

## Magnetic phase transition in epitaxial $\text{Ni}_{1-x}\text{Fe}_x$ alloy thin films

J. W. Freeland,\* I. L. Grigorov, and J. C. Walker

*Department of Physics and Astronomy, The Johns Hopkins University, 3400 N. Charles Street, Baltimore, Maryland 21218*

(Received 22 August 1997)

An investigation of fcc  $\text{Ni}_{1-x}\text{Fe}_x$  thin films utilizing a combination of Mössbauer spectroscopy and magnetometry presents clear evidence for the emergence of a low-spin antiferromagnetic state in the region of high Fe concentration, which coexists with a high-spin ferromagnetic state. The emergence of this state is observed by magnetometry as a drop in the saturation moment while Mössbauer spectroscopy reveals the appearance of a low-spin antiferromagnetic state. Evidence of superparamagnetic behavior indicates that the portion of the sample in the high-spin state may exist as clusters in a matrix of the low-spin state. [S0163-1829(98)05302-8]

Ever since the discovery of the Invar effect in fcc Ni-Fe alloys,<sup>1</sup> these alloys have been a subject of intensive study.<sup>2,3</sup> However, study of the rich magnetic behavior of these alloys in the region of high Fe concentration ( $x > 0.6$ ) has been complicated by the presence of a structural phase transition to the energetically favorable bcc phase.<sup>3</sup> In order to better understand the role of the Fe in the fcc  $\text{Ni}_{1-x}\text{Fe}_x$  alloys and its relation to the magnetic order, it is necessary to explore the order in the region of high Fe concentration while suppressing the structural phase transition. Using molecular beam epitaxy (MBE), this can be accomplished since fcc Ni-Fe has a close lattice match to Cu and can be prepared in the fcc phase by pseudomorphic growth on Cu substrates over the entire Fe concentration range.<sup>4-7</sup> Studies using *in situ* magneto-optic Kerr effect (MOKE) have found that thin pseudomorphic  $\text{Ni}_{1-x}\text{Fe}_x$  films on Cu(100) present a ferromagnetic signal over the entire concentration range,<sup>4,5</sup> in contrast to the behavior of bulk alloys. The behavior of the Curie temperature as a function of film thickness also provides an indication of a magnetic transition in the region of high Fe concentration.<sup>6</sup> However, since MOKE is not a measure of absolute total moment and only sensitive to the presence of a ferromagnetic signature, additional techniques are then necessary to determine the behavior of the total moment and whether or not magnetic transition involves the emergence of an antiferromagnetic phase.

In this study we utilized a combination of Mössbauer spectroscopy and superconducting quantum interference device (SQUID) magnetometry to provide direct evidence for a magnetic phase transition in pseudomorphic fcc  $\text{Ni}_{1-x}\text{Fe}_x$  thin films. Our results clearly show the emergence of a low-spin antiferromagnetic (AFM) state in the region of high Fe concentration, which coexists with a high-spin ferromagnetic (FM) state.

All of the samples were prepared by MBE in a Perkin-Elmer PHI 430 B MBE system, which has a base pressure of  $1 \times 10^{-10}$  Torr. The Cu(111) substrates were evaporated *in situ* on V-1 quality natural mica sheets at a substrate temperature of 200 °C. The mica sheets were cleaned in ethanol for 15 min, air-cleaved just prior to introduction into the UHV chamber, and then outgassed at 400 °C for several hours prior to growth. To facilitate removal of the sample from the mica substrate, which is required for transmission Mössbauer spectroscopy, a 300 Å epilayer of NaCl was de-

posited on the mica. The sample may then be removed from the mica substrate using a small amount of ultrapure water. For the (100) orientation the 1500 Å Cu base is grown directly on cleaved NaCl(100) at a substrate temperature of 350 °C.

The multilayer structures have the general form  $[\text{Ni}_{1-x}^{57}\text{Fe}_x(4 \text{ ML})/\text{Cu}(100 \text{ Å})]_N$ , where the 4-monolayer (ML) film thickness was 7.2 Å for the (100) films and 8.4 Å for the (111) films. The number of repetitions  $N$ , was 10 for the (111) orientation and 4 for the (100) orientation. The concentrations of Ni and Fe were varied by changing the Ni cell temperature and thus the Ni growth rates and were confirmed after film growth by electron microprobe analysis. To reduce intermixing with Cu at the interface, the substrate temperature was held at 300 K during growth using a  $l$ - $N_2$  cooling finger. Since we are interested in studying independent magnetic layers, the 4 ML  $\text{Ni}_{1-x}\text{Fe}_x$  layers were separated by a 100 Å Cu layer, which has been demonstrated previously to be sufficient to magnetically isolate the layers.<sup>8</sup>

The crystallinity and orientation of the Cu substrates were verified by *in situ* reflection high-energy electron diffraction (RHEED) prior to the multilayer growth. RHEED was also utilized during the multilayer growth to monitor the sample crystallinity. It was only possible to monitor one orientation during the multilayer deposition due to the presence of the  $l$ - $N_2$  cooling finger. However before capping the films the cooling finger was removed and sample was rotated to confirm that the surface had the expected symmetry [fourfold for the (100) and sixfold for the (111)]. In addition, the RHEED streak spacing, which is directly related to the in-plane lattice parameter, was monitored during growth using a K-Space CCD RHEED camera system.<sup>9</sup> In all cases the streak spacing varied by less than 0.05%. This indicates that the  $\text{Ni}_{1-x}\text{Fe}_x$  layers are growing pseudomorphically on the Cu substrate. X-ray diffraction was used as an additional check of the crystallinity and to confirm that no bcc phase was present in these films.

Figure 1 displays the saturation moment normalized to the volume of the film as measured by a SQUID magnetometer. As seen in Fig. 1, the samples display a ferromagnetic signature over the entire Fe concentration range. Below an Fe concentration,  $x$ , of 0.6 the behavior is similar to that of the bulk alloys (as shown by the solid line in Fig. 1). Above  $x = 0.6$ , there is a linear continuation of the increase in mo-

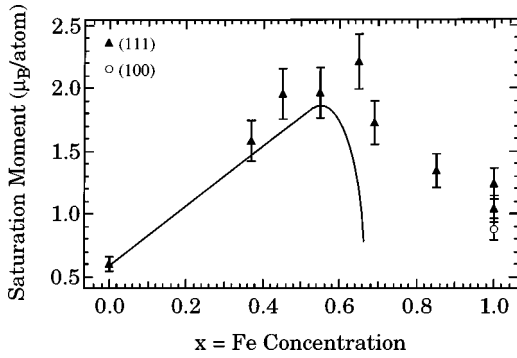


FIG. 1. The saturation magnetic moment normalized to the sample volume vs Fe concentration. The drop in the moment is due to the emergence of an antiferromagnetic state in the region of high Fe concentration. The solid line is the data for bulk  $\text{Ni}_{1-x}\text{Fe}_x$  alloys from Ref. 3 for comparison.

ment into the Invar region, where a precipitous drop in moment is seen in the bulk alloys caused by a transition to an antiferromagnetic state.<sup>3</sup> Presence of a high moment phase in this region has been previously observed in both sputtered<sup>10</sup> and epitaxial<sup>4-6</sup> thin films and is believed to be due to strain induced by the growth process. Expansion of the lattice parameter has been theoretically predicted to stabilize the alloy in the high-spin ferromagnetic state.<sup>11,12</sup> Moving to higher Fe concentrations there is a drop in the moment from a value of  $\sim 2.3 \mu_B$  for  $x=0.65$  to a value of  $\sim 1 \mu_B$  for  $x=1$ . The pure Fe ( $x=1$ ) saturation moment appears to be reproducible and independent of crystalline orientation as shown by three different measurements for films with (100) and (111) orientations. As will be seen the Mössbauer spectroscopy data, the drop in the magnetic moment at high Fe concentrations appears to be caused by the emergence of a low-spin antiferromagnetic state coexisting with the ferromagnetic state. Since this antiferromagnetic state is invisible to the magnetometry measurements, as more of the sample becomes AFM, the magnetic moment drops. The technique of Mössbauer spectroscopy is well suited to study the appearance of such a state due to its sensitivity to both types of magnetic order.

The low-temperature (13 K) Mössbauer data as a function of Fe concentration are shown in Fig. 2. These spectra are

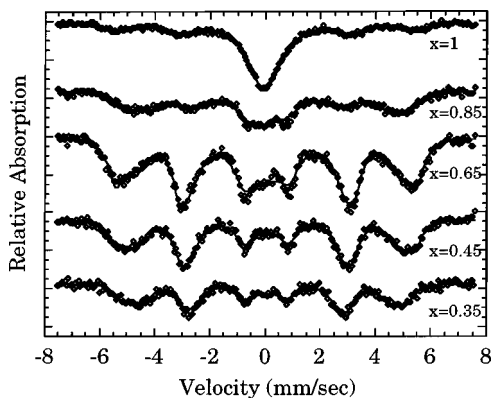


FIG. 2. Low-temperature (13 K) Mössbauer data as a function of Fe concentration. Note the emergence of the broad central feature in the region of high Fe concentration that is correlated to the drop in the saturation magnetic moment. Such a feature is due to the formation of an antiferromagnetic state.

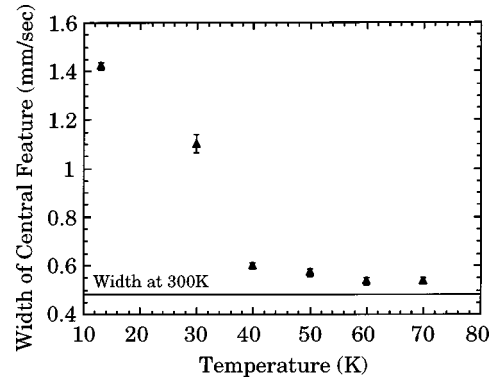


FIG. 3. Central feature width vs temperature for the pure Fe ( $x=1$ ) film. This figure shows the drastic reduction in the central feature width indicative of a Neél transition around 35 K. The solid line denotes the central feature width at 300 K for comparison.

well fit by high-spin magnetic sextet(s) with the inclusion of a broad singlet in the region of high Fe concentration. In the region of low Fe concentration the two high-spin site fit is consistent with that observed in bulk random alloy data.<sup>10,13</sup> The hyperfine field associated with the high-spin state remains constant around 300 kOe ( $\sim 2 \mu_B$ ) with a variation of less than 10%. Since the Fe local moment probed by the hyperfine field is not changing enough to explain the drop in the saturation moment, the drop must be associated with the emergence of the broad central feature in the region of high Fe concentration. This feature grows in intensity and can be well correlated with the drop in the saturation moment. To determine that this broad central feature is indeed caused by Fe in an antiferromagnetic state and not due to relaxation phenomena, the central feature width was studied as a function of temperature for the pure Fe film ( $x=1$ ). Figure 3 shows the dramatic reduction in the width of the central feature with increasing temperature consistent with a Neél transition at  $T_N \sim 35$  K. We find that the width drops from 1.1 mm/sec to a value 0.5 mm/sec as the temperature is raised from 30 to 40 K. The width then remains relatively constant near 0.5 mm/sec above 40 K. This proves conclusively that this feature is associated with an unresolvable low-spin antiferromagnetic state (moment  $\sim 0.5 \mu_B/\text{atom}$ ). From a comparison of the width and isomer shift of the central feature observed for the  $\text{Ni}_{15}\text{Fe}_{85}$  film at both 13 and 300 K to the pure Fe film, we conclude that the central feature present here is also due to an AFM state. This Neél temperature is significantly lower than the value of 65 K measured for fcc Fe precipitates<sup>14</sup> and thin films.<sup>15</sup> However, since the film thickness is only 4 monolayers, the finite size of the sample can affect the magnetic order and cause a suppression of the transition temperature.<sup>16</sup>

In addition, the temperature-dependent Mössbauer study of the  $\text{Ni}_{15}\text{Fe}_{85}$  and pure Fe films revealed the disappearance of the high-spin state as the temperature was raised to 300 K. This disappearance together with an observed ferromagnetic hysteresis at 300 K provides an indication of superparamagnetic behavior in this film. For both films we observed irreversible behavior of field cooled vs zero-field cooled magnetic moment as a function of temperature, which is a clear indication of superparamagnetic behavior. Additional confirmation of this is made by measuring the Mössbauer spectra

of the pure Fe film with a 5 kG applied field and observing the appearance of a sextet corresponding to a high-spin state. The applied field suppresses the relaxation of the magnetic clusters and causes the appearance of a magnetic site in the absorption spectra. From both of these measurements we conclude that the high-spin FM state may exist as clusters in a matrix of the low-spin AFM state.

This observation of coexisting magnetic states in the Ni-Fe alloys is in agreement with studies of bulk alloys in the invar region (65% Fe), where there is strong evidence for coexisting AFM and FM order.<sup>17,18</sup> In these studies it was postulated that there were Fe-rich clusters ordered AFM and coupled to a Ni-rich FM matrix. The spectrum of the Ni<sub>15</sub>Fe<sub>85</sub> film is well described by two high-spin states similar to the sites in the Ni<sub>63</sub>Fe<sub>37</sub> film (Ni rich) and a broad central feature corresponding to a low-spin AFM site as seen in the pure Fe film (Fe rich). This argues for Ni-rich and Fe-rich regions with different magnetic order. For the case of the pure Fe film, previous studies of fcc Fe(100) have seen evidence for coexisting magnetic order,<sup>19,20</sup> however the mode by which the two types of order coexist is not clear. One possible answer may be found in the complicated structures formed by the competition between structural and magnetic energies. Low-energy electron diffraction<sup>21,22</sup> and medium energy ion scattering<sup>23</sup> of fcc Fe(100) on Cu(100) have presented clear indications of complex strain waves forming in fcc Fe thin films on Cu(100).

In addition to the magnetic information contained in the Mössbauer data, there is a great deal of structural information. By comparing the low Fe concentration spectra qualitatively with those of bulk single phase fcc Ni-Fe random alloy spectra, it is inferred that the alloy films are indeed randomly ordering during codeposition of Fe and Ni and have not formed any ordered alloy phases.<sup>10,24</sup> The high-spin site has zero quadrupole splitting expected for a pure fcc

structure. Since we cannot resolve the sextet for the low-spin site, extraction of the quadrupole information is not possible, but the isomer shifts of the two sites can be compared. If the volume increases, the *s*-electron density in the nucleus drops causing the isomer shift to become more positive. For spectra in the region of high Fe concentration the high-spin FM site always has a more positive isomer shift than the low-spin AFM site. This may indicate that the FM regions have a larger volume than the low-spin AFM state. This is consistent with both experimental observations<sup>19,20</sup> and theoretical predictions<sup>12,25</sup> that the lower volume favors the low-spin state.

Information concerning the structure of the pure Fe film can also be inferred by comparing our results to those of uncovered fcc Fe(100) films studied *in situ* by both Mössbauer spectroscopy<sup>20</sup> and magnetometry.<sup>26</sup> For uncovered 4-ML fcc Fe(100) films the magnetic order is ferromagnetic while the structure is fct. But for the case of our 4-ML Fe films, the order is predominantly antiferromagnetic. Both studies of the uncovered films indicate that the AFM order is associated with the fcc structure. This is a good indication that the multilayers are stabilizing the 4-ML Fe films in a more pure fcc state. Such a conclusion is consistent with an x-ray-absorption study of fcc Fe(100) on Cu(100), which found that a Cu cap layer relaxes fct Fe into fcc Fe.<sup>27</sup>

In summary, our investigation of fcc Ni<sub>1-x</sub>Fe<sub>x</sub> thin films gives clear evidence for the emergence of a low-spin antiferromagnetic state in the region of high Fe concentration in coexistence with a high-spin ferromagnetic state. The emergence of this state is observed by magnetometry as a drop in the saturation moment in this region while Mössbauer spectroscopy reveals the appearance of a low-spin antiferromagnetic state. Together with the evidence of superparamagnetic behavior, there is strong evidence that high-spin state exists as clusters intermixed with the low-spin state.

\*Present address: Naval Research Laboratory, NSLS Bldg. 725A/U4B, Brookhaven National Lab., Upton, NY 11973.

<sup>1</sup>Ch. Éd. Guillaume, C. R. Hebd. Seances Acad. Sci. **125**, 235 (1897).

<sup>2</sup>*Physics and Applications of Invar Alloys*, edited by Hideo Saito (Maruzen, Tokyo, 1978).

<sup>3</sup>E. F. Wassermann, in *Ferromagnetic Materials*, Vol. 5, edited by K. H. J. Buschow and E. P. Wohlfarth (Elsevier, Amsterdam, 1990).

<sup>4</sup>G. J. Mankey, S. Z. Wu, F. O. Schumann, F. Huang, M. T. Kief, and R. F. Willis, *J. Vac. Sci. Technol. A* **13**, 1531 (1995).

<sup>5</sup>F. O. Schumann, S. Z. Wu, G. J. Mankey, and R. F. Willis, *J. Appl. Phys.* **79**, 5635 (1996).

<sup>6</sup>F. O. Schumann, S. Z. Wu, G. J. Mankey, and R. F. Willis, *Phys. Rev. B* **56**, 2668 (1997).

<sup>7</sup>J. Dresselhaus, M. Möller, Th. Kleeman, and E. Kisker, *J. Magn. Magn. Mater.* **148**, 172 (1995).

<sup>8</sup>J. W. Freeland, D. J. Keavney, D. F. Storm, I. L. Grigorov, J. C. Walker, M. G. Pini, P. Politi, and A. Rettori, *Phys. Rev. B* **54**, 9942 (1996).

<sup>9</sup>D. Bartlett *et al.*, *Rev. Sci. Instrum.* **62**, 1263 (1991).

<sup>10</sup>G. Dumpich, E. Becker, K. Schletz, W. Stamm, W. Keune, W. Kiauka, and S. Murayama, *J. Magn. Magn. Mater.* **74**, 237 (1988); G. Dumpich, E. F. Wassermann, V. Manns, W. Keune,

S. Murayama, and Y. Miyako, *ibid.* **67**, 55 (1987).

<sup>11</sup>R. J. Weiss, *Proc. R. Soc. London, Ser. A* **82**, 281 (1963).

<sup>12</sup>I. A. Abrikosov, O. Eriksson, P. Söderlind, H. L. Skriver, and B. Johansson, *Phys. Rev. B* **51**, 1058 (1995).

<sup>13</sup>B. Window, *J. Appl. Phys.* **44**, 2853 (1973).

<sup>14</sup>U. Gonser, C. J. Meechan, A. H. Muir, and H. Wiedersich, *J. Appl. Phys.* **34**, 2373 (1963).

<sup>15</sup>W. A. A. Macedo and W. Keune, *Phys. Rev. Lett.* **61**, 475 (1988).

<sup>16</sup>M. E. Fisher and A. E. Ferdinand, *Phys. Rev. Lett.* **19**, 169 (1967); D. S. Ritchie and M. E. Fisher, *Phys. Rev. B* **7**, 480 (1973); D. P. Landau, *ibid.* **13**, 2997 (1976).

<sup>17</sup>H. Zähres, M. Acet, W. Stamm, and E. F. Wassermann, *J. Magn. Magn. Mater.* **72**, 88 (1988).

<sup>18</sup>H. Murayama, R. Pauthenet, J. C. Picoche, and O. Yamada, *J. Phys. Soc. Jpn.* **55**, 3218 (1986).

<sup>19</sup>D. J. Keavney, D. F. Storm, J. W. Freeland, I. L. Grigorov, and J. C. Walker, *Phys. Rev. Lett.* **74**, 4531 (1995).

<sup>20</sup>R. D. Ellerbrock, A. Fuest, A. Schatz, W. Keune, and R. A. Brand, *Phys. Rev. Lett.* **74**, 3053 (1995).

<sup>21</sup>P. Bayer, S. Müller, P. Schmailzl, and K. Heinz, *Phys. Rev. B* **48**, 17 611 (1993).

<sup>22</sup>S. Müller, P. Bayer, C. Reischl, K. Heinz, B. Feldmann, H. Zillgen, and M. Wüttig, *Phys. Rev. Lett.* **74**, 765 (1995).

<sup>23</sup>J. V. Barth and D. E. Fowler, *Phys. Rev. B* **52**, 1528 (1995).

<sup>24</sup>S. Tomiyahsi, H. Yamamoto, and H. Watanabe, *J. Phys. Soc. Jpn.* **30**, 1605 (1971).

<sup>25</sup>V. L. Moruzzi, P. M. Marcus, and J. Kübler, *Phys. Rev. B* **39**, 6957 (1989).

<sup>26</sup>D. Li, M. Frietag, J. Pearson, Z. Q. Qiu, and S. D. Bader, *Phys. Rev. Lett.* **72**, 3112 (1994).

<sup>27</sup>H. Magnan, D. Chandesris, B. Villette, O. Heckmann, and J. Lecante, *Phys. Rev. Lett.* **67**, 859 (1991).