

Suppression of ferromagnetic order of Fe overlayers on the Rh(001) surface

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The magnetic phase of thin Fe overlayers on top of a Rh(001) surface has been probed using the surface magneto-optical Kerr effect. Quite surprisingly, we have found a suppression of ferromagnetic order up to six atomic layers of Fe. Not until Fe coverage reaches above seven layers does a ferromagnetic order start to develop. The suppression of ferromagnetic order is attributed to the tetragonally distorted cubic structure, which has been predicted to favor antiferromagnetic ordering from our first-principles calculation using the full potential linearized augmented plane-wave method. [S0163-1829(99)12943-6]

The study of surface magnetism has been made more accessible over the last decade since the introduction of surface magneto-optical Kerr effect (SMOKE) in surface physics.¹ This has allowed for the fast growing field and many new insights. Among several interesting areas in this field are the magnetic and structural properties of novel metastable systems, which are potentially important in fabrication of magnetic devices.² One of the easiest ways to manipulate an overlayer film is to use a substrate with a different lattice parameter as compared to the overlayer film. Since the partially filled *d*-band in transition metal films is strongly influenced by the number and the distance to nearest-neighbor atoms, different magnetic characteristics can also be expected from substrates with different lattice spacings.³ As has been reported by Moruzzi,⁴ the magnetic state vs lattice spacing can be discontinuous and multivalued even without consideration of surface alloying.

Recently, the correlation between magnetic properties and atomic structures has drawn considerable attention. One of the most controversial systems is fcc (or fcc-like) Fe.⁵ The zero field magnetic moment of fcc Fe has been calculated by Moruzzi, Marcus, and Kübler⁶ using total energy spin-polarization band calculations. Face centered cubic Fe is expected to have a very complex magnetic phase diagram depending on the Wigner-Seitz radius of the Fe atoms. An interesting change in the magnetic state can be found near a Wigner-Seitz radius of 2.7 a.u., where the antiferromagnetic low-spin state and ferromagnetic (FM) high-spin state are closely located in energy. The lattice spacing of Cu(001) ($a=3.61$ Å) corresponds to a Wigner-Seitz radius of 2.7 a.u. and as expected, the magnetic structure of Fe on Cu(001) has proved to be very complicated.⁶ The magnetic state of the Fe film is very sensitive to the growth condition and the Fe thickness, and changes in the magnetic state is closely related to subtle changes in the structure.⁷ Further expansion of the lattice constant is of interest since lattice expansion has been predicted to yield an increase in magnetic moment

of a fcc Fe film.⁶ Previously, it has been shown that Fe overlayers on Cu₃Au(001) are ferromagnetic starting at 1.1 monolayer (ML).⁸ The lattice constant of Cu₃Au is 3.75 Å so that the overlayer of Fe is expanded laterally by 4% more than a Fe overlayer on Cu(001).

The initial thickness where the ferromagnetic order starts to form is closely related to both the growth mode of the film and the hybridization of electronic states between the overlayer and the substrate. However, on transition metal substrates, the hybridization is not strong enough to suppress ferromagnetic order in Fe films above 1-2 ML, which we will show later. The growth mode can affect the percolation threshold of the overlayer and hence also contribute to a delayed onset of ferromagnetism.

In this study, we have used a Rh(001) crystal since it has a fcc lattice spacing of $a=3.80$ Å, potentially enabling an enhancement or diminishment of the magnetic moment depending on its structure. A previous study using neutron scattering to examine the magnetization of 5 ML Fe overlayers on Rh(001) and Cu(001) showed no in-plane magnetization.⁹ For the case of Cu(100), later studies showed FM order for 1-4 ML with perpendicular magnetization.⁷ Earlier result from photoemission work by Kachel *et al.* has shown induced magnetization of Rh films on top of Fe(001) up to 2 ML.¹⁰ From these results, an onset of FM with the magnetization direction along the surface normal for 1-2 layers Fe thickness is expected based on the above observations of induced magnetic moment from Rh and the expanded lattice spacing. Unexpectedly, we have found no ferromagnetic order in this system up to 6 ML of Fe, neither in the out-of plane nor in-plane direction. We attribute the absence of ferromagnetism to the tetragonally distorted cubic structure of the Fe film; according to calculations by Peng and Jansen,^{11,12} the magnetic phase of face centered tetragonal iron could be antiferromagnetic depending on the ratio between a (the side of square cross section) and c (the height of the unit cell). We will comment on the

controversy in determining the structure of a few atomic Fe overlayer. In this paper, we present a simple model to predict the structure of the Fe overlayer depending on the (001) substrate lattice parameter with implications on the magnetic structure.

The experiment have been performed in an ultrahigh vacuum (UHV) chamber equipped with instruments to perform surface magneto-optical Kerr effect (SMOKE) measurements, spot-analysis low energy electron diffraction (LEED) and LEED measurements, and Auger electron spectroscopy (AES) measurements with a cylindrical mirror analyzer. The base pressure of this chamber was maintained at 1.0×10^{-10} Torr or below. The Fe evaporation was performed using a water-cooled evaporator equipped with a flux monitor. No pressure rise during evaporation was observed. The growth of Fe took place at room temperature. The actual coverage of Fe has been estimated using AES and is estimated to be accurate to within 30%. The evaporation rate was 0.33 ML/min. The Rh(001) crystal was prepared by repeated Ne sputtering(600V) and annealing cycles. Carbon contamination was effectively removed by temperature cycling of the sample in 5×10^{-9} Torr O_2 to 1000 °C, followed by flashing to 1300 °C. To prevent possible H contamination, the clean surface was flashed shortly before the start of deposition. Kerr effect measurement was performed using a He-Ne laser (632.8 nm) with an incident angle of 45° with linear polarization in the plane of incidence (*p* polarization). Both polar and longitudinal geometry have been applied to check the onset of magnetization vs Fe thickness. Most Kerr measurements were performed at 80 °K.

The growth of Fe overlayer on Rh(001) gives a (1×1) LEED pattern with some increase of the background signal with increasing Fe thickness. A structural study of Fe/Rh(100) by Jona and coworkers using dynamic LEED, has shown that the Fe films grows pseudomorphically at least till 8 ML Fe thickness.¹³ This is quite compatible with our observation.

We show the SMOKE data in Fig. 1. These are the Kerr loops for 0, 5, and 8 ML of Fe on top of Rh(001), measured in the polar geometry. For comparison, we have added a Kerr loop from 3 ML Fe/Ag(001). Here, the most important fact is the suppression of any ferromagnetic signal up to 6 ML of Fe oriented either in the plane of the film or perpendicular to it. For thick layers larger than 7 monolayers, it undergoes a structural and magnetic phase transition as in Fe/Cu(001). The fully relaxed bcc phase of Fe starts to appear above 12 monolayers, where the LEED spot becomes broad with increase of the background intensity. The details on the magnetic and structural phase transition vs thickness of Fe overlayer will be reported elsewhere.¹⁴ For a pure Fe film of few atomic layers, this is quite surprising. To check for serious alloy formation, which could explain the missing ferromagnetism, AES has been used to follow the Rh and Fe peak intensities. Exponential growth and decay of Fe and Rh signal indicate there is no severe alloy formation in this system. Films grown at 80 °K has also been checked with AES and SMOKE. At this temperature, any motion of the atoms is expected to be more frozen out. Hence, alloying can be excluded as the reason for the lack of the FM signal.

To understand the correlation of Fe overlayer structure and its magnetism, we have assumed the misfit strain of Fe

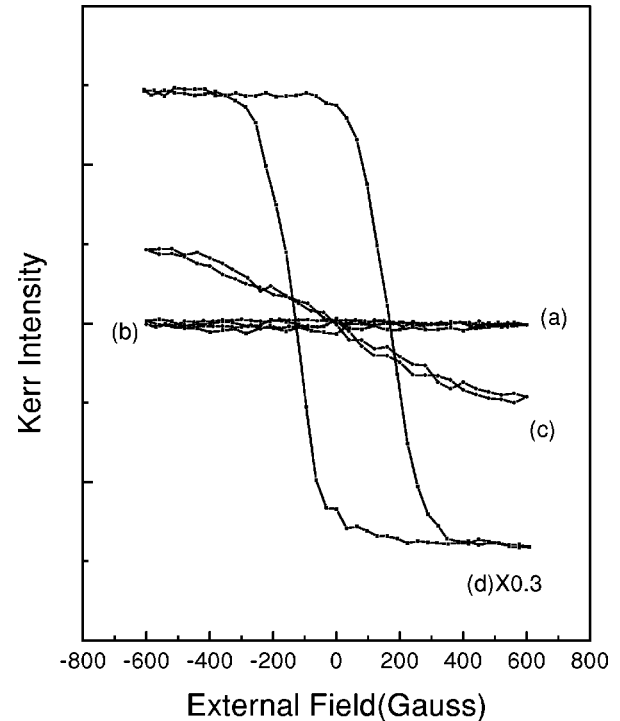


FIG. 1. Surface Magneto-optic Kerr intensity of various overlayer (a) clean Rh(001), (b) 5 ML of Fe on Rh(001) (c) 8 ML Fe on Rh(001), (d) For comparison, 3 ML Fe/Ag(001), note the change in scale.

to be the dominant factor in determining the overlayer structure. For our strain analysis we have used the bulk value of the lattice spacing of fcc and bcc structure of Fe, and we assumed pseudomorphic growth. Measurements of the Poisson ratio of bulk iron and thin iron films indicate that thin Fe overlayers are quite elastic so that the atomic volume is almost conserved.^{15,16} Both fcc(001) and bcc(001) surfaces have a square surface unit cell. For pseudomorphic growth, the layer separation determines if the film grows in bcc or fcc structure, with $d_{bcc} = a/2$, and $d_{fcc} = a/\sqrt{2}$, where a denotes the surface nearest neighbor distance. In Fig. 2, the lateral misfit strain for an Fe film is plotted when the overlayer grows pseudomorphically on top of a fcc(001) surface with the lattice spacing along the x axis. We have used the bulk value lattice spacing of bcc and fcc Fe, i.e., 2.88 Å and 3.6 Å, respectively. For a perfect match between the Fe bcc lattice spacing, $a_{bcc} = 2.88$ Å, the fcc lattice should have a lattice spacing $d_{fcc} = \sqrt{2}a_{bcc} = 4.06$ Å. So Fe on a fcc substrate with a lattice spacing of 3.60 Å is expected to grow in the fcc structure, and on a fcc substrate with lattice spacing of 4.06 Å, Fe is expected to be bcc. This is actually the case for Cu(100), ($a = 3.61$ Å), where Fe grows as fcc and Ag(100), ($a = 4.09$ Å) where Fe grows as bcc. But what happens for Fe growth on substrates with lattice spacings in between 3.6 and 4.06 Å? Is it stretched from a fcc structure or compressed from a bcc structure? In Fig. 2, we have plotted the misfit strain for (a) fcc Fe and (b) bcc Fe vs fcc substrate lattice spacing. Figure 2(c) shows (a) - (b), i.e., the relative strain. Based on this curve, when the relative strain is less than zero, the fcc lattice is the preferred structure. When the relative strain is larger than zero, the bcc structure has a smaller lateral strain. We notice that the cross-over lattice

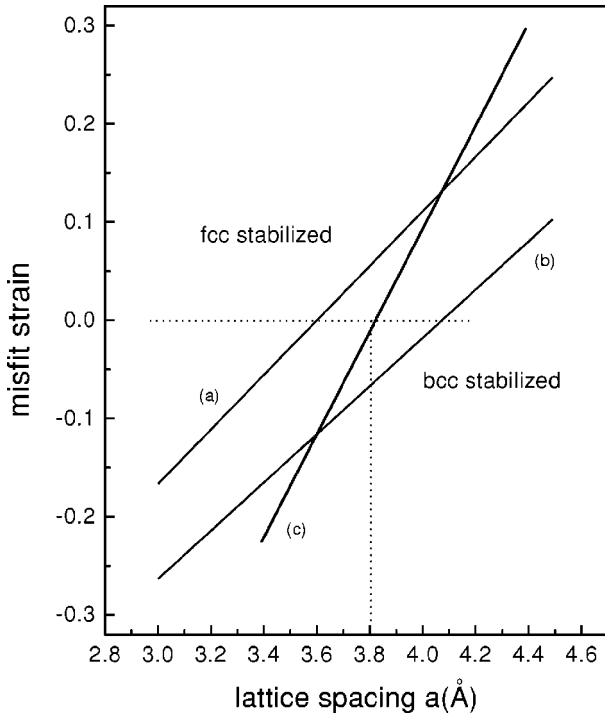


FIG. 2. Relative strain of Fe overlayer with varying lattice parameter of cubic (001) lattice of (a) fcc surface, (b) bcc lattice converted to fcc, (c) (a)+(b).

spacing is slightly above 3.8 Å. So assuming commensurate growth and using this simple argument one would predict that Fe would grow in a fcc structure on substrates with lattice spacings less than 3.81 Å, and for substrates with larger lattice spacings the bcc structure would be preferred. This actually holds for a range of substrates, listed in Table I. We need to be more specific in describing the structure here. If there exists a surface relaxation, there is no absolute cubic structure on top surface. And with this relatively large lattice mismatched system, the actual shape of overlayer cannot be a real cubic one. Thus, it is more appropriate to use tetragonally distorted cubic (fcc or bcc) here.

Knowing the overlayer structure, the magnetic structure can be correlated with different Wigner-Seitz radii of the Fe atom. First principles calculation of the ground state of iron by Wang, Klein, and Krakauer showed that for Fe in the bcc structure, the ferromagnetic state is the lowest energy state over a large range of Wigner-Seitz radius centered at 2.76 Å (or 3.90 Å in terms of a fcc lattice).¹⁷ Hence, bcc Fe film grown on substrate with around 4.17 Å, should be ferromagnetic starting from the first layer just above the magnetic percolation threshold unless alloying or electronic hybridization quenches the magnetization. This has been shown to be the case for Fe/Pd(001), Fe/Pt(001), Fe/Ag(001), and Fe/Au(001).¹⁸ These systems are predicted to be bcc (tetragonally distorted bcc) from the strain argument in Fig. 2 and

TABLE I. Lattice parameter of the various fcc crystals for the growth of bcc and fcc Fe.

Samples	Ni	Cu	Rh	Pd	Pt	Au	Ag
a (Å)	3.52	3.61	3.80	3.89	3.92	4.08	4.09

have all proved to be ferromagnetic starting from the monolayer. Even in the case of Fe/Au(001), where Au atoms segregate on top of the iron surface, the film proves to be ferromagnetic. On the other hand, the magnetic structure of fcc iron is very complicated especially near the lattice spacing of 3.6 Å.⁶ Indeed, the Fe/Cu(001) system exhibits a range of different magnetic structures depending on the relaxation perpendicular to the growth plane.⁷

Interestingly, our Rh(001) surface has a lattice spacing of 3.8 Å, which is located near the border between the bcc and fcc structure. According to the above simple strain analysis the fcc structure is predicted to be more stable than the bcc structure. However, independent of its structure, it is expected to be ferromagnetic. If the iron grows as fcc, its magnetic state is predicted to be ferromagnetic, since its lattice spacing is well above that of Cu.⁶ And if it is bcc, it should be ferromagnetic since the ferromagnetic state is more favorable even in this range. However, a fcc Fe with $a=3.8$ Å results in an 18% increase in the atomic volume. To reduce the volume expansion, the lattice will be contracted, resulting in distorted cubic structure with $c/a < 1$, where c is the inter-planar distance along the growth direction. Feng and Jansen have calculated the stability in magnetic structure for iron in the tetragonally distorted fcc lattices with varying c/a ratio, using the full potential linearized augmented plane-wave (FLAPW) method.¹¹ Their calculations showed that under certain conditions ($V/V_o < 1, 0.8 < c/a < 1.2$), the antiferromagnetic state is energetically favorable. They calculated energy values in the above phase space for both ferromagnetic and antiferromagnetic state. A problem with their calculation is that in the ferromagnetic state, the fcc structure minimum comes out with a lower energy than the bcc state, which suspects the validity of this results. The unreasonable results may come from the well-known deficiency¹⁶ of local spin density approximation (LSDA), used in their calculation, in predicting ground-state crystal structure.

We have calculated the total energy of 1 ML of Fe on Rh(001) surface using the FLAPW method in order to get some physical insight on the magnetism and atomic structure of a thin film of Fe on Rh(001). In this study general gradient approximation (GGA) was employed for exchange-correlation potential, instead of LSDA. GGA is known to predict better a ground-state crystal structure, compared to LSDA. About 1000 basis functions and 10 special k -points in the two-dimensional (2D) irreducible Brillouin zone were used. In Fig. 3, the calculated total energies are plotted as a function of the interlayer spacing between Fe and Rh layers with the fixed in-plane lattice constant same as that of Rh. The open and solid circles represent the total energies in ferromagnetic and antiferromagnetic states, respectively. As shown in Fig. 3, the antiferromagnetic state is energetically favorable by 3 mRy compared to the ferromagnetic. The interlayer spacing at total energy minimum in antiferromagnetic state is 3.267 a.u. (1.729 Å), while in ferromagnetic state, the interlayer spacing is 3.508 a.u. (1.856 Å). The c/a ratios at the minimum energy position for antiferromagnetic and ferromagnetic states are 0.915 and 0.98, respectively. These results are quite consistent that the atomic volume in ferromagnetic state is slightly larger than that in antiferromagnetic state.

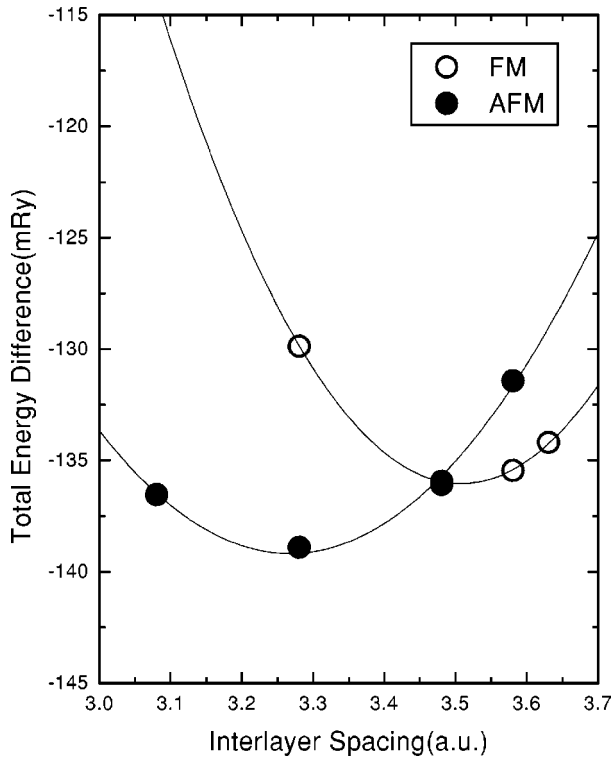


FIG. 3. The calculated total energy of 1Fe/Rh(001) on the interlayer spacing between Fe and Rh layers. The solid and open circles stand for the antiferromagnetic and ferromagnetic states, respectively.

So far, we have not considered the actual structural studies. In case of tetragonal distortion in overlayer structure, it is difficult to distinguish whether it is face-centered tetragonal or body-centered tetragonal. Also it is not possible to distinguish if the overlayer thickness is less than three layers. In this case, one of the clear ways to distinguish the structure is to find out the neighboring distance between the atoms in the same plane and adjacent plane, especially in (001) surface. If these distances are similar, which is the case of face-centered-structure, it can be considered as tetragonally distorted fcc structure. Or if the distance to an atom in adjacent plane is much shorter than that from the atoms in plane, it should be considered to be tetragonally distorted bcc structure. For example, in fcc, the ratio between the two distances mentioned above should be 1. In bcc, this ratio is 1.15. In our case, this ratio is 1.05.

But the accurate determination of atomic structure at the surface should measure the relaxed layers near the surface. A damped oscillatory relaxation and contraction could be present in many metallic system. Obviously, relaxation can be very strong for the top layers where the spacing could be quite different from that of the bulk. This surface relaxation is controversial problem even for clean metal surfaces especially in Rh(001). Even quite recent experimental value shows relaxation outwards while the theoretical values are controversial with the degree of contraction.^{19,20} The energy scale involved in misfit strain is in the few hundreds meV range. Also the energy scale involved in relaxation is in few tens meV. Hence, the displacement becomes less small in strained system. For this reason, recent experimental studies

on the structure of Fe/Rh(001) and Fe/Cu₃Au(001) (Refs. 8,13, and 21) could be very interesting.

To validate our simple strain analysis, we have extended its use to an interesting magnetic moment-volume instability problem; the Invar effect. Fe_xNi_{1-x} has drawn a lot of attention since its discovery.²² As the Fe concentration reaches 65%, the magnetic moment collapses down to zero. Using the bulk lattice constant of Ni (fcc, $a = 3.52 \text{ \AA}$), we can apply the simple strain relation illustrated in Fig. 2 to predict the concentration for the structural transition associated with the Invar effect. According to Fig. 2, the structural transition takes place at the lattice spacing of 3.81 \AA , which corresponds to a Fe concentration of 51%. Here, the average lattice spacing has been assumed to be linear in concentration between the Ni and Fe lattice spacings. Assuming the same elastic property of the NiFe alloy as Fe and using Fig. 3, the transition between the ferromagnetic and the antiferromagnetic state takes place at 3.77 \AA . The correlation between overlayer strain and structural transition is quite consistent with the value determined by a first-principles calculation.²³ To make more accurate estimate, we need to consider the variation of the Poisson ratio. Also this discrepancy depends on the hybridization between two components. However, at the surface, if there is no segregation, this misfit analysis is more accurate than in bulk alloy.

The onset thickness of ferromagnetic order is related to a structural transition. At some critical thickness (in our case it is about 6-7 ML), the pseudomorphic growth will not be possible due to strain relaxation by defect formation or charge transfer etc.²⁴ To maintain a tetragonal structure rather than the conversion to a relaxed cubic phase, a stability condition for the stressed structure needs to be fulfilled, i.e., $(c_{11} + c_{12})c_{33} - 2c_{13}^2 > 0$ where c_{ij} 's are the usual elastic coefficients.²⁵ This condition breaks down at a critical thickness. Then the pseudomorphic tetragonally distorted structure becomes unstable and reverts to a cubic structure. This break point of the structural change can be found at $(c_{11} + c_{12})c_{33} - 2c_{13}^2 = 0$. Near this transition point, we can assume the cubic phase, so that $c_{11} = c_{33}$ and $c_{12} = c_{13}$.²⁶ Then, the condition for the transition becomes $c_{11} + 2c_{13} = 0$. This case corresponds to a uniaxial stress, where there is no in plane stress. Also this implies a collapse of the bulk modulus, similar to what is observed in Invar effect.

In conclusion, we have shown the suppression of ferromagnetic order of iron overlayers on Rh(001) surface up to 6 monolayers. A simple strain analysis predict that Fe overlayer on Rh(001) is expected to form a tetragonally distorted fcc structure. Our first principles calculation shows that antiferromagnetic state is energetically favorable compared with the ferromagnetic state. Our simple misfit strain analysis explains quite well the Invar effect as well as the magnetic state of Fe overlayer.

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