Magnetic Instability of Ultrathin fcc Fe_xNi_{1-x} Films

F. O. Schumann and R. F. Willis
The Pennsylvania State University, Department of Physics, 104 Davey Lab, University Park, Pennsylvania 16802

K. G. Goodman and J. G. Tobin
Department of Chemistry and Material Science, Lawrence Livermore National Laboratory, Livermore, California 94550

(Received 1 May 1997)

The "invar effect" in Fe_xNi_{1-x} alloys occurs when the Fe content approaches 65%. At this point, the magnetization falls to zero, and a martensitic structural transformation from a fcc to a bcc lattice occurs. This paper addresses the question: "What happens if the structural transformation is suppressed in an ultrathin alloy film?" We present results to this effect, showing the variation of the magnetization with changing composition in ultrathin films grown on Cu(100). We find a new low-spin, ferromagnetic phase of matter, which is a sensitive function of the atomic volume. [S0031-9007(97)04889-8]

PACS numbers: 75.70.Ak, 75.50.Bb, 79.60.Dp

Recent experimental results of the properties of fcc Fe/Cu(100) have stressed the importance of the correlation between magnetic properties and the atomic volume [1–4]. These moment-volume instabilities for fcc Fe had been calculated a few years ago [5] and were the driving force for many subsequent experiments. Moment-volume instabilities are also known in fcc Fe_xNi_{1-x} alloys. In the bulk, Fe_xNi_{1-x} alloys show anomalous behavior at a Fe content of ~65%, which is usually referred to as the "invar effect" [6]. It has been observed that the structure changes from the fcc into the bcc phase as the Fe content increases. Simultaneously the Curie temperature T_c and the magnetic moment collapse [6]. The question arises whether a moment collapse still takes place if the fcc phase stability is extended beyond 65% Fe. This question has been theoretically answered by Abrikosov *et al.* [7]. They find that a moment collapse still takes place at a Fe content of 75%, which is accompanied by a reduction of the atomic volume of ~9%. Experimentally an extended regime of fcc stability can be achieved via epitaxy on a Cu(100) substrate [8] which allows us to test the prediction of Abrikosov *et al.*

In this Letter we report on the concentration dependence of the magnetic dichroism of the Fe $3p$ core level in photoemission with linearly polarized light [x-ray magnetic linear dichroism (XMLD)] for metastable fcc Fe_xNi_{1-x} alloy films and the correlation to their atomic volume [9].

We will show that a moment-volume instability exists, but the atomic volume changes are significantly smaller than predicted. We will also show that the moment stays finite since we observe a ferromagnetic response in the form of surface magneto-optic Kerr effect (SMOKE) hysteresis loops and XMLD. Moreover, our results stress the importance of a changing atomic volume on the magnetic instability of fcc Fe_xNi_{1-x} alloys and indicate the existence of magnetic phases not considered by Abrikosov *et al.*

We performed extensive studies on the structural and magnetic properties of Fe_xNi_{1-x}/Cu(100) alloys films, which we found to grow layer by layer [8]. Details of the apparatus can be found elsewhere [8]. The dichroism experiments were performed at the SpectroMicroscopy Facility on Beamline 7 at the Advanced Light Source, Berkeley [10]. The alloy films were grown at 300 K and the concentration and thickness were determined using a MgK_α source. For photoemission of the $3p$ core levels we utilized 190 eV photons (p-polarized) and collected electrons in normal emission with an angular resolution of 2°. The angle of incidence of the photon beam was 60° with respect to the surface normal and the magnetization was in the "transverse" geometry [11] which is sensitive to an in-plane orientation of the magnetization. A field pulse from a coil near the sample magnetized the sample along the {001} direction. Magnetization reversal could be achieved by reversing the direction of the field pulse. SMOKE experiments have shown that Fe_xNi_{1-x} films with the magnetic field along the {001} direction have almost square loops. We performed two series of experiments: First we grew uniform films with a given thickness and concentration; then, in order to explore the thickness dependence at a given concentration, we grew wedged samples with a gradient of ~2 ML/mm. The spot size of the light was ~100 μm which results in a thickness resolution of ~0.2 ML (monolayers).

We have systematically changed the concentration of fcc Fe_xNi_{1-x} alloy films and measured the dichroism of the Fe $3p$ core level. In Fig. 1 the result for a 7 ML $Fe_{59}Ni_{41}$ film is shown in which we observe dichroism in both the Ni and the Fe $3p$ levels. Similar spectra were obtained with the focus on the Fe-rich side. The results are displayed in the upper panel of Fig. 2 [12]. The distinctive feature is a high asymmetry for concentrations below ~60% followed by a transition into a low asymmetry at higher Fe concentrations [13]. The lower panel of Fig. 2 shows the concentration dependence

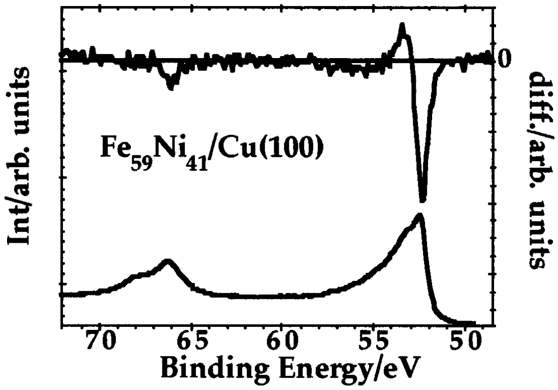

FIG. 1. Difference spectrum and single spectrum of a 7 ML $Fe_{59}Ni_{41}$ alloy film taken at 300 K. Dichroism is also observed for the Ni $3p$ core level.

of the atomic volume of 6 ML thick alloy films as determined by low-energy electron diffraction (LEED) and reflection high-energy electron diffraction (RHEED). The perpendicular lattice constant has been deduced from the Bragg peaks of the $(0,0)$ LEED spot [14]. This simple kinematic picture has been shown to be sufficiently accurate for determining the perpendicular lattice constant for two different phases in fcc Fe/Cu(100) [2]. The in-plane lattice constant was measured by the peak separation of the $(1,0)$ and $(-1,0)$ RHEED beam [15]. We have observed that for up to 66% Fe content, Fe_xNi_{1-x} alloys grow pseudomorphically on the Cu(100) substrate [16]. But $Fe_{80}Ni_{20}$ alloys show a gradual decrease of the in-plane lattice constant of ~0.7% between 1–4 ML.

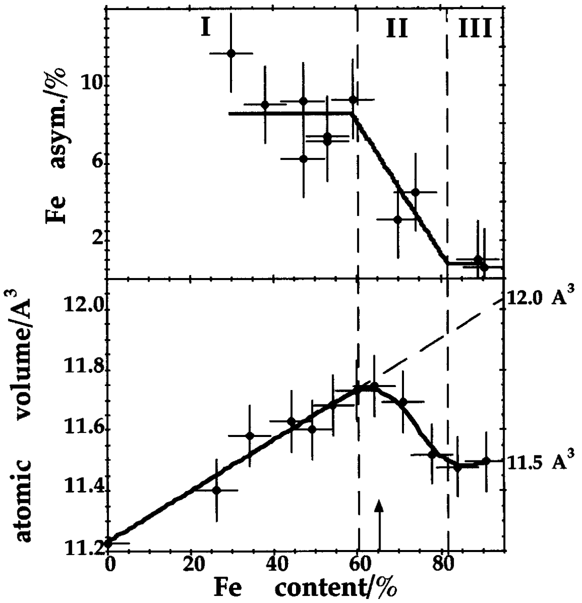

FIG. 2. The upper panel shows the concentration dependence of the Fe $3p$ asymmetry at 300 K; the film thickness was 5.5–9.0 ML. Solid line is a fit as explained in the text. The dashed vertical lines separate the different regimes labeled I, II, and III. The lower panel shows the atomic volume of 6 ML thick alloy films.

We now want to discuss what we can learn from the variation of the atomic volume. First we extrapolate the atomic volume for the pure Fe case and compare it with the results of a full LEED I-V analysis of Fe/Cu(100) [1]. Müller *et al.* found 12.1 Å^3 for films up to 4 ML and 11.4 Å^3 for the interior of thicker films [1]. Interestingly our values derived from Fig. 2 (12.0 and 11.5 Å^3) are in good agreement with Müller *et al.* and show that our simplified structural analysis is essentially correct. In the case of Fe/Cu(100) the two atomic volumes are representative for two different magnetic phases; the larger volume refers to a ferromagnetic high spin (HS) state and the smaller to an antiferromagnetic low spin (LS) state [3,4] in agreement with theory [5]. We can immediately see that if Fe were to stay in a HS state for all concentrations the atomic volume would follow the curve which extrapolates to 12.0 Å^3 for pure fcc Fe. Since the atomic volume curve deviates towards smaller values we conclude that a ferromagnetic LS state exists for concentrations beyond ~70% Fe. It should be noted that we are able to observe hysteresis loops and magnetic dichroism, so we can rule out a fully antiferromagnetic phase. In fact, the results of Keavney *et al.* suggest that a coexistence of phases is a possibility. They observed that by increasing the lattice constant of the substrate the average moment increases from $(0.3-2.0)\mu_B$ [3,17]. However, they found that the hyperfine field is not systematically dependent on the lattice constant. They described this as a change in the population of two coexisting phases. For Fe concentrations above 80% the atomic volume changes only very little due to the fact that the atomic volumes of Fe and Ni are now very similar. From the atomic volume plot in Fig. 2 we can now derive a model for the Fe asymmetry. For concentrations up to ~65% Fe we expect a constant value followed by a transition region to smaller values. Finally, a regime at constant value starts at ~80% Fe content. The solid line in the upper panel of Fig. 2 is a fit to the data by assuming two regimes of constant asymmetry joined by an intermediate regime with linearly varying asymmetry [18].

We can distinguish three regimes; for Ni-rich alloys we observe a high asymmetry of ~8% followed by a transition regime towards smaller values which finally stays constant at ~1%. These regimes have been indicated in Fig. 2 as I–III.

We clearly observe a close connection between the magnetic asymmetry and the atomic volume which shows in the transition interval a reduction by ~2%. This confirms the expected moment-volume instability. However, the variation of the atomic volume is significantly smaller than predicted by Abrikosov *et al.* [7].

In order to further explore the volume instability we have investigated the thickness dependence of the asymmetry for concentrations near the boundary of regimes II and III. We were guided by ancillary SMOKE experiments on a $Fe_{75}Ni_{25}$ alloy which have shown a change in the thickness dependence of T_c at around 4 ML [8]. In Fig. 3 we show the results for two Fe concentrations of 72% and 80%, respectively. In both cases we notice that by reducing the thickness, the asymmetry reaches a value of $\sim$8%–10% which coincides with the value for Fe concentrations below 60%; see Fig. 2. In other words the reduction of the asymmetry is suppressed at a thickness of 2–3 ML. If we indeed observe a moment-volume instability for Fe_xNi_{1-x} alloys, we have to expect an increase of the atomic volume if the thickness is decreased from $\sim$7 to $\sim$2 ML. This is exactly what we have observed and we compare in Fig. 4 the atomic volume for 2 and 6 ML films [19]. We see that an increase of the atomic volume by $\sim$3%–4% is sufficient to result in an increased asymmetry. As pointed out before these results are in agreement with the observation of Keavney *et al.* although they could not give a value of the change in the atomic volume [3].

Again we observe that the magnitude of the asymmetry depends in a very sensitive way on the atomic volume. We therefore conclude that our data show the existence of two magnetic phases which are separated by a small variation of the atomic volume ($\sim$3%). This is significantly smaller than the prediction of Abrikosov *et al.* and also smaller than the change observed for Fe/Cu(100) [1,2].

The observed close connection between the magnetic asymmetry and atomic volume clearly suggests that the element specific asymmetry tracks the average moment. In fact, we find that the element-specific asymmetry for Co_xNi_{1-x}/Cu(100) alloy films is independent of the concentration. Recently it has been shown experimentally that XMLD of the Fe $3p$ core level probes the magnetization [11,20], which agrees with the findings of van der Laan [21], and the data shown in Fig. 2 would suggest a strong variation of the average Fe moment. As shown in Fig. 3 the asymmetry increases by a factor of $\sim$6 when reducing the thickness from $\sim$7 to $\sim$2 ML for Fe concentrations of 72% and 80%, respectively. This factor is more or less what Keavney *et al.* observe for the average moment (or magnetization) upon increasing the lattice constant [3]. We can make this point clearer by considering the following. In the Ni-rich regime we can assume the value of $\sim 2.5\mu_B$ for Fe; this follows from Abrikosov *et al.* and the variation of the atomic volume shown in Fig. 2. With this "calibration" we get a value of $\sim 0.4\mu_B$ in the limit of pure Fe/Cu(100). This is in fair agreement with the result of Keavney *et al.* [3]. In other words, extrapolating the magnetic asymmetry signal towards the pure Fe case results in a variation which is strongly correlated to the magnetization.

Although the available cooling was rather limited (250 K) we can rule out variations in T_c as the cause of the asymmetry behavior. Our SMOKE measurements have shown that T_c increases only slowly with thickness for $Fe_{75}Ni_{25}$/Cu(100) (after a steep initial increase) and is above 250 K for thicknesses larger than $\sim$2 ML [8]. In other words, there is no drop of T_c as a function of thickness as is observed for Fe/Cu(100) [22].

The question might arise as to whether the observation of a reduced asymmetry is due to "magnetic live surface layers" as reported by Thomassen *et al.* [22] rather than a "volume" effect. The thickness dependence of the asymmetry shown in Fig. 4 does not support this view. We do see a continuous change rather than a jump at a critical thickness, which is $\sim$4 ML for Fe/Cu(100). This is confirmed by our SMOKE measurements and similar results for fcc Fe_xCo_{1-x}/Cu(100) alloys [23], which show that the sample is uniformly magnetized [8]. It turns out that a small amount ($\sim$20%) of Ni or Co is sufficient to suppress the existence of magnetic live surface layers. The existence of magnetic live layers is closely connected to the structural instability of

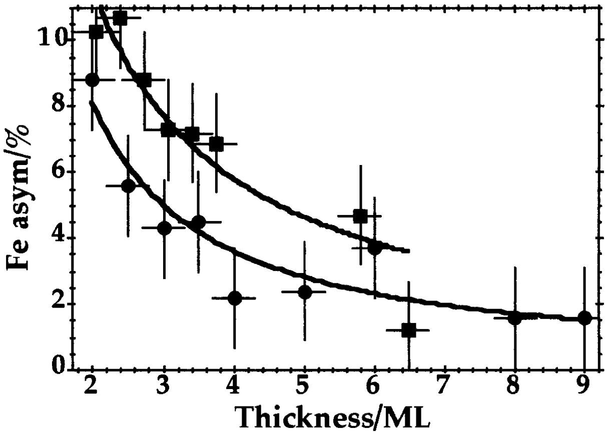

FIG. 3. Thickness dependence of the Fe $3p$ asymmetry for wedge-shaped films of $Fe_{80}Ni_{20}$ (squares) and $Fe_{72}Ni_{28}$ (circles) alloys taken at $\sim$250 K.

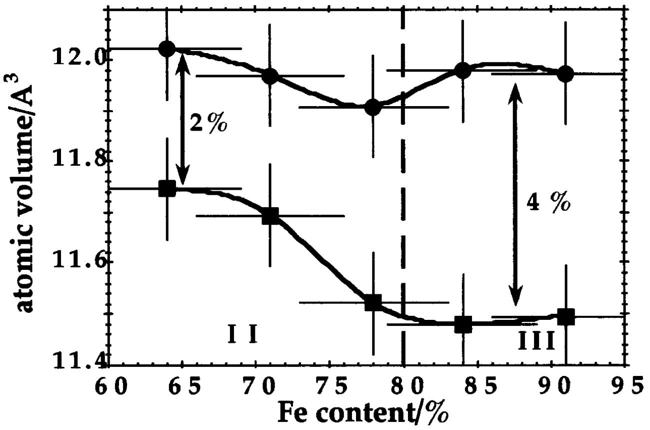

FIG. 4. Comparison of the variation of the atomic volume of 2 ML (circles) and 6 ML (squares) thick alloy films near the critical invar concentration.

fcc Fe/Cu(100) which results in reconstructions of the surface as seen with LEED [1,22]. The lack of these reconstructions for $\mathrm{Fe}_x\mathrm{Ni}_{1-x}/\mathrm{Cu}(100)$ are a manifestation of a higher structural stability. From this point of view we do not expect magnetic live surface layers in $\mathrm{Fe}_x\mathrm{Ni}_{1-x}$ alloys.

Also a rotation of the magnetization from in plane to out of plane is not responsible for the reduced Fe $3p$ asymmetry. This follows from our SMOKE experiments in the longitudinal and polar geometry [8]. We also checked this point with the XMLD technique by employing a geometry which is sensitive to a perpendicular magnetization orientation. A suppression of a perpendicular magnetization has also been observed for $\mathrm{Fe}_x\mathrm{Co}_{1-x}/\mathrm{Cu}(100)$ alloys upon alloying with a small amount of Co [23].

The growth of $\mathrm{Fe}_x\mathrm{Ni}_{1-x}/\mathrm{Cu}(100)$ alloys has been thoroughly studied and we found good epitaxial growth [8]. In particular, we did not observe different growth regimes as it is known for Fe/Cu(100) [22]. Therefore our measurements reflect the "true" intrinsic properties of $\mathrm{Fe}_x\mathrm{Ni}_{1-x}$ alloys.

We have shown that $\mathrm{Fe}_x\mathrm{Ni}_{1-x}$ alloys can be stabilized in the fcc phase on a Cu(100) substrate. Furthermore, we observe a variation of the atomic volume with concentration. We report on the first systematic study of the magnetic behavior of ultrathin alloy films utilizing the element specificity of core-level photoemission with linear polarized light. We have observed a close connection between the Fe $3p$ asymmetry and the atomic volume. The observed reduction of the atomic volume at ~60%–80% Fe content is significantly smaller than predicted by Abrikosov *et al.* [7]. Our results clearly show that additional magnetic phases other than a nonmagnetic and high-spin ferromagnetic HS phases must exist for fcc $\mathrm{Fe}_x\mathrm{Ni}_{1-x}$ alloys. We also conclude that XMLD measures a quantity closely related to the magnetization.

Funding was provided via NSF Grant No. DMR-95-21126. This work was also performed under the auspices of the U.S. Department of Energy by LLNL under Contract No. W-7405-ENG-48. We also thank Dr. D. Waddill for his help.

---

[1] S. Müller *et al.,* Phys. Rev. Lett. **74**, 765 (1995).
[2] M. Zharnikov *et al.,* Phys. Rev. Lett. **76**, 4620 (1996).
[3] D. J. Keavney *et al.,* Phys. Rev. Lett. **74**, 4531 (1995).
[4] R. D. Ellerbrock *et al.,* Phys. Rev. Lett. **74**, 3053 (1995).
[5] V. L. Moruzzi, P. M. Marcus, and J. Kübler, Phys. Rev. B **39**, 6957 (1989).
[6] E. F. Wassermann, in *Invar: Moment-Volume Instabilities in Transition Metals and Alloys,* edited by K. H. J. Buschow and E. P. Wohlfarth, Ferromagnetic Materials (North-Holland, Amsterdam, 1990).
[7] I. A. Abrikosov *et al.,* Phys. Rev. B **51**, 1058 (1995).
[8] F. O. Schumann *et al.,* Phys. Rev. B **56**, 2668 (1997).
[9] A suppression of the martensitic transition is reported in G. Dumpich *et al.,* Phys. Rev. B **46**, 9258 (1992); Th. Kleemann *et al.,* in *Metallic Alloys: Experimental and Theoretical Perspectives,* edited by J. S. Faulkner and R. G. Jordan (Kluwer Academic Publishers, Dordrecht, 1994). However the variation of the atomic volume is not described.
[10] J. G. Tobin *et al.,* J. Appl. Phys. **79**, 5626 (1996).
[11] F. Sirotti and G. Rossi, Phys. Rev. B **49**, 15 682 (1994).
[12] The Fe asymmetry is the ratio of the difference spectrum over twice the mean peak height. We cannot use the expression $I(\mathrm{up}) - I(\mathrm{down})/I(\mathrm{up}) + I(\mathrm{down})$ due to the concentration dependence of Fe $3p$ height.
[13] For magnetization reversal the sample is moved into a second position and then back to the measurement position. The associated error is more significant than the statistical noise.
[14] J. B. Pendry, *Low Energy Electron Diffraction* (Academic Press, London, New York, 1974).
[15] J. Fassbender *et al.,* Phys. Rev. Lett. **75**, 4476 (1995).
[16] Fassbender *et al.* observe an oscillation of the peak separation. However the minimum coincides with the value of the Cu(100) substrate. This is also observed for $\mathrm{Fe}_x\mathrm{Ni}_{1-x}$ alloys up to 66% Fe content.
[17] They were not able to determine the perpendicular lattice constant. Hence we do not know the atomic volume.
[18] Find that the Ni asymmetry stays constant for up to 60% Fe content. Because of the decreasing peak height dichroism on the Ni site can no longer be detected for higher Fe concentrations.
[19] For 2 ML thick films the Cu substrate makes a contribution to the perpendicular lattice constant. We have corrected this by assuming a Cu bulk value for the top 2 ML of the Cu crystal and the same weight as for the 2 ML alloy film. This is a reasonable assumption which is confirmed by a LEED I-V study including the (1, 0), (1, 1), and (2, 0) beams.
[20] F. Sirotti, G. Panaccione, and G. Rossi, Phys. Rev. B **52**, R17 063 (1995).
[21] G. van der Laan, Phys. Rev. B **51**, 240 (1995).
[22] J. Thomassen *et al.,* Phys. Rev. Lett. **69**, 3831 (1992).
[23] M. Zharnikov *et al.,* Thin Solid Films **275**, 262 (1996).