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Simple structure and soft elastic behavior of Mn on Fe{001}

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Ultrathin films of Mn grow epitaxially and pseudomorphically on Fe{001}. Low-energy electron diffraction (LEED) experiments show that with increasing thickness the films contain defects and disorder, but a substantial portion remains well crystallized. A quantitative LEED analysis of a 23-Å-thick film finds that the film has a body-centered-tetragonal structure with lattice parameters: $a=2.866$ Å and $c=3.228$ Å, hence with an axial ratio $c/a=1.13$ and atomic volume 13.3 Å^3/atom. Strain analysis using both the LEED results and the tetragonal structure from dilute Mn alloys determines the Poisson ratio of the film to be near 0.5, hence the film is elastically soft. Both the face-centered- and the body-centered-cubic structures are consistent with the data as underlying phases of the grown film. LEED intensity data show that the distance between Mn layers is small (about 1.3 Å) when the epitaxial film is only two- or three-layers thick, and then increases to become 1.614 Å in the bulk of 14-layer thick films. [S0163-1829(96)06231-5]

I. INTRODUCTION

Manganese is probably the strangest of the $3d$ metals and has many features that are not well understood. It has four allotropes: a cubic α phase with 58 atoms/cell, stable up to 727 °C; a cubic β phase with 20 atoms/cell, stable between 727 and 1095 °C; a face-centered-cubic (fcc) γ-phase, stable between 1095 and 1133 °C; and a body-centered-cubic (bcc) δ-phase, stable between 1133 °C and the melting point at 1244 °C.

The high-temperature allotropes have attracted much attention, because their simple structures make them accessible to theory. Many unsuccessful attempts have been made to quench them directly to room temperature from the high temperatures at which they are stable. However, they remain virtual phases that cannot be prepared in bulk form at room temperature and can only be studied by extrapolation. Of the two high-temperature phases, the γ phase is the one which has attracted the most attention, since it can be stabilized at room temperature, albeit in strained form, by adding impurities.

The stabilization by impurities is done by alloying Mn with other metals. Many alloys have been prepared of Mn with Cu, Fe, Ni, Pd, Pt, etc. which on the Mn-rich end are antiferromagnetic at low temperatures and for low concentrations of impurities undergo a martensitic transformation from the fcc to a face-centered-tetragonal (fct) structure upon cooling through the Néel temperature. The lattice parameters of pure fct Mn at room temperature can then be obtained by extrapolation of alloy data to a zero impurity content. The older literature[1] gives somewhat different values for the parameters a_{fct} and c_{fct} of pure fct Mn depending on the alloy involved: from a MnCu alloys, one finds $a_{\text{fct}}=3.782$ Å and $c_{\text{fct}}=3.547$ Å (but also $c_{\text{fct}}=3.533$ Å). More recent values, which we will adopt for the discussion of the results of the present work, are those obtained by Endoh and Ishikawa[2] in a study of γ-MnFe alloys by extrapolation to a zero Fe content, namely, $a_{\text{fct}}=3.796$ Å and $c_{\text{fct}}=3.592$ Å.

Different γ-Mn alloys have different properties. For example, in γ-MnCu alloys the martensitic transformation is always accompanied by the onset of antiferromagnetism, and the *bulk* modulus softens at the transition temperature,[3] whereas γ-MnNi alloys behave differently depending on the alloy composition: for Ni concentrations less than 10 at. %, the magnetic and structural transitions also occur together, the body-centered-tetragonal (bct) structure has $c/a<\sqrt{2}$ and the *shear* modulus softens at the transition temperature, but for Ni concentrations greater than 10% the magnetic transition occurs at a higher temperature than the martensitic transition and has $c/a>\sqrt{2}$; above 22 at. % Ni there is no structural transition.[4] It may be of interest to point out that even α-Mn is particularly notable for its small bulk modulus, and is almost as soft as copper.[5]

Stabilization of the γ and δ phases by epitaxy has been attempted by a few authors. Thus, Heinrich *et al.*[6] have grown Mn films on Ru(0001), Ni{001}, and Fe{001}, and report the formation of complex phases on the former two substrates and infer from the surface net of Fe{001} that bcc Mn grew on the latter substrate (but no structure or strain analysis was done). Egelhoff *et al.*[7] have grown Mn films on Cu{001} and Ag{001}, and found that the atomic structure of the films is bct; they also determined the atomic volume as a function of film thickness. Tian *et al.*[8] have grown Mn films on Pd{001} and determined their bct atomic structure by quantitative low-energy electron diffraction (QLEED), concluding from a strain analysis that the structure results from a distortion of the fcc-Mn phase caused by the epitaxial plane tensile strain. Purcell *et al.*[9] have grown 15–25-Å films of Mn on Fe{001} by molecular-beam epitaxy and found them to have a bct structure with $a=2.87$ Å and $c=3.27$ Å.

The motivation for the present work, which is also concerned with the epitaxial growth of Mn on Fe{001}, has two origins. One is that a calculation of Wu and Freeman[10] finds an unusually small interlayer distance of 1.30 Å in a bilayer of Mn on Fe{001}, in contrast to the experimental bulk value of 1.635 Å reported by Purcell *et al.*[9] Since the latter authors used a simple (rather unconventional) method to arrive at their result (viz., a plot of the energies of the primary Bragg LEED reflections along the 00 rod versus the square of the reflection index—a method the accuracy of which is not known and which does not give surface relaxations), it seemed appropriate to try and determine the atomic structure of Mn films on Fe{001} by QLEED, a method which has been repeatedly shown to be precise and reliable and which also gives surface relaxations. The second motivation stems from the desire to establish which of the two high-temperature phases (γ or δ) is stabilized on Fe{001}, a question that might be answered by the strain analysis of the bct structure of the epitaxial Mn films.

The experimental tools used in this work are QLEED and Auger electron spectroscopy (AES). We present in Sec. II, the experiments; in Sec. III, the QLEED analysis; in Sec. IV, the strain analysis; in Sec. V, a discussion of the results; and in Sec. VI, the conclusions.

II. EXPERIMENTS

The experiments were done in an ultrahigh-vacuum chamber capable of reaching a base pressure of about 1×10^{-10} Torr and provided with front-view LEED optics which were used both for crystallographic studies and, in the retarding-field analyzer mode, for AES measurements. The Fe{001} substrate was a small platelet with approximate size $6\times6\times0.5$ mm^3. In the experimental chamber, the Fe sample could be heated either by radiation from a hot filament located behind the sample or by electron bombardment of the sample's back surface. The temperature of the sample was measured by means of an infrared radiometer with an accuracy estimated at ±50 °C. The LEED intensity data needed for quantitative structure analysis [the so-called $I(V)$ curves] were measured with a video-LEED system described elsewhere.[11]

The sample surface was cleaned *in situ* by a series of Ar-ion bombardments (about 2×10^{-5} Torr, 375 eV, 0.3μA/cm^2), and high-temperature anneals (about 700 °C for 1 to 2 h), and its chemical state was monitored by AES. The Mn source consisted of small 99.95%-pure chips contained in a tungsten spiral, which could be electrically heated. During deposition of Mn on the substrate surface the tungsten spiral was heated to about 1000 °C, with the temperature of the Mn chips estimated at about 600 °C. The deposition rates were kept slow at approximately 1 Å/min or lower. During deposition the substrate was neither heated nor cooled—its temperature was monitored with an infrared pyrometer and was never at or above the minimum temperature measurable with this instrument (~150 °C). Previous experiments using identical sources and a thermocouple showed that the substrate was always at room temperature during short depositions and was heated only a few degrees above room temperature by radiation from the source during long (~1 h) depositions. In any case, the LEED observations clearly indicated that the substrate temperature was not interfering with the epitaxial growth of the Mn films.

The thickness of the Mn films was estimated from the decrease of the Fe AES signal and the increase of the Mn AES signal, as described elsewhere (see, e.g., Ref. 12). Upon deposition of Mn, the LEED pattern, which for the clean Fe{001} surface is a fourfold-symmetric, high-contrast, low-background pattern, persisted as 1×1, with a progressive increase of the background, which became very high for Mn films of 20–25 Å, the thickest films grown in this work.

Intensity data were collected at various stages of deposition in order to follow the evolution of the $I(V)$ curves with increasing thickness of the Mn film, but the data used for the determination of the bulk atomic structure of the film were collected from a 23-Å film. This thickness is larger than the penetration depth of the incident electrons [a fact confirmed by the stability of the $I(V)$ curves with increasing thickness], so that the film could be considered semi-infinite for the purposes of QLEED analysis.

III. QLEED INTENSITY ANALYSIS

The intensity calculations were performed with Jepsen's full-dynamical CHANGE program[13] and the following nonstructural parameters: Mn potential taken from the collection of Moruzzi, Janak, and Williams;[14] eight phase shifts and 69 beams up to 360 eV; inner potential $V_0=-(10+4i)$ eV, with the real part adjustable in the fitting process [it became $-(7\pm3)$ eV after refinement]; and isotropic root-mean-square amplitude of thermal vibrations of 0.15 Å. Evaluation of the agreement between theoretical and experimental curves was done both by visual inspection and by R-factor analysis. Three R factors were used, namely, the Van Hove–Tong R_{VHT} (Ref. 15), the Zanazzi-Jona r_{ZJ} (Ref. 16), and the Pendry R_P (Ref. 17) factors.

The intensity calculations assumed as a model a semi-infinite Mn crystal with an in-plane lattice constant equal to that of Fe, namely, 2.866 Å, as required by the observed pseudomorphism (shown by the 1×1 LEED pattern). In the calculations, both the bulk interlayer spacing d_{bulk} and the first- and second-interlayer spacing d_{12} and d_{23}, respectively, were varied: d_{bulk} initially from 1.30 to 1.90 Å in steps of 0.1 Å and later from 1.56 to 1.66 Å in steps of 0.02 Å; and the changes Δd_{12} of d_{12} and Δd_{23} of d_{23} from -0.2 to $+0.2$ Å in steps of 0.05 and 0.02 Å, respectively. The three R factors used here did not reach their global minima for exactly the same values of the structure parameters (R_{VHT} and r_{ZJ} did, while R_P pointed to a value of d_{bulk} 0.02-Å different), but we quote the best averaged result as

$$d_{\mathrm{bulk}}=1.614 \text{ Å}, \;\; \Delta d_{12}=+0.15 \text{ Å}, \;\; \Delta d_{23}=0,$$

with a precision of the order of 0.005 Å for d_{bulk}, but with an accuracy estimated at ±0.03 Å for d_{bulk} and Δd_{12}, and ±0.05 Å for Δd_{23}. The minimum values of the R factors are $R_{\mathrm{VHT}}=0.24$, $r_{\mathrm{ZJ}}=0.11$, and $R_P=0.47$. The calculated $I(V)$ curves are compared to the experimental ones in Fig. 1.

IV. STRAIN ANALYSIS

The QLEED intensity analysis of a 23-Å 1×1 Mn film shows that the bulk has a body-centered-tetragonal structure with $a=2.866$ Å and $c=2\times1.614=3.228$ Å, hence with $c/a=1.13$ (Ref. 18) and volume 13.3 Å^3/atom. This structure might be a distortion of either the γ phase (fcc between 1095 °C and 1134 °C) or the δ phase (bcc between 1134 °C and the melting point at 1244 °C). With strain analysis, we will evaluate the Poisson ratio of the film, and then the lattice constant of the underlying cubic structure. The lattice constant will have different values depending on whether the underlying phase is fcc or bcc. Comparison of these values

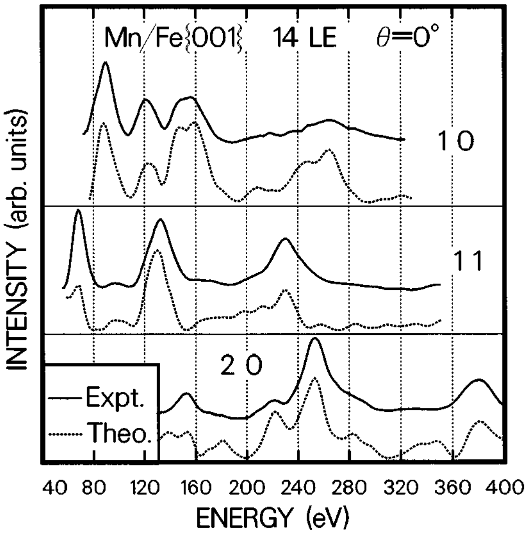

FIG. 1. Normal-incidence experimental LEED spectra (solid curves) from a 23-Å film of Mn on Fe{001} and theoretical LEED spectra (dotted curves) for a semi-infinite Mn crystal with the parameters given in the text.

with estimates from other sources could then determine if that cubic structure is fcc or bcc.

Assuming that all tetragonal states can be treated as strained states of an underlying cubic lattice, we find the relation between in-plane and out-of-plane (i.e., perpendicular) strains produced by epitaxial strains on a given tetragonal state of the film as

$$\frac{\delta c}{c} = -\alpha \frac{\delta a}{a}, \tag{1}$$

where $\alpha=2\nu/(1-\nu)$, and ν is the Poisson ratio of the underlying cubic structure (see, e.g., Ref. 19).

Now within tetragonal structures, the equilibrium state of Mn is an fct structure with lattice constants $a_{\mathrm{eq}}^{\mathrm{fct}}=3.796$ Å, $c_{\mathrm{eq}}=3.592$ Å, obtained from Fe-stabilized alloy crystals by extrapolation to pure Mn.[2] (We use subscripts eq to refer to the equilibrium phase of the grown films, and the superscript fct to differentiate the lattice constant from that of a bct structure.) Hence integration of Eq. (1) from this fct structure of pure free tetragonal Mn when epitaxial strain is introduced gives

$$\frac{c}{c_{\mathrm{eq}}} = \left(\frac{a^{\mathrm{fct}}}{a_{\mathrm{eq}}^{\mathrm{fct}}} \right)^{-\alpha}, \tag{2}$$

where c and a^{fct} are the lattice constants of the Mn film as determined by LEED, namely, $c=3.228$ Å and $a^{\mathrm{fct}}=2.866\times\sqrt{2}=4.053$ Å. With these values, we get from Eq. (2) $\alpha=1.631$ and then $\nu=0.45$.

Note that this determination of ν, and of the values of the in-plane strain from 3.796 to 4.053 Å of 6.8% and the out-of-plane strain from 3.592 to 3.228 Å of -10.1%, does not depend on whether the underlying cubic structure is bcc or fcc. The value of ν is larger than the average value of Poisson's ratio for most metals (which is about 0.3) and indicates that cubic Mn is elastically soft with a small ⟨110⟩ shear modulus (like the dilute MnNi alloys, but unlike the MnCu alloys).

V. DISCUSSION

(1) The bulk behavior. The value $\nu=0.45$ will now be reinforced by comparison with other evaluations. Then ν will be used to determine the lattice constant of the underlying cubic phase if it is bcc and if it is fcc. These lattice constants will then be compared with extrapolated values from the high-temperature γ and δ phases to see which is the more likely underlying phase.

Our earlier study of pseudomorphic films of Mn on Pd{001} (Ref. 8) had found by QLEED the values $a^{\mathrm{fct}}=3.891$ Å and $c=3.430$ Å. Using Eq. (2) again, we find $\alpha=1.867$ and whence $\nu=0.48$. Again the Mn is elastically soft with a small shear modulus.

Other estimates of the magnitude of Poisson's ratio can be made from the measurements of elastic constants of MnNi alloys as made by Lowde *et al.*[4] Reading data from the plots in Figs. 2, 3, and 4 of Ref. 4, we find $\nu=0.39$, 0.43, and 0.44 for $\mathrm{Mn_{83}Ni_{11}C_6}$, $\mathrm{Mn_{84.7}Ni_{9.2}C_{6.1}}$, and $\mathrm{Mn_{85.3}Ni_{8.8}C_{5.9}}$, respectively, clearly showing that Mn-rich alloys have a Poisson ratio near 0.5.

Now assume that the equilibrium tetragonal structure of pure Mn found by the extrapolation of MnFe alloys is made tetragonal by a uniaxial stress in a ⟨001⟩ direction acting on an underlying cubic structure of Poisson ratio ν. Such a stress is expected in the antiferromagnetic phase of Mn made up of {001} planes alternating in moment direction. Then in place of Eq. (2), which is produced by an in-plane *biaxial* stress, we have

$$\frac{a_{\mathrm{eq}}}{a_0} = \left(\frac{c_{\mathrm{eq}}}{c_0} \right)^{-\nu}, \tag{3}$$

where $a_0=c_0$ is the lattice constant of the underlying cubic structure.

If the underlying structure is fcc, then $a_{\mathrm{eq}}=a_{\mathrm{eq}}^{\mathrm{fct}}=3.796$ Å, $c=3.592$ Å, and with $\nu=0.5$ Eq. (3) gives $a_0^{\mathrm{fcc}}=3.73$ Å. If the underlying structure is bcc, then $a_{\mathrm{eq}}=a_{\mathrm{eq}}^{\mathrm{fct}}=3.796/\sqrt{2}=2.684$ Å, $c=3.592$ Å, and with $\nu=0.5$ Eq. (3) gives $a_0^{\mathrm{bcc}}=2.94$ Å.

We can estimate the magnitude of the fcc and bcc lattice constants by extrapolating the values measured at high temperatures and using appropriate thermal-expansion coefficients. These coefficients must be corrected for the fact that they exhibit a decrease at lower temperatures (the linear extrapolation of the lattice parameter of the α-phase from 1000 K to room temperature is too low by about 1.5% with respect to the measured value).[20] Using the high-temperature data reported by Pearson[1] and applying a 1.5% correction, we find at room temperature for δ-Mn, $a_0^{\mathrm{bcc}}=2.98$ Å (Purcell *et al.*[9] quote 2.95 Å) and for γ-Mn, $a_0^{\mathrm{fcc}}=3.73$ Å.[21]

The extrapolated values of a_0 from high temperatures for both the bcc and fcc phases are close to the values found above by the strain analysis. Hence, we cannot determine the underlying cubic phase from these data, although perhaps there is a small preference for fcc.

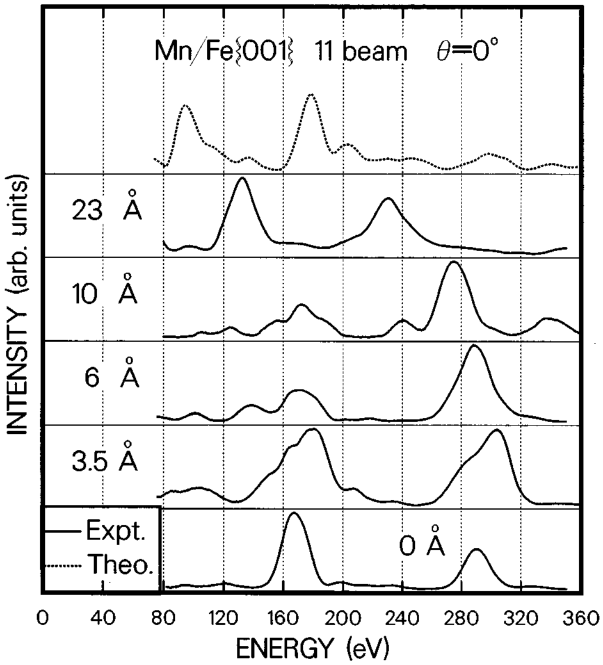

FIG. 2. Evolution of the 11 LEED spectrum with increasing thickness of Mn films (solid curves) on Fe{001}. The film thickness is given in each panel, hence the bottom curve is the 11 spectrum of clean Fe{001}. Note the trend of the major peaks to shift toward higher energies (implying a shorter interlayer distance) for the thinnest films and toward smaller energies for the thicker films. The upper dotted curve is a theoretical 11 spectrum calculated for a bilayer of Mn with an interlayer distance of 1.3 Å on Fe{001}.

(2) The interlayer spacing. The QLEED analysis finds $d_{\mathrm{bulk}}=1.614$ Å, in fair agreement with the value 1.635 Å found by Purcell *et al.*[9] with a less accurate procedure (namely, a plot of the energies of the primary Bragg LEED reflections along the 00 rod versus the square of the reflection index). Our result is not consistent, however, with the calculations of Wu and Freeman[10] for a bilayer of Mn on Fe{001}: these authors find that the distance between the two Mn layers is 1.30 Å, and conclude from the strong disagreement with the value reported by Purcell *et al.*[9] that ''experiments using other techniques are highly desired to clarify this discrepancy.''

Now the spacing of a bilayer contains relaxation effects due to the presence of a vacuum interface. Such relaxations on {001} surfaces are generally contractions of only a few percent from d_{bulk}, whereas the bilayer spacing of Ref. 10 has a 20% smaller value than the d_{bulk} found here and in Ref. 9. Hence it is of interest to show that our LEED measurements confirm the unusually small bilayer spacing, which appears then to be a result of the special magnetic structure of the bilayer on Fe{001}.

As mentioned in Sec. II, we have also collected intensity data to follow the evolution of the $I(V)$ curves with an increasing thickness of the Mn film. A study of this evolution indicates that the interlayer distance changes with increasing thickness of the film, being initially smaller than the bulk interlayer distance in Fe{001} and becoming larger in thicker films.

We show in Fig. 2, as an example, the evolution of the 11 spectrum of the clean Fe{001} surface (bottom curve, labeled 0 Å for 0 coverage by Mn) with increasing thickness of the Mn films. Two caveats should first be pointed out about Fig. 2: one is that the thickness values given in Fig. 2, measured with AES, are estimated to be accurate perhaps only within about 50%, and the other is that the $I(V)$ curves shown in the figure, with the exception of the clean Fe{001} and of the 23-Å curve, should be considered significant only with regard to the positions of the major peaks (because we did not optimize the signal-to-noise ratio, as we normally do for curves intended for intensity analysis, and we achieved only approximately normal-incidence conditions, as we did not expect to use these curves for intensity analysis). But Fig. 2 is sufficiently reliable to show that with increasing film thicknesses, the intensity peaks shift first toward higher electron energies and then toward lower energies. A peak shift toward higher energies from the position in the clean Fe{001} spectrum means that the interlayer spacing is *smaller* than in clean Fe{001} (1.433 Å), hence we conclude that the interlayer distances in two- or three-layer-thin Mn films are smaller than 1.433 Å, although as we have seen, the bulk interlayer distance in a 23-Å film is, at 1.614 Å, larger.

Precise quantification of the interlayer spacing in the thinner films is not possible with the available data because, even apart from the unsuitability of the data for quantitative intensity analysis (see the caveat mentioned above), it is very probable that the films were *not* of uniform thickness, having regions (islands) with one, two, or three layers simultaneously present in unknown proportions. Nevertheless, we have calculated the $I(V)$ curves expected from a bilayer of Mn on the Fe{001} surface with an interlayer distance of 1.30 Å (the value proposed by Wu and Freeman[10]). The top (dotted) curve in Fig. 2 is the result of such a calculation for the 11 spectrum. The peak positions in the calculated curve are roughly in agreement with the peak positions in the 3.5-Å film (other spectra, not shown, have peak positions between those of the 3.5-Å and those of the 6-Å films).

A conclusion that can be drawn at this point is that there is no contradiction between the results of Wu and Freeman's calculation and the results of Purcell *et al.* or of our QLEED analysis. The data indicate that the distance between Mn layers is about 1.3 Å in the early stages of film growth (two or three layers), but then increases steadily to reach 1.614 Å in thicker films (12 to 14 layers). It may be worth pointing out that this change of interlayer spacing with thickness may play a role in the antiferromagnetic exchange coupling between Fe layers separated by ultrathin Mn layers, which is presently of interest in some laboratories.

VI. CONCLUSION

A QLEED analysis of a 23-Å-thick film of Mn on Fe{001} finds that amidst disorder and defects the film has pseudomorphic ordered regions with a body-centered-tetragonal structure. The lattice parameters of this structure are $a=2.866$ Å and $c=3.228$ Å, hence with an axial ratio $c/a=1.13$ and atomic volume 13.3 Å^3/atom, and with a 9%-expanded first-interlayer spacing (d_{12}). Strain analysis shows that this structure may be considered a deformation of either fcc Mn with a lattice constant of 3.73 Å or of bcc Mn with a lattice constant of 2.94 Å. In either case the Poisson ratio is 0.45 and Mn is found to be elastically soft with a small $\langle 110\rangle$

shear constant. LEED intensity data also show that the distance between Mn layers is about 1.3 Å when the epitaxial film is only two- or three-layers thick, but then increases to become 1.614 Å in the bulk of 14-layers thick films.

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