

Structure of ultrathin films of Fe on Cu{111} and Cu{110}

D. Tian and F. Jona

College of Engineering and Applied Science, State University of New York, Stony Brook, New York 11794

P. M. Marcus

IBM Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598

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A study of the growth of Fe on Cu{111} and on Cu{110} has been carried out with low-energy electron diffraction (LEED) and Auger electron spectroscopy. We find that on Cu{111}, Fe grows first pseudomorphically as γ -Fe{111} to a thickness of about five layer equivalents (LE), and then forms six bcc Fe{110} domains rotationally related in the Kurdjumov-Sachs orientation. The pseudomorphic film has the same bulk interlayer spacing, within experimental error, as the Cu{111} substrate ($2.08 \pm 0.03 \text{ \AA}$) and a slightly contracted first interlayer spacing ($2.03 \pm 0.03 \text{ \AA}$). With increasing thickness more and more defects are introduced in the film, but a 13-LE film still produces a good LEED pattern. On Cu{110}, the Fe film grows also pseudomorphically, with the same bulk interlayer spacing as the substrate (1.27 \AA) and a contracted first interlayer spacing (1.17 \AA), but a precise structure analysis is not possible because the film has relatively large {111} facets. Defects and disorder increase with film thickness, so that the LEED pattern is practically obliterated when the thickness exceeds about 20 LE.

I. INTRODUCTION

The vacuum deposition of iron on single-crystal copper has attracted considerable attention during the past 20 years because the close match between the lattice constant of fcc copper ($a_0 = 3.61 \text{ \AA}$) and the lattice constant of the metastable fcc modification of iron (γ -Fe, $a_0 = 3.59 \text{ \AA}$) stabilizes the epitaxial growth of thin films of γ -Fe, which are not attainable as macroscopic crystals. The major portion of the work on this subject has been concentrated on studies of the growth of Fe on the {001} surface of Cu (see the references cited in Ref. 1). It is generally accepted by now that on a clean Cu{001} surface iron films can be grown pseudomorphically with thicknesses of 15 to 20 layers. The films are slightly strained by the epitaxial stress so that their structure is a small tetragonal distortion of the fcc lattice with $a = 3.61 \text{ \AA}$ (imposed by the Cu substrate) and $c = 3.54 \text{ \AA}$ (Ref. 1).

Less attention has been devoted to the growth of Fe on Cu{111} and on Cu{110}. It was established early on that on Cu{111} the Fe films grow initially pseudomorphic (i.e., probably with the structure of slightly distorted γ -Fe), but then convert to bcc α -Fe with "bcc $[\bar{1}11]$ parallel to fcc $[10\bar{1}]$ in sixfold complementation."² Most of the subsequent work was concentrated on the study of the epitaxial relationships between the Fe{110} deposits and the Cu{111} substrate (Ni{111} and Ag{111} have also been used as substrates). This work involved growth in relatively poor vacuum (approximately 10^{-5} Torr) of rather thick films (100–300 \AA) and the films were studied with electron microscopes.^{3–6} Thus, it was found both theoretically and experimentally that the epitaxial relationships between bcc Fe{110} films and fcc {111} substrates (Cu{111} in particular) produced two special cases of one-dimensional matching: the Nishiyama-Wasserman orientation⁷ (NW, diagonals

of the primitive rhombic unit meshes of substrate and film are parallel) and the Kurdjumov-Sachs orientation⁷ (KS, sides of the rhombic unit meshes are parallel), both orientations occurring at the same time.^{3–6}

Magnetic measurements of the γ -Fe{111} films grown on Cu{111} found them to be ferromagnetic^{8,9} with magnetic moments of approximately $1\mu_B/\text{atom}$. Similar results were obtained for Fe films electrodeposited on Cu{110}.¹⁰

What seems to be lacking is a clear and quantitative description of the atomic structure of the Fe films, whether it is pseudomorphic (and hence probably strained fcc) or incommensurate (equilibrium bcc). Quantitative structural studies were done by Montano and co-workers^{11,12} for both Fe on Cu{111} and Fe on Cu{110}, but only at the monolayer level. Thus, the purpose of the work described herein was to characterize quantitatively both the structure of the pseudomorphic Fe films and the epitaxial relationships between the bcc Fe films and the underlying pseudomorphic layers. We show that on Cu{111} the Fe films grow pseudomorphically to thicknesses of about 4 to 5 layers (in agreement with the earlier work of Gradmann and Tillmanns²) and we determine the interatomic distances. Thicker films assume the structure of stable bcc Fe, with domains consistent with the KS orientation, and we find that the NW orientation did *not* occur. We also show that on Cu{110} pseudomorphism occurs as well, but the films are not flat—they exhibit identifiable {111} facets which make an accurate determination of the atomic structure of the films both difficult and uncertain.

II. EXPERIMENT

The experiments were done in an ultrahigh-vacuum chamber with base pressure of 7×10^{-11} Torr. The low-

energy-electron-diffraction (LEED) observations and measurements were made with a rearview unit, and the $I(V)$ spectra were collected with a video-LEED system as described elsewhere.¹³ The Auger electron spectroscopy (AES) scans were done by means of a cylindrical mirror analyzer (CMA) provided with an axial electron gun.

A Cu{111} and a Cu{110} surface were cleaned *in situ* by series of Ar-ion bombardments (5×10^{-5} Torr, 400 eV, 15 μ A) followed by anneals at 650°C. After elimination of all impurity lines (C,N,O) from the AES spectra, both surfaces produced clear, low-background 1×1 LEED patterns.

The Fe source was a 99.999%-pure Fe wire wrapped around a W spiral which was heated electrically. The rate of deposition was approximately 1 Å/min. The thickness of the Fe deposit was determined from the ratio $R = I_{\text{Fe}(651 \text{ eV})} / I_{\text{Cu}(920 \text{ eV})}$ between the AES intensities $I_{\text{Fe}(651 \text{ eV})}$ and $I_{\text{Cu}(920 \text{ eV})}$ of the Fe AES line at 651 eV and the Cu AES line at 920 eV, respectively, by means of the formula

$$R = R_{\infty} \frac{1 - e^{-d/\lambda_{651 \text{ eV}}}}{e^{-d/\lambda_{920 \text{ eV}}}}, \quad (1)$$

where $R_{\infty} = I_{\text{Fe}(651 \text{ eV})}^{\infty} / I_{\text{Cu}(920 \text{ eV})}^{\infty} = 0.84$ (Ref. 14); I^{∞} denotes the intensity of the AES line from a very thick sample of Fe (Cu) at 651 (920) eV; the λ 's are the inelastic mean free paths of electrons with 651 (920) eV energy traveling in Fe; $\lambda_{651 \text{ eV}} = 13.8$ Å and $\lambda_{920 \text{ eV}} = 16.4$ Å (Ref. 15); and d is the thickness of a film of Fe assumed to be uniform over the Cu surface.

The thickness of the Fe films as determined with Eq. (1) are quoted below in layer equivalents (LE), representing the number of *uniformly distributed* layers of Fe that would produce the same value of the ratio R in Eq. (1) as that measured in the actual experiments. The conversion from angstroms to LE was done on the basis of the relation 1 LE = 2.08 Å for Fe/Cu{111} and 1 LE = 1.27 Å for Fe/Cu{110} (justified by the LEED results presented below), but it should be emphasized that 1 LE is not necessarily equal to one layer, or, in the notation used by other authors, 1 ML. The error bars in the determination of film thickness are estimated to be about $\pm 50\%$, primarily because of uncertainties in the values of the inelastic mean free paths.

III. RESULTS

Fe/Cu{111}. The threefold-symmetric 1×1 LEED pattern from Cu{111} persisted, upon deposition of Fe, until a coverage of about 5 LE, with the background increasing slightly with coverage. Above 5 LE, new spots became visible near and around the integral-order beams. At about 7 LE the integral-order beams disappeared, the symmetry of the pattern became sixfold, and the configuration of the new spots became equal to the one produced by thick films of Fe on Ru(0001) (Ref. 16).

Figures 1(a) and 1(b) show two photographs, for 67 and 70 eV, respectively, of the LEED patterns obtained from a 13-LE film of Fe (the thickest film studied in this work). It can be shown that these patterns are those expected

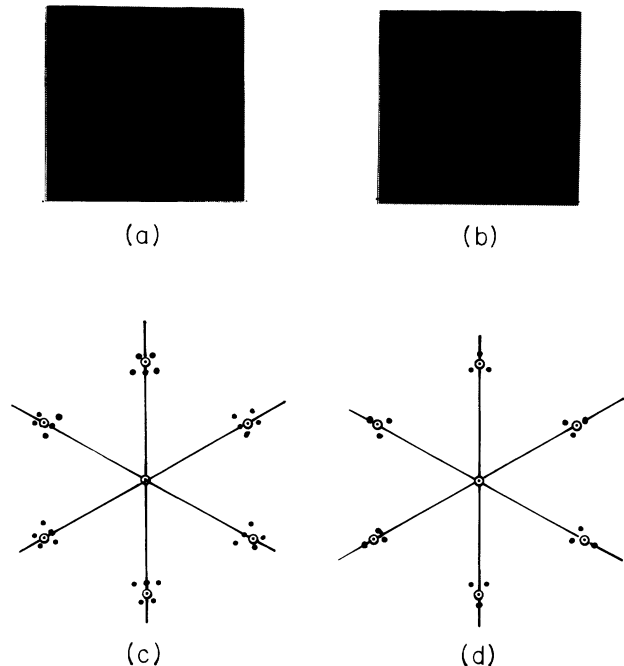


FIG. 1. (a) and (b) Photographs of LEED patterns from a 13-LE-thick film of Fe on Cu{111} (67 and 70 eV, respectively). (c) and (d) Schematic LEED patterns expected from bcc Fe{110} domains in the KS orientation (c) and in the NW orientation (d), rotationally related through the threefold-symmetric substrate. The open circles arise from the Cu{111} substrate, the full circles from the bcc Fe{110} domains.

from a uniform distribution of three-dimensional domains of bcc Fe{110} grown onto the hexagonal net of pseudomorphic Fe on Cu{111} in the KS orientation (see also Gradmann and Tillmanns²). The phenomenon is the same as the one observed in the case of thicker films of Fe on Ru(0001) (Ref. 16) with one difference: for bcc Fe{110}/Ru(0001) the interrow distances are almost identical to one another [2.340 Å for bcc Fe{110} and 2.343 Å for Ru(0001), see Fig. 4 of Ref. 16], hence the fit for the KS orientation is almost perfect, whereas for bcc Fe{110}/Cu{111} the interrow distances differ by 5.4% (2.213 Å for Cu{111}). Figure 1(c) depicts a schematic LEED pattern expected in the present case: the full circles are the (new) spots produced by the bcc Fe{110} domains. They appear in clusters of five spots (three inner and two outer spots) which correspond to the 10- and 11-type beams from Fe{110} (see Ref. 16). Since beam intensities vary with electron energy, the five spots are not all clearly observable at the same energy. For example, the three inner spots are best observed at 67 eV [Fig. 1(a)] whereas the two outer spots are visible at 70 eV [Fig. 1(b)]. In Fig. 1(c), the open circles are the spots produced by the underlying Fe layers pseudomorphic with Cu{111}. With thicker Fe films the open circles were not observed, as the substrate was no longer reached by the electron beam.

Additional proof that the observed pattern was in fact produced by bcc Fe{110} domains, and that such

domains had the same (unstrained) structure as those grown on Ru(0001), is provided by Fig. 2: the integrated intensities of the five-spot clusters produced by thick films of Fe on Ru(0001) (Ref. 16) and by thick films of Fe on Cu{111} (present work) are essentially identical to one another, and both are equal to the combined intensities of 10 and 11 beams from bulk bcc Fe{110} (Ref. 17).

In contrast to the expectations and the observations reported in the literature,³⁻⁶ the NW orientation did not appear in the present experiments. In fact, the LEED pattern expected from rotationally related domains of bcc Fe{110} in the NW orientation is depicted in Fig. 1(d), and such a pattern was never observed in the present experiments.

We now discuss the structure of the low-coverage (1×1) deposits. In order to determine this structure, we assumed initially that the 1×1 LEED pattern which we observed on 5-LE films was in fact produced by homogeneous films with thicknesses of four to five layers. An assumption about the effective number of Fe layers was necessary because the intensity calculations are not helpful in determining the coverage: the intensity-versus-energy [so-called $I(V)$] curves from either semi-infinite Cu{111} or semi-infinite fcc Fe{111}, or one, two, or three layers of Fe on Cu{111}, are almost equal to one another—LEED cannot distinguish well between isostructural crystals of elements with similar atomic numbers. The assumption of four- to five-layer films was also convenient because it allowed us to compare the experimental $I(V)$ curves with curves calculated for a semi-infinite fcc Fe{111} crystal (four to five atomic layers are practically equivalent to semi-infinite material as far as LEED is concerned). But of course the assumption should (and will later) be justified by the experiment.

About the structure of the film we know at the outset only that the in-plane lattice constant is that of Cu{111} ($a = 2.55 \text{ \AA}$). Unknown are the interlayer spacings, both in the bulk (d_{bulk}) and at the surface (d_{12}). The intensity calculations were done for values of Δd_{bulk} (the change in

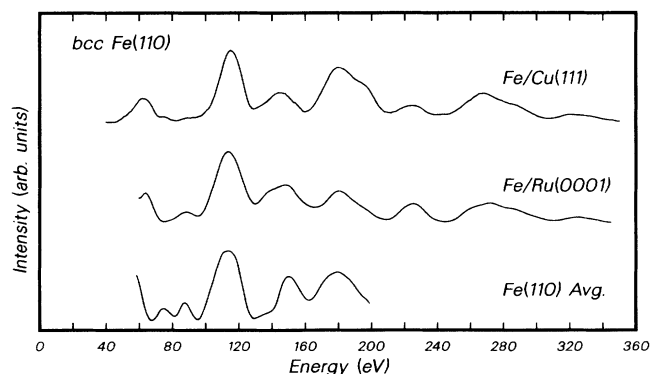


FIG. 2. Experimental integrated LEED intensities of the five-spot clusters around the Cu{111} spots measured on a 13-LE Fe film [top curve, cf. Fig. 1(c), but without the open circles], compared to the equivalent curve from a 6-LE Fe/Ru(0001) film (middle curve, Ref. 16) and to the sum of 10 and 11 spectra from bulk Fe{110} (Ref. 17).

d_{bulk}) varying from -0.1 to $+0.04 \text{ \AA}$ in steps of 0.02 \AA , while Δd_{12} (the change in the first interlayer spacing) was varied between -0.2 and $+0.2 \text{ \AA}$ in steps of 0.05 \AA . The best fit to experiment was found to correspond to a bulk interlayer spacing equal to that of Cu{111} within experimental error, namely, $d_{\text{bulk}} = 2.08 \pm 0.03 \text{ \AA}$, and a slightly contracted first interlayer spacing, $\Delta d_{12} = -0.05 \pm 0.03 \text{ \AA}$. Figure 3 depicts theoretical and experimental $I(V)$ spectra: the corresponding reliability factors [Pendry's R_p (Ref. 18), Zanazzi and Jona's r_{ZJ} (Ref. 19), and Van Hove and Tong's R_{VHT} (Ref. 20)] are $R_p = 0.15$, $r_{ZJ} = 0.13$, and $R_{\text{VHT}} = 0.23$.

But we still have to answer the following question: was the pseudomorphic film a monolayer or a multilayer film? The question is important because on Ru(0001) we could prove that only one layer of Fe grew pseudomorphically on the substrate—the additional Fe formed immediately the bcc {110} domains on top of this single layer. That proof was possible and convincing because in that case the $I(V)$ curves changed considerably from those of the clean substrate to those of one, then two, etc., layers of Fe on the substrate, and therefore the identification of the coverage and of its structure was unambiguous. But in

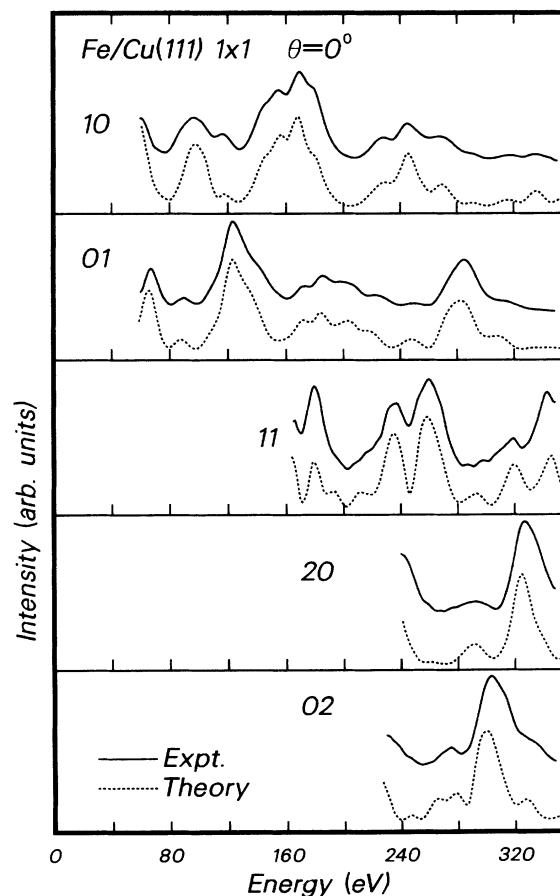


FIG. 3. Experimental and theoretical LEED spectra for normal electron incidence on a 5-LE film of Fe on Cu{111}. The theoretical spectra were calculated for a semi-infinite γ -Fe{111} crystal.

the present case the problem is more difficult, as mentioned above, because Fe and Cu have similar atomic numbers and therefore in general the $I(V)$ curves from different coverages are almost indistinguishable from one another. Fortunately, we have found that for at least one $I(V)$ curve, the 00 spectrum for non-normal incidence ($\theta=10^\circ, \phi=0^\circ$), the changes with Fe coverage, while small, are detectable. Figure 4 shows that in the range between 120 and 160 eV the shape of the $I(V)$ curve changes visibly with increasing coverage by Fe from 0 to 5 LE. The calculations for a semi-infinite γ -Fe{111} match the 5-LE $I(V)$ curve best, as shown in Fig. 5. The corresponding R -factor values are $R_p=0.11$, $r_{ZJ}=0.11$, and $R_{VHT}=0.19$. We conclude therefore that in the present case, in contrast to the Fe/Ru(0001) case, the pseudomorphic film of Fe grew in thickness to include four to five layers.

Fe/Cu{110}. Upon deposition of Fe, the 1×1 pattern from Cu{110} persisted, but extra spots appeared almost immediately (i.e., for less than 1 LE), which moved with varying voltage along directions parallel to the $\langle 100 \rangle$ axis. These extra spots (which were called "maverick" spots in the early LEED literature) are indicative of the presence of facets on the surface. Their intensities increased with coverage by Fe and their size, initially large (elongated along $\langle 100 \rangle$) 6×3 nm at 0.8 LE, decreased to 2×2 nm at 15 LE. The overall LEED pattern, however, remained 1×1 , albeit with increasing background, until about 20 LE, and became practically invisible in the high background thereafter.

The energy dependence of the motion of the extra spots suggests that the spots were due to the presence of {111} facets, which are inclined 35.5° to the {110} surface. In fact, rotation of the sample by 35.5° around the $\langle 110 \rangle$ axis in the plane of the surface allowed us to observe directly the 00 spot of the {111} facets and the convergence of the extra spots toward that 00 spot. The fact that the extra spots appeared very early in the deposition process suggests that the iron agglomerated to form islands, while the behavior of the spots showed that the islands were bounded on top and on two sides by {110}

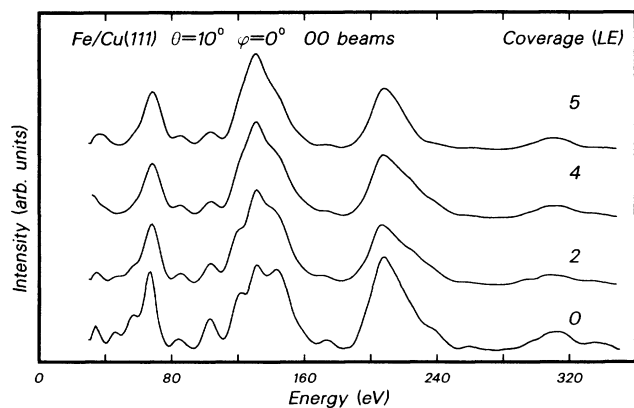


FIG. 4. Experimental 00 spectra from Fe/Cu{111}. Coverage given in LE (0 means clean Cu{111}).

planes and on the remaining two sides by {111} planes. From the size of the extra spots we can estimate the size of the {111} facets by using a modified Scherrer formula.²¹ We find that at 0.8 LE the {111} facets were about 35×70 Å across, and at 15 LE they had grown to be 100×100 Å across.

The faceting of the Fe film had a disappointing consequence: the $I(V)$ curves of the pseudomorphic Fe film were "contaminated" by the moving extra spots and were therefore not to be entirely trusted for a reliable intensity analysis aimed at the determination of the atomic structure. We did collect several $I(V)$ curves anyway (from an 11-LE film) and compared them with calculations on a semi-infinite γ -Fe{110} crystal (with Δd_{bulk} and Δd_{12} varied as for the {111} film). Refinement with R factors was not justified in this case, owing to the disturbing presence of the extra spots, but visual evaluation was used to find the best possible fit. Figure 6 depicts such a best fit between experiment and a calculation done with $\Delta d_{\text{bulk}}=0.0$ (i.e., $d_{\text{bulk}}=12.7$ Å) and $\Delta d_{12}=-0.1$ Å.

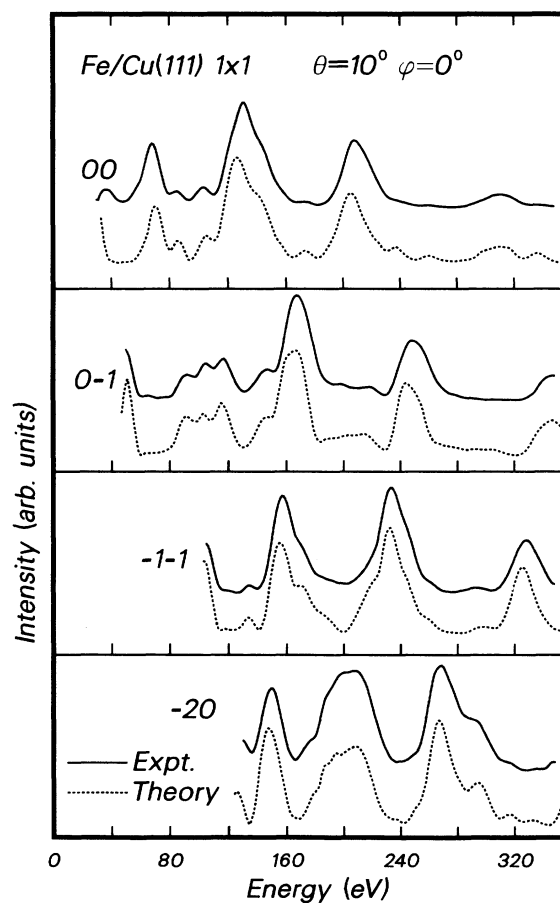


FIG. 5. Experimental and theoretical LEED spectra for incidence at $\theta=10^\circ$ and $\phi=0^\circ$ on a 5-LE film of Fe on Cu{111}. The theoretical spectra were calculated for a semi-infinite γ -Fe{111} crystal.

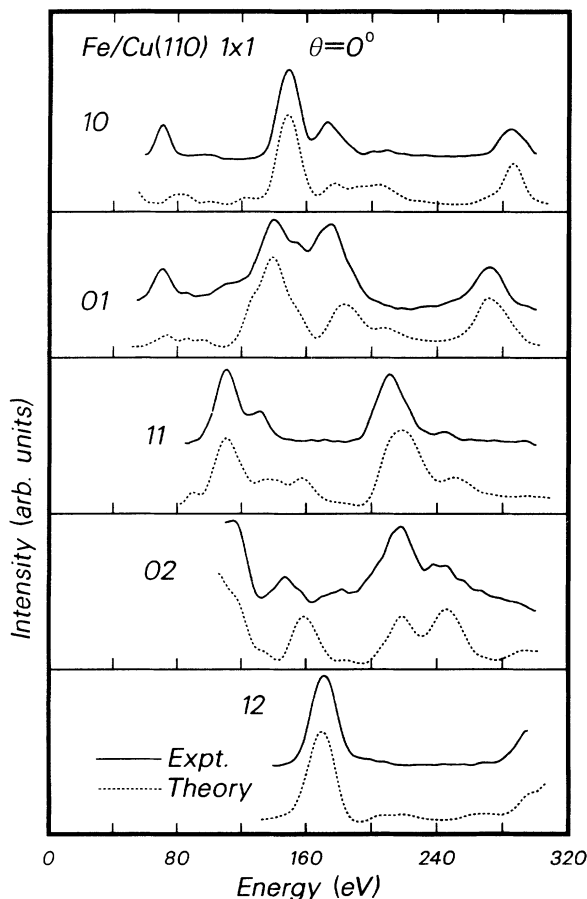


FIG. 6. Experimental and theoretical LEED spectra for normal electron incidence on an 11-LE film of Fe on Cu{110}. The theoretical spectra were calculated for a semi-infinite γ -Fe{110} crystal.

IV. CONCLUSION AND DISCUSSION

Our experiments show that the growth of Fe on Cu{111} occurs first by formation of a pseudomorphic film of γ -Fe{111} about five layers thick and then by growth of bcc Fe{110} domains in the KS orientation and rotationally related to one another through the three-fold symmetry of the substrate. The pseudomorphic film has the same bulk interlayer spacing, within experimental error, as the Cu{111} substrate (2.08 ± 0.03 Å) and a slightly contracted first interlayer spacing (2.03 ± 0.03 Å). With increasing thickness beyond about five layers the film consists of six rotationally related bcc Fe{110} domains, more and more defects are introduced

in the film, but a 13-LE film still produces a good LEED pattern.

For epitaxy of bcc {110} on fcc {111}, the ideal ratio of cubic lattice constants $a^{\text{fcc}}/a^{\text{bcc}}$ for KS orientation²² is 4/3 [the equivalent ratio for the case of bcc Fe{110} on hcp Ru(0001) is 1.335, see Ref. 16], while the ideal ratio for NW orientation²² is either $2/\sqrt{3}=1.155$ or $\sqrt{2}$. Now, the ratio of the cubic lattice parameters of fcc Cu and bcc Fe is 1.261, hence it is not surprising that bcc Fe{110} grows on Cu{111} in the KS orientation, since the ratio is closer to ideal KS than to ideal NW. In addition, an atomistic calculation²² with assumed pair potentials shows that the energy is minimized at both the KS and the NW orientation, but the KS energy minimum is lower than the NW minimum. Van der Merwe and Braun⁷ also predicted the occurrence of the KS orientation for the epitaxy of α -Fe on Cu{111}.

As pointed out by Kobayashi and Das Sarma,²² the special feature of the KS and NW orientations that produces minima of the interfacial energy at these orientations is that, for favorable lattice-constant ratios, the bcc {110} and fcc {111} lattices are commensurate in a direction perpendicular to particular lattice rows, although they remain incommensurate in the direction parallel to these lattice rows. Hence, the interaction energy of the two lattices is averaged uniformly over a line in the incommensurate direction rather than uniformly over the entire unit mesh as in the general case in which all directions are incommensurate. For minimal interfacial energy that line will be midway between the lattice rows, thus avoiding the vicinity of substrate atoms where the potential is larger; the KS line, which goes through the center of the rhombic mesh and is parallel to the close-packed rows, has somewhat lower energy than the NW line, which connects midpoints of adjacent edges of the rhombic unit mesh.

On Cu{110} the Fe film grows also pseudomorphically, with the same bulk interlayer spacing as the substrate (1.27 Å) and a contracted first interlayer spacing (1.17 Å), but a reliable structure analysis is not possible because the film features relatively large {111} facets. The film thickness can grow up to about 20 LE, but with increasing amounts of defects that practically obliterate the LEED pattern above 20 LE.

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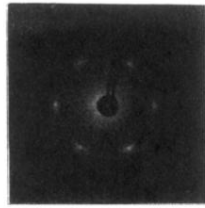
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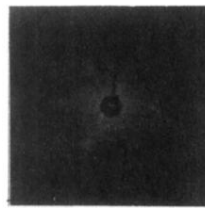
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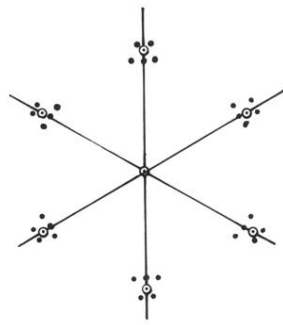
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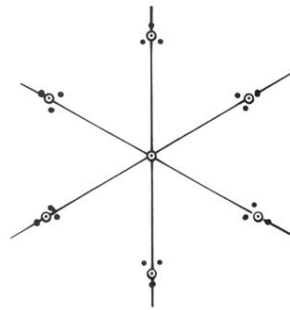
(a)



(b)



(c)



(d)

FIG. 1. (a) and (b) Photographs of LEED patterns from a 13-LE-thick film of Fe on Cu{111} (67 and 70 eV, respectively). (c) and (d) Schematic LEED patterns expected from bcc Fe{110} domains in the KS orientation (c) and in the NW orientation (d), rotationally related through the threefold-symmetric substrate. The open circles arise from the Cu{111} substrate, the full circles from the bcc Fe{110} domains.