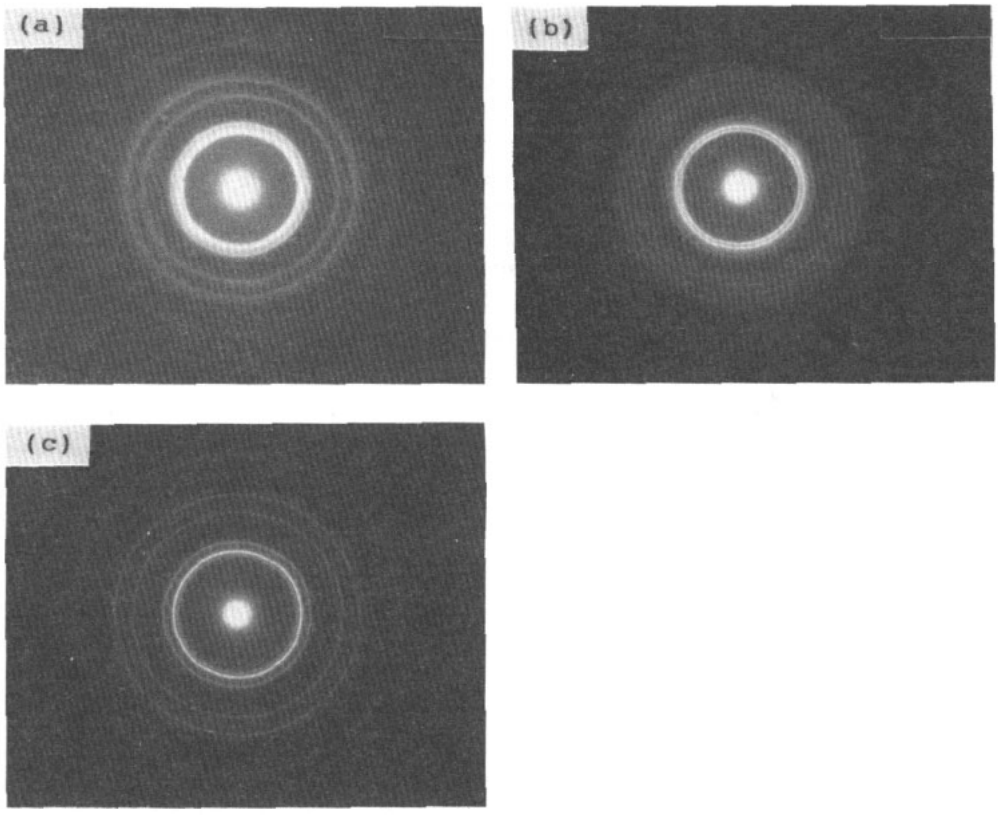

Figure 6. Some typical SAD patterns of the Fe/Pd multilayers: (a) Fe(1.2 nm)/Pd(6.5 nm); (b) Fe(3 nm)/Pd(6.5 nm) and (c) Fe(6.5 nm)/Pd(6.5 nm).

Table 2. Indexing results of the diffraction lines of figure 6.

d_{obs} (nm)	d_{cal} (nm)	Visual intensity[a]			Indices	
		Figure 6(a)	Figure 6(b)	Figure 6(c)	New phase (a = 0.360 nm)	Pd (a = 0.389 nm)
0.223	0.224	s	s	w		111
0.208	0.208	w	s	s	111	
0.194	0.195	m	m	vw		200
0.181	0.180	vw	m	m	200	
0.139	0.138	m	m	vw		220
0.128	0.127	vw	m	m	220	
0.118	0.117	m	m	vw		311
0.112	0.112	w	w	vw		222
0.109	0.109	vw	m	m	311	
0.105	0.104	vw	w	w	222	

[a] s, strong; m, medium; w, weak; vw, very weak.

For Fe/Pd films, the highest magnetic moment per Fe atom reported in the literature is only about $2.8\mu_B$ [9]. However, in this work, the highest magnetic moment per Fe atom reached $3.27\mu_B$. To probe the reason for the magnetic enhancement, the microstructure of

the films was investigated by means of TEM SAD and x-ray diffraction. Figure 6 shows some typical SAD patterns of the Fe/Pd multilayers with different thicknesses of the Fe layer while the Pd layer thickness was fixed at 6.5 nm. The corresponding spacing distances were measured and are listed in table 2, in which the camera constant of the TEM SAD was calibrated by x-ray diffraction results. From figure 6 and table 2 it can be seen that the SAD patterns of all the films consist of two sets of sharp diffraction rings from two FCC phases, i.e. one is the FCC Pd phase and the other is an Fe-enriched Fe/Pd metastable solid solution. Their lattice parameters were about 0.389 ± 0.005 nm and 0.360 ± 0.005 nm, respectively. From figure 6, it can also be seen that the diffraction intensity of the new Fe/Pd phase increased rapidly with increasing Fe layer thickness. When the thicknesses of the Fe and Pd layers were 3 nm and 6.5 nm, respectively, the diffraction intensities of the two phases were very similar. When the Fe layer thickness increased to 6.5 nm, the same as the Pd layer thickness, the diffraction intensity of the Pd phase became very weak, indicating that more Pd was dissolved into the Fe layers. As a result, the new phase with FCC structure was found to be an Fe/Pd solid solution formed at the Fe/Pd interfaces, whose Pd concentration was less than the average Pd content (44 at.%) of the Fe(6.5 nm)/Pd(6.5 nm) multilayers. It should be emphasized that the Fe layer did not have a BCC structure, but an FCC structure with a lattice parameter less than that of the Pd phase. This new phase formed at the Fe/Pd interfaces has not been reported previously.

It is generally assumed that the enhancement of the magnetic moment in Pd/magnetic-metal (Fe, Co) multilayers could be due to the polarization of the Pd atoms [12, 14, 15], because Pd is a strong paramagnet and a small addition of magnetic elements will induce a magnetic moment at Pd atom sites. A neutron diffraction study has indicated that Pd atoms carried magnetic moments of about $0.36\mu_B$ in Pd/Fe alloys [16], and the total magnetic moment in this alloy increased to $2.8\mu_B$ [17]. In our experiment, assuming the Pd atoms carry a magnetic moment of $0.36\mu_B$, the magnetic moments of the Fe(6.5 nm)/Pd(6.5 nm) and Fe(3 nm)/Pd(6.5 nm) multilayers were estimated to be $2.44\mu_B$ and $2.77\mu_B$, respectively, which are obviously lower than the experimental values, i.e. $2.85\mu_B$ for Fe(6.5 nm)/Pd(6.5 nm) and $3.04\mu_B$ for Fe(3 nm)/Pd(6.5 nm) films. Therefore, in addition to the magnetic moment resulting from the polarization of the Pd atoms, there was another factor raising the total magnetic moment. According to the calculation reported by Freeman and Fu [18], Fe in thin-film form with an FCC structure can exhibit ferromagnetic behaviour, in contrast to its bulk FCC phase, which exhibits no ferromagnetic behaviour, because the ferromagnetic state has a lower total energy than the anti-ferromagnetic state. Fe thin films with FCC structure have a higher magnetic moment than α-Fe. Gradman and Isbert [19] also gave a similar prediction. Thus, the calculation of Freeman and Fu can serve as a possible explanation for the magnetic moment enhancement in the Fe/Pd nano-multilayers, similar to our recent results obtained in the Fe/Cu system [6]. The growth of the new Fe/Pd FCC phase at the interfaces in the Fe/Pd multilayers might be related to the medium difference of covalent radius between Fe and Pd. However, it is quite interesting that this new FCC phase has a lattice parameter different from that of the FCC Pd. This microstructure–magnetic-property correlation certainly needs much more study.

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References

[1] Stinson D G and Shin S-C 1990 *J. Appl. Phys.* **67** 4459
[2] Magnan H, Chandesris D, Villette B, Heckman O and Lecante J 1991 *Phys. Rev. Lett.* **67** 859
[3] Sporl K and Weller D 1991 *J. Magn. Magn. Mater.* **93** 379
[4] Krishnan R and Tessier M 1990 *J. Appl. Phys.* **67** 5391
[5] Muir W B, Cochran J F, Rudd J M, Heinrich B and Celinski Z 1991 *J. Magn. Magn. Mater.* **93** 229
[6] Pan F, Tao K, Yang T and Liu B X 1993 *Phys. Status Solidi* a **135** 753
[7] Pan F, Yang T, Tao K and Liu B X 1992 *J. Phys.: Condens. Matter* **4** L519
[8] Pan F, Tao K and Liu B X 1993 *J. Appl. Phys.* at press
[9] den Broeder F J A, Donkersloot H C, Draaisma H J G and de Jonge W J M 1987 *J. Appl. Phys.* **61** 4317
[10] Boufelfel A, Emrick R M and Falco C M 1991 *Phys. Rev.* B **43** 13 152
[11] Dublon G, Rosenblum M P and Vetterling W T 1990 *IEEE Trans. Magn.* **MAG-16** 1126
[12] Draaisma H J G, de Jonge W J M and den Broeder F J A 1987 *J. Magn. Magn. Mater.* **66** 351
[13] Gutierrez C J, Mayer S H and Walker J C 1989 *J. Magn. Magn. Mater.* **80** 299
[14] Oswald A, Zeller R and Dederichs P H 1986 *Phys. Rev. Lett.* **56** 1419
[15] Wu Ruqian, Li Chun and Freeman A J 1991 *J. Magn. Magn. Mater.* **99** 71
[16] Cable J W, Wollan E O and Koehler W C 1965 *Phys. Rev.* **138** A755
[17] Zhang S L, Sumiyama K and Nakamura Y 1988 *J. Magn. Magn. Mater.* **73** 58
[18] Freeman A J and Fu C L 1987 *J. Appl. Phys.* **61** 3356
[19] Gradman U and Isbert H O 1980 *J. Magn. Magn. Mater.* **15–18** 1109