Site-Specific Mössbauer Evidence of Structure-Induced Magnetic Phase Transition in fcc Fe(100) Thin Films

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The magnetic phases of fcc Fe(100) in Fe(100)/$Cu_{1-x}Au_x$(100) multilayers with lattice parameters in the range $a = 3.606$ to 3.704 Å have been studied using Mössbauer spectroscopy and SQUID magnetometry. The Fe layers have a two-phase structure consisting of a low-spin antiferromagnetic (AF) and a high-spin ferromagnetic (FM) phase. The average Fe moment and the relative population of FM Fe both increase with a, but the hyperfine magnetic field for the FM phase is not dependent on a, indicating that the increase in moment comes only from the FM phase population increase.

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The magnetic properties of metastable fcc Fe have been explored for some time [1,2]. Recently, new interest in this controversial material has arisen, due to the ability to fabricate higher quality films, and new predictions for the magnetic structures based on modern computational methods. In general, total magnetic moment calculations predict a fairly complex phase diagram consisting of as many as three magnetic states, with a sensitive dependence on the lattice parameter [3]. These include a nonmagnetic state, a low-spin antiferromagnetic state, and a high-spin ferromagnetic state. Experimentally, the measurement of the moments of these states has been characterized by a sensitivity to growth conditions, such as substrate temperature and surface conditioning, with conflicting reports of the magnetic structure and moments coming from different laboratories. This situation is attributed to the complexity of the phase diagram near the lattice parameter of most of the experimental studies, i.e., at the lattice parameter of Cu. To complicate matters further, there are structural transitions that fcc Fe undergoes at certain film thicknesses, with corresponding changes in the magnetic properties [4–6], and magnetic phase transitions [7,8]. Not least among the structural transitions is the fcc-bcc transition which occurs above a critical thickness of 10–11 monolayers (ML). Therefore, small variations in structure between samples can produce the widely varying results that have been reported. In this Letter the transition between the high- and low-spin phases of fcc Fe(100) is studied by growth on substrates with varying lattice parameter, and local information on the magnetic states is obtained by Mössbauer spectroscopy.

While the explanation for the experimental discrepancies based on sensitive dependence of magnetic properties on structure is most probably correct, it does not answer any questions concerning the structure—property relations in fcc Fe. This situation strongly indicates the need for the determination of reliable phase diagrams for fcc Fe. Li *et al.* [9] have recently explored the thickness dependence of the magnetic structure and moments in uncapped ultrathin Fe wedges grown on Cu(100), and have identified several magnetic states of fcc and face-centered tetragonal (fct) Fe(100). In addition, they have explored the growth temperature dependence of the magnetic properties. For growth at 0 °C, as used in this study, Li *et al.* suggest that the initial growth is fct up to about 5 ML, fcc between 6 and 11 ML, and reconstructs to bcc Fe above 11 ML. Kerr effect measurements determined that the fct phase is ferromagnetic, and the fcc phase is antiferromagnetic with a high-moment "live" surface layer similar to previous observations by Thomassen *et al.* [10].

Typically, the magnetic moment calculations give the predicted moment and total energy for each state as functions of the Wigner-Seitz radius. Experimental maps of such curves are rare, however, probably because many workers use single-crystal substrates and cannot obtain many different lattice parameters. Keune and co-workers have studied fcc Fe(100) on Cu(100) and Cu_3Au(100) using Mössbauer spectroscopy [11,12], and reported a two-phase structure similar to the observations in this study. Gradmann and Isbert [13], and subsequently Mitani *et al.* [14], used $Cu_{1-x}Au_x$(100) alloy substrates to vary the lattice parameter, and reported that the total moment of their films increases with lattice parameter. Alloying studies permit a more continuous distribution of lattice parameter values between that of Cu and Cu_3Au, which is the most interesting regime due to the expected transition from the low-spin to the high-spin state. However, until now only the average moment per Fe atom has been measured in this regime, without sensitivity to the possible coexistence of multiple magnetic states. In this work Mössbauer spectroscopy is used to study separately the behaviors of the low-spin and high-spin states in fcc Fe(100) films grown on alloy substrates with increasing lattice parameter.

The alloy substrates were codeposited *in situ* on air-cleaved NaCl(100) wafers by molecular beam epitaxy from two different pure metal sources, allowing the composition to be varied by changing one or both of the growth rates. Each NaCl(100) wafer was outgassed in vacuum at 350 °C for 15 min, followed by

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the deposition of a ~300 Å layer of pure NaCl(100) and a ~5000 Å $Cu_{1-x}Au_x$ substrate layer. On these substrates, 6.5 ML of Fe(100) were deposited at 0 °C, followed by ~40 ML of $Cu_{1-x}Au_x(100)$ with the same composition as the substrate, and the bilayer structure is repeated 4 times to increase the Mössbauer signal. Within the 6.5 ML Fe layers, the 2 ML regions of the Fe layers nearest the $Cu_{1-x}Au_x$ layers are composed of natural Fe, while the interior region is composed of ~95% enriched ^{57}Fe. In this arrangement, the Mössbauer spectra correspond to the interior region only. Each multilayer is capped with ~3000 ÅCu, for a resultant structure of NaCl(100)/$Cu_{1-x}Au_x$(~5000 Å)/[Fe(6.5 ML)/$Cu_{1-x}Au_x$(~40 ML)]$_4$/Cu(~3000 Å) for the system studied.

The crystallinity and orientation of the alloy substrates were verified by reflection high energy electron diffraction (RHEED) prior to the multilayer growth. During growth, RHEED was also used to monitor the crystallinity of the fcc Fe(100) and the alloy layers. It was only possible to monitor the ⟨10⟩ azimuthal direction with RHEED during deposition (due to the presence of the l-N_2 cold finger), but from the patterns observed the evidence is that the Fe grows pseudomorphically. Along the ⟨10⟩ azimuth, no shifts were observed upon deposition of Fe on the alloy substrates. Postgrowth azimuthal scans also show none of the additional reflections that would be expected from a bcc Fe component. The RHEED patterns from the Fe layers showed broadened streaks as compared to the alloy substrate, which sharpened upon deposition of the alloy on Fe.

X-ray diffraction was used on the finished samples as an additional check on the crystallinity and to determine the substrate lattice parameter. These measurements detected no formation of the intermetallic compounds that might be expected for this alloy system, such as Cu_3Au or CuAu. A minority $Cu_{1-x}Au_x(111)$ component was detected, but this is most likely due to the initial polycrystalline growth on NaCl, because the in-plane symmetry of the substrate surfaces was determined to be fourfold by RHEED. We conclude then that the substrate surfaces formed a crystalline, homogeneously disordered, (100) oriented binary alloy. The lattice parameter was varied from that of Cu at $a = 3.606$ to 3.704 Å, which corresponds to a composition range of $x = 0$ to 0.2. Unfortunately, the x-ray diffraction measurements could not be used to measure the perpendicular spacing of the fcc Fe(100) due to coincident diffraction peaks from the substrates. However, the absence of bcc Fe peaks is further evidence for pseudomorphism.

The local magnetic environment of the Fe was investigated by ^{57}Fe transmission Mössbauer spectroscopy. Specifically, the low temperature and temperature dependent magnetic hyperfine fields at the ^{57}Fe nuclei in the films were measured, providing information on the magnetic structure and moments. The site-specific Mössbauer technique described above was employed to minimize any effects of interdiffusion, gold surface segregation, or sample to sample differences in interface band structure caused by different Au concentrations. To connect these microscopic measurements with bulk measurements, SQUID magnetometry measurements were also taken at ~5 K to determine the average moment per Fe atom.

First we consider the temperature dependent Mössbauer spectra for the fcc Fe(100) on pure Cu(100), as shown in Fig. 1. At room temperature, the film shows only a single spectral line, indicating that it is not magnetically ordered. As the temperature is reduced, the central line undergoes a broadening transition between 50 and 150 K. The linewidth is more than doubled in this transition. We interpret this as the same low-spin antiferromagnetic phase that has been observed by Macedo and Keune [11] in fcc Fe thin films, and by others in small particle fcc Fe precipitates [2,15–17], with a Néel temperature of ~67 K. This phase does not appear as a sextet because the moment is too low to result in resolvable Zeeman-split spectral lines. This makes it difficult to fit to a definite hyperfine field, but the linewidth shown is consistent with the moment previously reported for low-spin antiferromagnetic fcc Fe of $\sim 0.7\mu_B$ per atom [12]. We also note that upon cooling a high-spin magnetic sextet appears in the spectrum. The hyperfine splitting of the sextet corresponds to a bulklike moment, but its ordering temperature is reduced from bulk to about

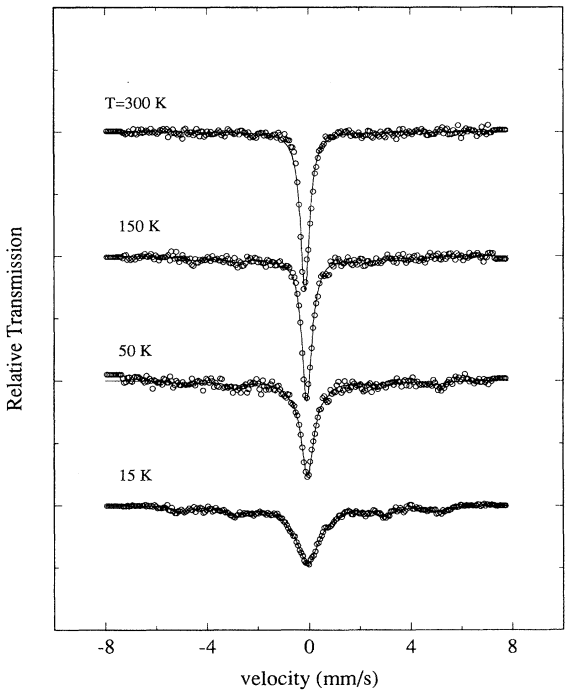

FIG. 1. Temperature dependent Mössbauer spectra (open circles) and fits (solid lines) for 6.5 ML fcc Fe(100) films grown on pure Cu(100). The central linewidth doubles upon cooling to 15 K, indicating the AF ordering of the low-spin site. Also, a small amount of high-spin Fe exists, as seen in the low intensity sextet.

150 K. The intensity ratios of the sextet lines are 3:4:1:1:4:3, indicating in-plane magnetization. We associate this sextet with a high-moment phase of fcc Fe reported previously [11,12]. The high-spin site shows a small but nonzero negative quadrupole splitting ($\varepsilon < 0$), indicating that it may be tetragonally contracted to compensate for the in-plane expansion that results from the growth on Cu(100).

The two sites observed at the Cu lattice parameter undergo significant intensity changes when the substrate lattice parameter is increased. Spectra taken at ~15 K for six films with different substrate compositions are shown in Fig. 2. The intensity of the high-spin magnetic site is clearly increasing with increasing substrate lattice parameter relative to that of the low-spin site. The fraction of high-spin Fe, as calculated by integrating the six Lorentzian lines to which the magnetic site has been fitted and comparing to the total spectrum area, is shown in Fig. 3(a). The calculated area of the high-spin contribution increases from 33% of the total spectrum at $a = 3.606$ Å to 80% at $a = 3.702$ Å. However, it is also clear from Figs. 2 and 3(b) that the hyperfine field of the high-spin site is *not* systematically dependent on substrate lattice parameter. This result is in apparent disagreement with the predictions, based on total-moment calculations, of a monotonic increase in moment with nearest neighbor distance for both the ferromagnetic and antiferromagnetic phases of fcc Fe. However, there is no systematic dependence of the quadrupole splitting or isomer shift values on the substrate lattice parameter, indicating that the structure of the high-spin site is not actually changing when the substrate composition changes. This leads to the conclusion that there are two metastable phases of face-centered Fe(100) that can be stabilized on Cu(100), and that an in-plane expansion drives the system closer to one of the two states. In this picture a monotonic increase of the hyperfine field would not be expected. Finally, the intensity of the high-spin site in all the samples decreases with temperature, which is suggestive of blocking behavior in a film with a distribution of island sizes. Since the Néel temperature of the low-spin Fe is only 67 K, high-spin Fe islands could behave superparamagnetically above this temperature. In this case, a small external field should provide a sufficient reversal energy barrier to the islands to completely split the islands contribution to the Mössbauer spectra even at room temperature [18], unless the islands are extremely small. However, a Mössbauer spectrum taken from the $a = 3.606$ Å film in an external field of ~5 kG at room temperature, which is not consistent with very small islands. This apparent contradiction with the Mössbauer results can be reconciled if a very small fraction of Fe exists in the high-spin phase under these conditions, such

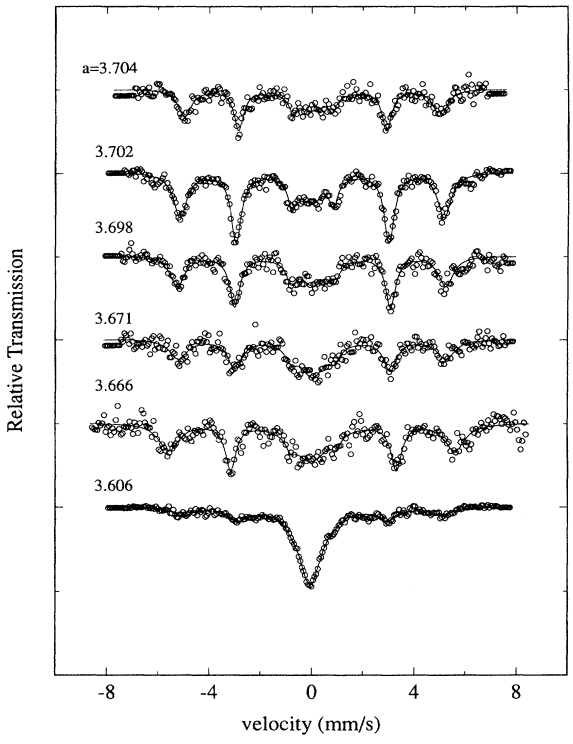

FIG. 2. Low temperature (~15 K) Mössbauer spectra for 6.5 ML fcc Fe(100) films grown on $Cu_{1-x}Au_x(100)$ for six different lattice parameters in the range $a = 3.606$ to 3.704 Å. Note that the spectral lines do not move out with increasing lattice parameter, but the intensity of the sextet relative to the singlet does increase. This is interpreted as an increase in the population of a constant-moment FM site with lattice parameter.

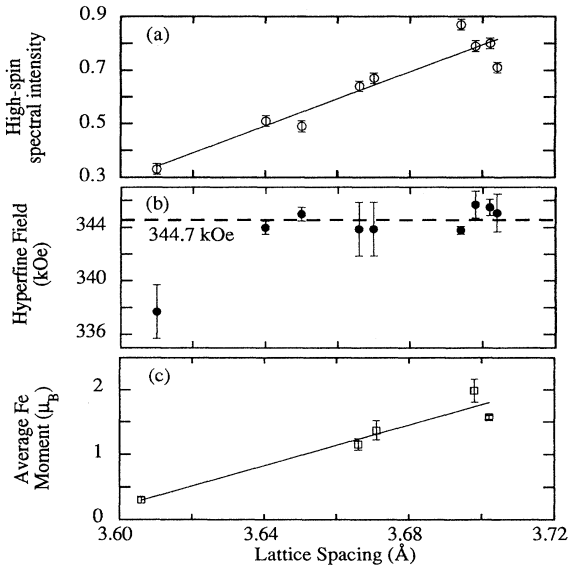

FIG. 3. Intensity of the fitted sextet at 15 K relative to the total fit spectrum (a), hyperfine field of the high-spin contribution (b), and average Fe saturation moment (c) vs substrate lattice parameter. The moment increase is similar to previous reports [13,14], but the hyperfine field data show that it is due to the dependence of the relative population of high-spin Fe as shown in (a), not an actual increase in Fe moment.

that the sextet intensity is below the detection limit of the Mössbauer experiments. Therefore, at lower lattice parameters the high-spin Fe may exist in islands within a low-spin matrix.

To compare these spectroscopic results with total moment measurements that have been performed by other groups, SQUID magnetometry hysteresis curves were obtained at ~5 K for many of the samples. These measurements show ferromagnetic loops with a dramatic increase in both the saturation and remnant magnetization as the substrate lattice parameter is increased from $a = 3.606$ to 3.704 Å. As in Fig. 3(b), the average saturation moment per Fe atom increases from $\sim 0.3\mu_B$ to $\sim 2.0\mu_B$. This shows that the high-spin site is ferromagnetic. The increase in moment is consistent with the average moment increase reported previously [13,14], but the Mössbauer data show that the increase in moment is due to an increase in the *population* of the high-spin Fe site rather than to a change in the Fe moment itself.

Owing to the bulklike hyperfine field of the high-spin site, the possibility that the high-spin Fe is bcc should be considered. In this picture the martensitic fcc(100)-to-bcc(110) transformation (for which evidence has recently been observed [19] for films above the critical thickness) would result in distorted bcc(110)-like grains in an fcc(100) Fe matrix. The thicknesses of all the Fe layers are significantly lower than the 11 ML critical thickness, but, since the structure is perturbed away from the equilibrium lattice parameter, a reduction in the critical thickness would not be surprising. Depending on the island size, such a transformation should result in superparamagnetic behavior of the high-spin Fe, for which some evidence was presented above. Although RHEED could miss a small amount of bcc Fe(110), this interpretation would require bcc islands large enough to be detectable by RHEED, especially at the higher lattice parameters where the high-spin phase accounts for up to 8% of the Fe. Also, the x-ray diffraction studies did not detect any peaks attributable to bcc Fe(110) in any sample. The absence of these two pieces of evidence suggests that the martensic transformation does not occur even with the in-plane lattice expansion, and that the high-spin Fe is an fct phase.

In conclusion, Mössbauer spectroscopy has been used to determine that the magnetic structure of fcc Fe(100) grown on Cu(100) and $Cu_{1-x}Au_x(100)$ disordered alloys is characterized by two magnetic phases: a high-spin ferromagnetic phase and a low-spin antiferromagnetic phase. The high-spin phase is most likely the metastable fct phase which is energetically favored when grown with an in-plane expansion, while the low-spin phase is fcc. As the lattice parameter of the substrate is increased, the population of the high-spin phase increases relative to that of the low-spin phase. Total moment SQUID measurements detect this increase in the amount of high-spin Fe as an increase in the *average* moment per Fe atom, in agreement with previous observations [13,14] and predictions by total energy calculations [3]. However, the Mössbauer data show that the moments on the sites themselves do not change with the substrate lattice parameter.

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[1] W. A. Jesser and J. W. Matthews, Philos. Mag. **15**, 1097 (1967).
[2] P. Ehrhart, B. Schönfeld, H. H. Ettwig, and W. Pepperhoff, J. Magn. Magn. Mater. **22**, 79 (1980).
[3] V. L. Moruzzi, P. M. Marcus, K. Schwartz, and P. Mohn, Phys. Rev. B **34**, 1784 (1986); V. L. Moruzzi, P. M. Marcus, and J. Kübler, Phys. Rev. B **39**, 6957 (1989).
[4] J. Thomassen, B. Feldmann, and M. Wuttig, Surf. Sci. **264**, 406 (1992).
[5] W. Daum, C. Stuhlmann, and H. Ibach, Phys. Rev. Lett. **60**, 2741 (1988).
[6] D. P. Pappas, K. P. Kämper, and H. Hopster, Phys. Rev. Lett. **64**, 3179 (1990).
[7] S. H. Lu, J. Quinn, D. Tian, F. Jona, and P. M. Marcus, Surf. Sci. **209**, 364 (1989).
[8] P. Xhonneux and E. Courtens, Phys. Rev. B **46**, 556 (1992).
[9] D. Li, M. Freitag, J. Pearson, Z. Q. Qiu, and S. D. Bader, Phys. Rev. Lett. **72**, 3112 (1994).
[10] J. Thomassen, F. May, B. Feldmann, M. Wuttig, and H. Ibach, Phys. Rev. Lett. **69**, 3831 (1992).
[11] W. A. A. Macedo and W. Keune, Phys. Rev. Lett. **61**, 475 (1988).
[12] W. Keune, T. Ezawa, W. A. A. Macedo, U. Glos, K. P. Schletz, and U. Kirschbaum, Physica B **161**, 269 (1989); W. A. A. Macedo, W. Keune, and E. D. Ellerbrock, J. Magn. Magn. Mater. **93**, 552 (1991).
[13] U. Gradmann and H. O. Isbert, J. Magn. Magn. Mater. **15–18**, 1109 (1980).
[14] S. Mitani, A. Kida, and M. Matsui, J. Magn. Magn. Mater. **126**, 76 (1993).
[15] S. C. Abrahams, L. Guttman, and J. S. Kasper, Phys. Rev. **127**, 2052 (1962).
[16] U. Gonser, C. J. Meechan, A. H. Muir, and H. Wiedersich, J. Appl. Phys. **34**, 2373 (1963).
[17] G. J. Johanson, M. B. McGirr, and D. A. Wheeler, Phys. Rev. B **1**, 3208 (1970).
[18] Z. Q. Qiu, S. H. Mayer, C. J. Gutierrez, H. Tang, and J. C. Walker, Phys. Rev. Lett. **63**, 1649 (1989).
[19] K. Kalki, D. D. Chambliss, K. E. Johnson, R. J. Wilson, and S. Chiang, Phys. Rev. B **48**, 18 344 (1993).