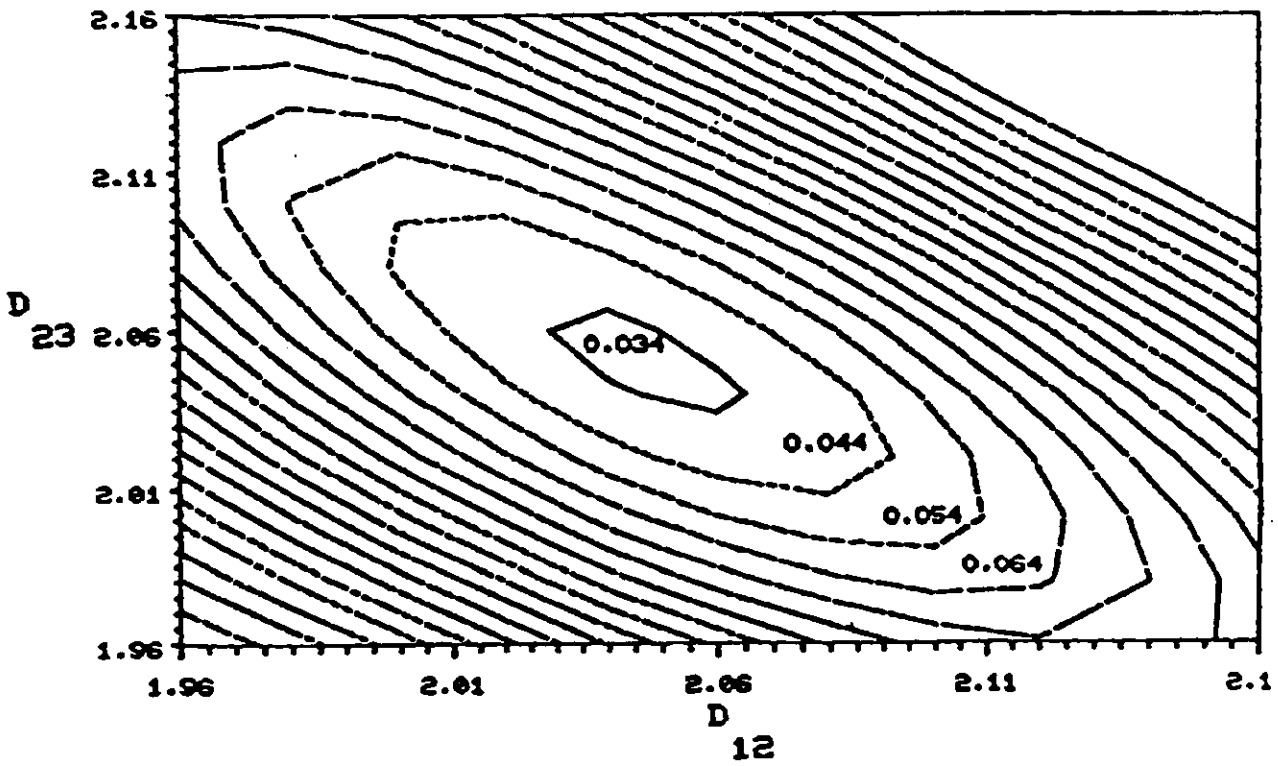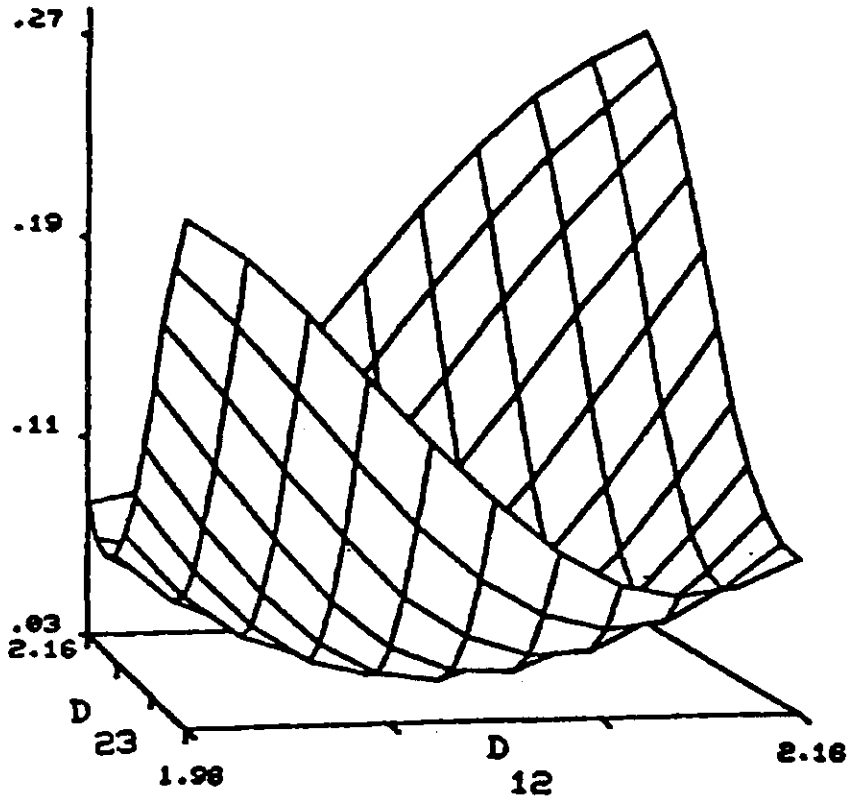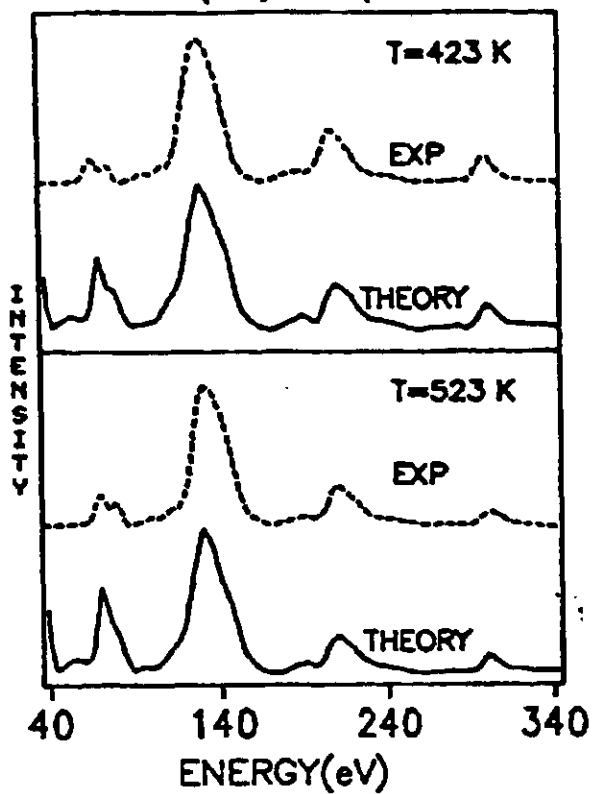# RELIABILITY FACTOR FOR CU(111)

BEAM (00) Temperature
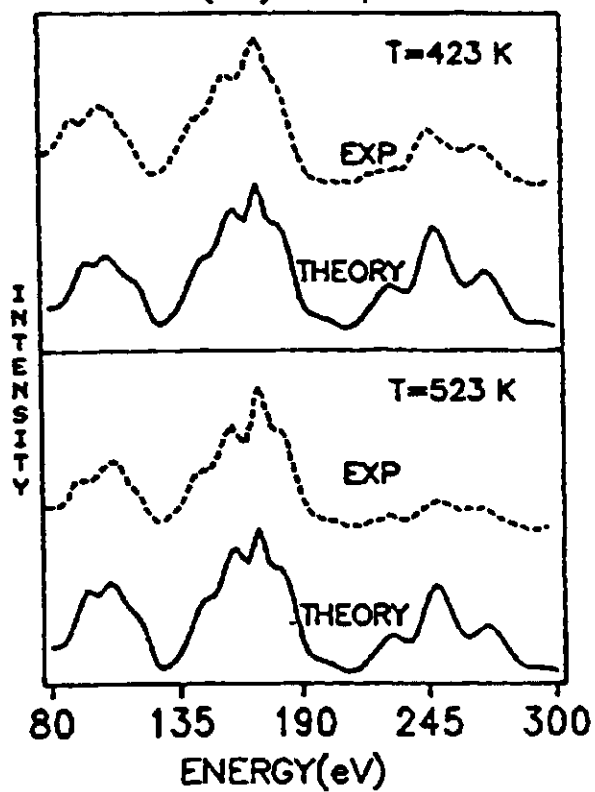
T=423 K
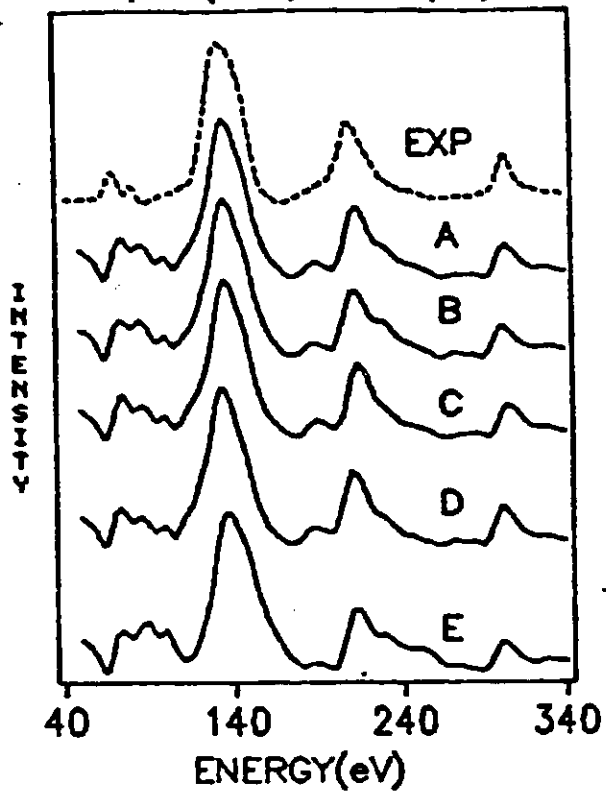
EXP

THEORY

T=523 K

EXP

THEORY

INTENSITY

40   140   240   340
ENERGY(eV)

BEAM (10) Temperature

T=423 K

EXP

THEORY

T=523 K

EXP

THEORY

INTENSITY

80   135   190   245   300
ENERGY(eV)

BEAM (01) Temperature

T=423 K

EXP

THEORY

T=523 K

EXP

THEORY

INTENSITY

50   140   230   320
ENERGY(eV)

Fe/Cu(111) SPOT (00)

INTENSITY

EXP

A

B

C

D

E

40   140   240   340

ENERGY(eV)

Fe/Cu(111) SPOT (10)

INTENSITY

EXP

A

B

C

D

E

80   135   190   245   300

ENERGY(eV)

Fe/Cu(111) SPOT (01)

INTENSITY

EXP

A

B

C

D

E

50   140   230   320

ENERGY(eV)

Fe/Cu(111) SPOT (11)

INTENSITY

EXP

A

B

C

D

E

160   240   320   400

ENERGY(eV)
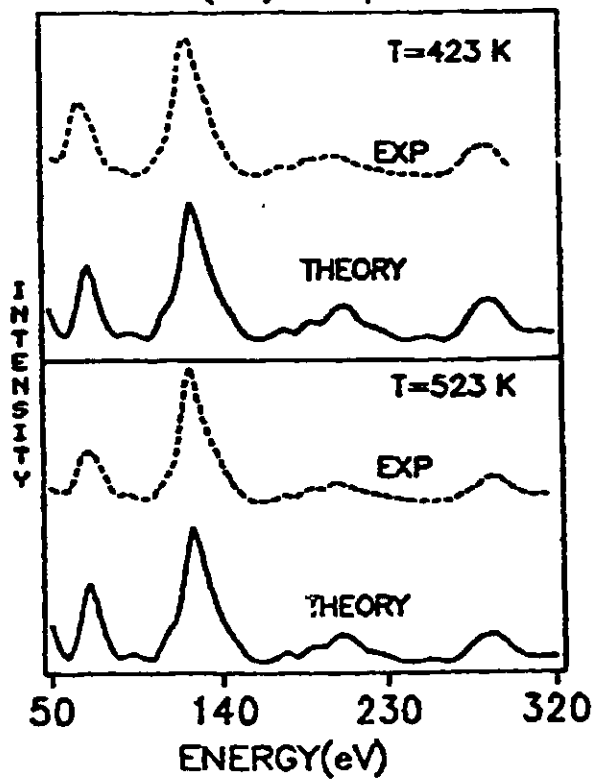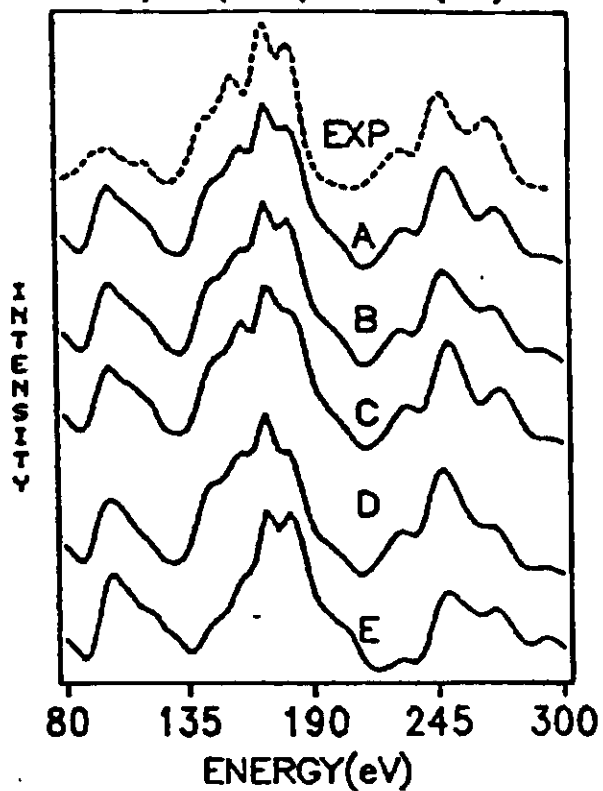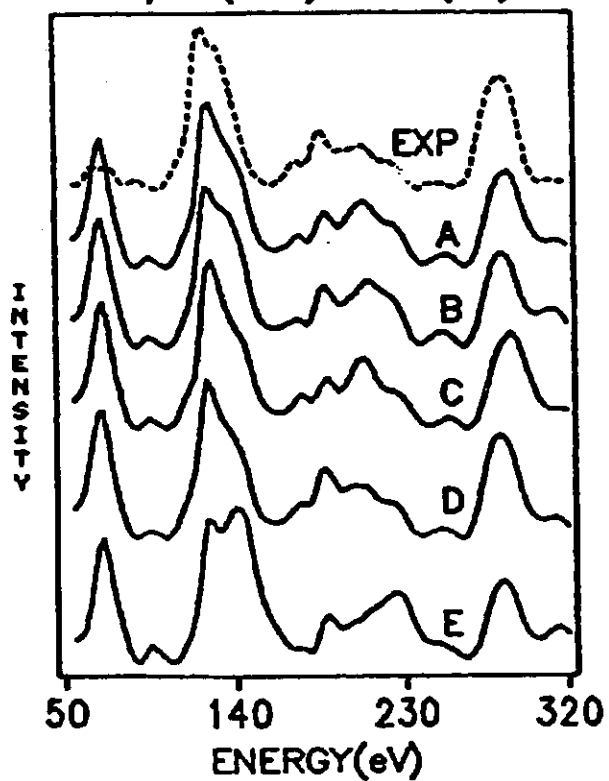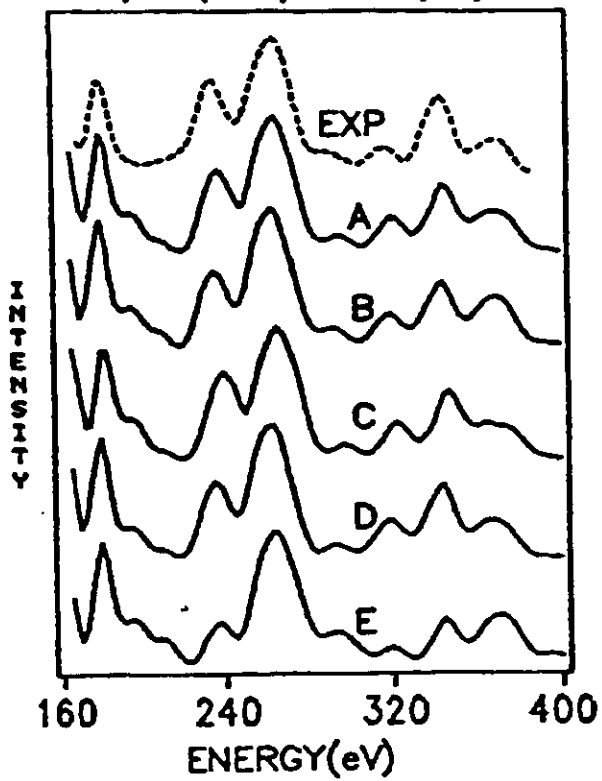
RELIABILITY FACTOR (1ML FE/CU)

EXPERIMENT (10) BEAM

INTENSITY

Cu(111) 300 K

Cu(111) 523 K

1 L Fe/Cu 473 K

1 L Fe/Cu 373 K

1 L Fe/Cu 300 K

80   135   190   245   300
ENERGY(eV)

EXPERIMENT (01) BEAM

INTENSITY

Cu(111) 300 K

Cu(111) 523 K

1 L Fe/Cu 473 K

1 L Fe/Cu 373 K

1 L Fe/Cu 300 K

50   140   230   320
ENERGY(eV)

RATIO(FE/CU) VS TIME

2ML AT 200 C

FE(47 EV)/CU(107 EV)

RATIO

TIME (MIN.)
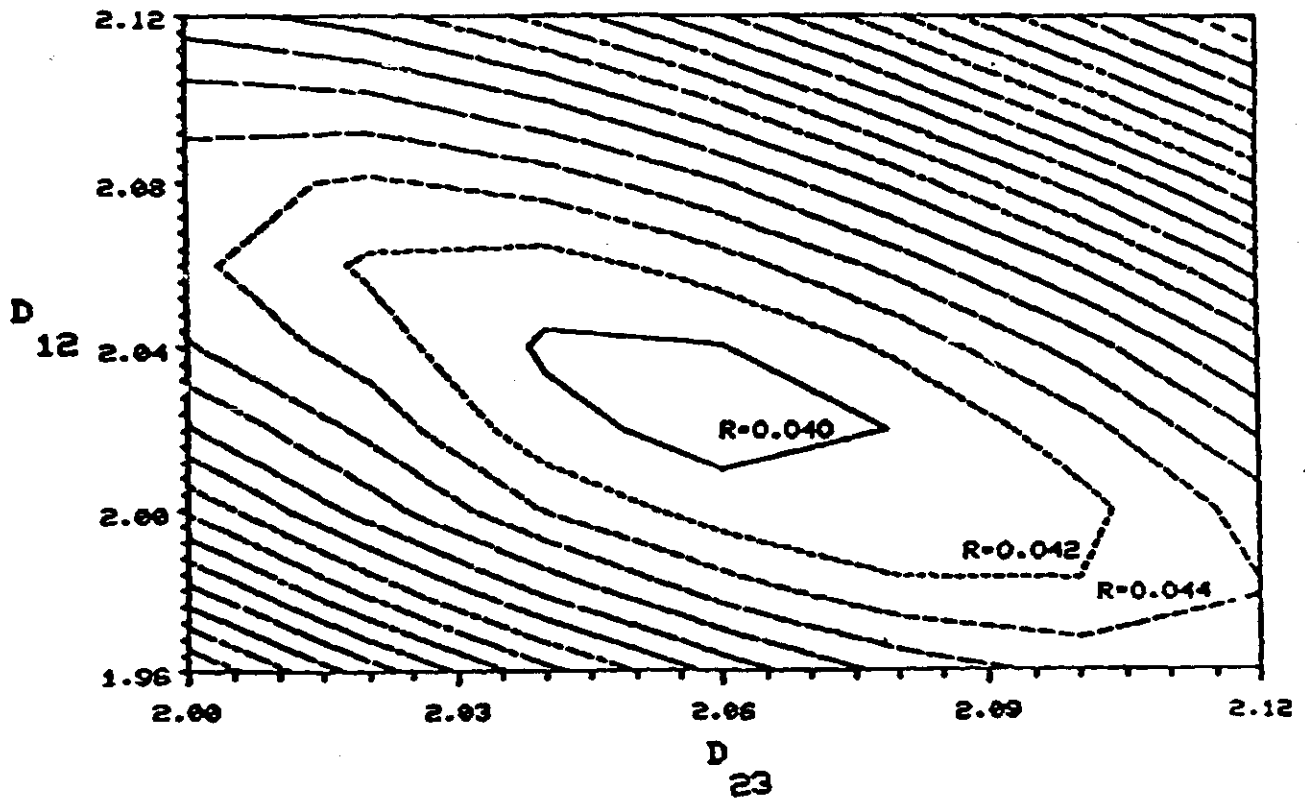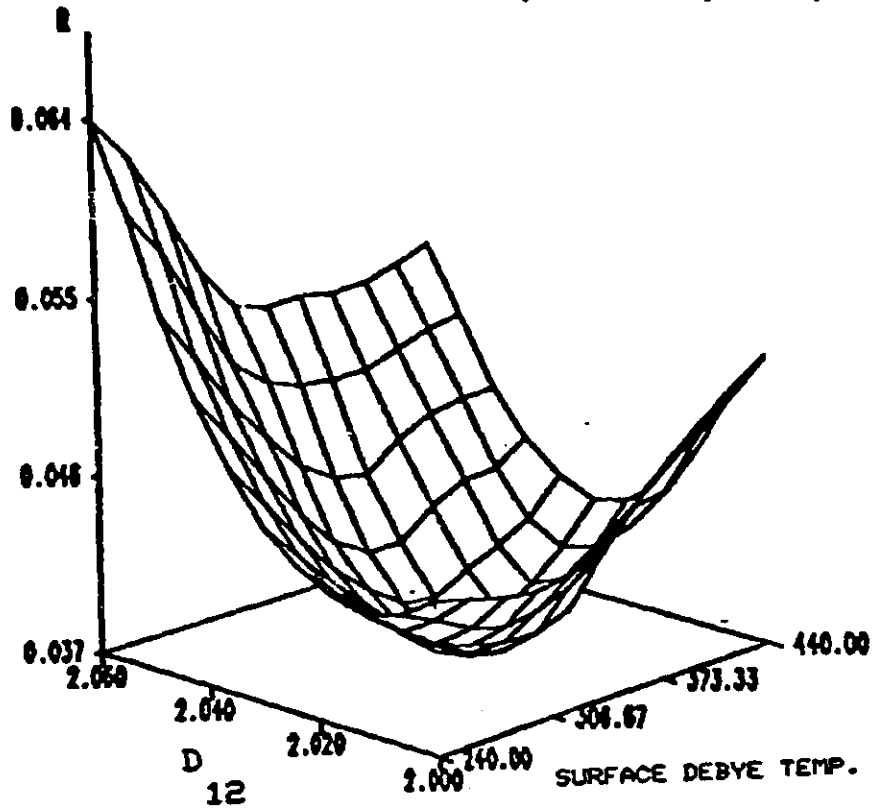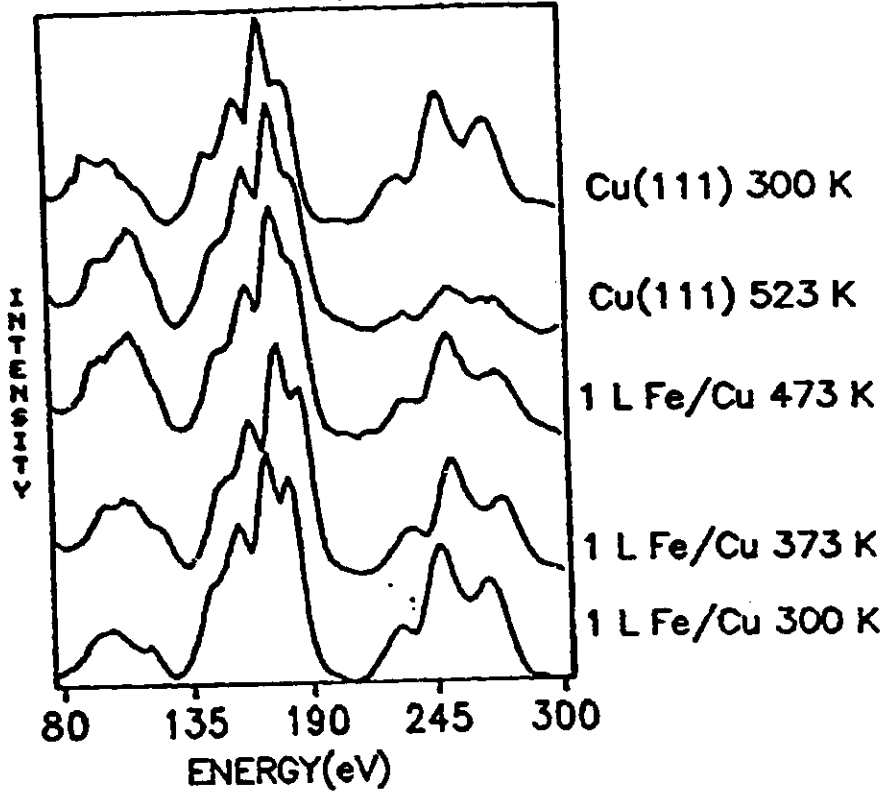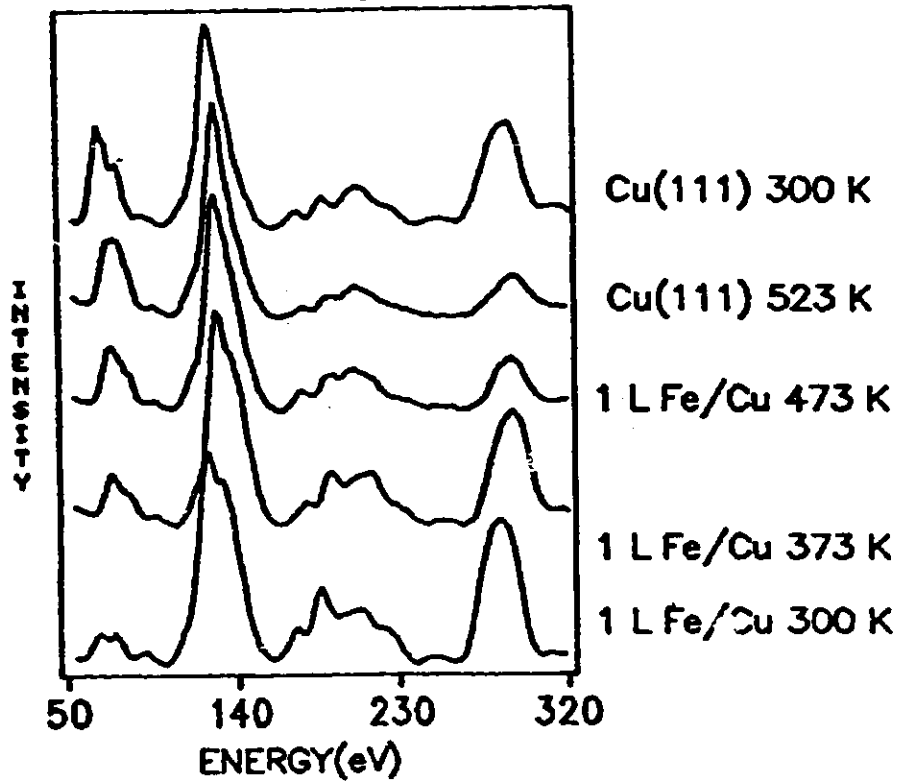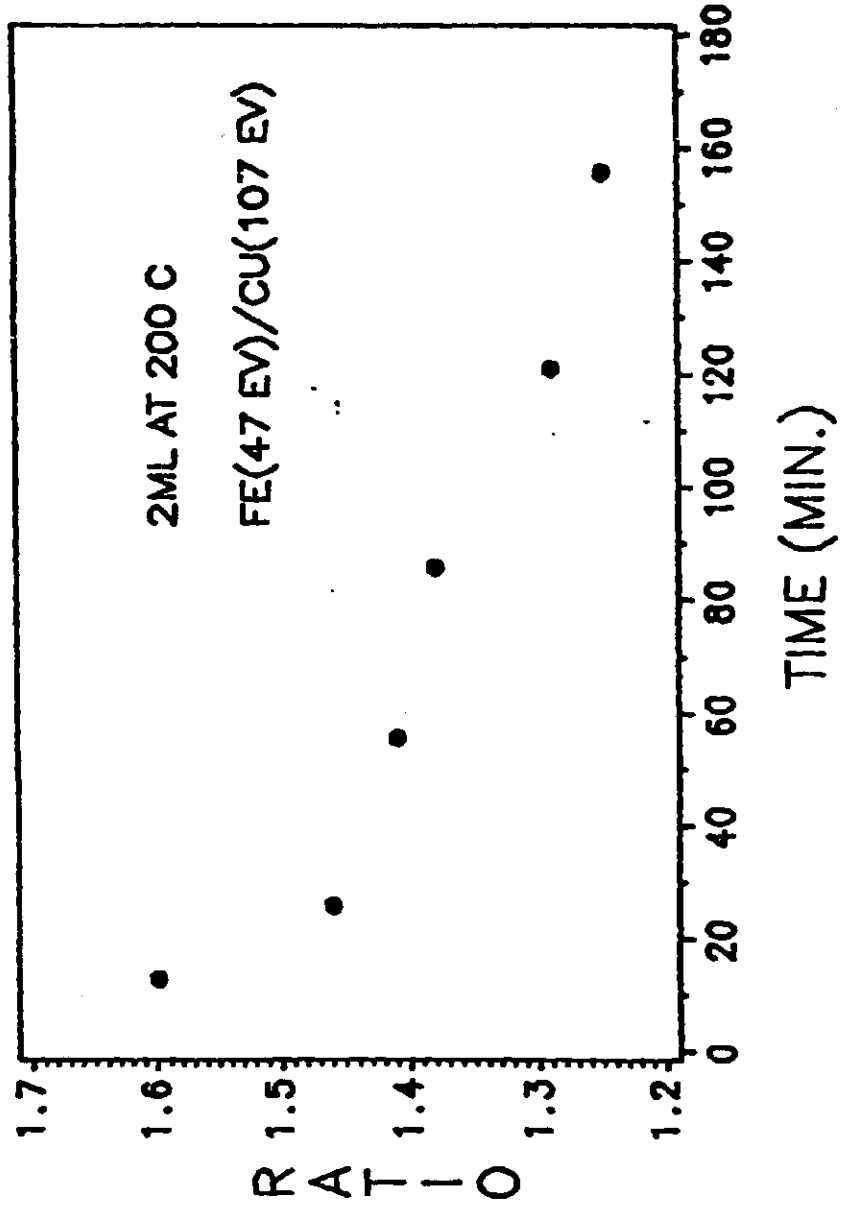
8. ELECTRONIC AND CRYSTALLOGRAPHIC STRUCTURE OF IRON FILMS
   EPITAXIALLY GROWN ON Cu SINGLE CRYSTALS

ABSTRACT

The crystallographic and electronic structure of iron films epitaxially grown on Cu single crystals was investigated by LEED, AS, EELS and UPS. The Cu(100), Cu(110) and Cu(111) faces were used as substrates for the growth of the iron films. In our study emphasis was placed on the modification of surface properties due to the Fe/Cu interface. Significant variation with respect to α-Fe was observed in the electronic structure of fcc iron formed on the various crystal faces.

INTRODUCTION

The epitaxial growth of one metal on another is a challenging and interesting problem of considerable technological importance. It is known that bimetallic systems differ in their properties from that of bulk materials. The surface determines the reactivity and selectivity of bimetallic catalysts [1]. These epitaxially grown systems are accessible to new advanced theoretical calculations, [2] which make the evaluation of experimental results more feasible. Recent experimental work on epitaxially grown films includes a LEED study of Ni on Cu(111) [3] and of Cu on Ni(100) [4]. Electron energy loss spectroscopy (EELS) and Auger measurements were also performed on Cu/Ni(100) [5]. Angular resolved photoelectron spectroscopy was used to study Ni epitaxially grown on Cu(100) [6]. A very important system from their potential catalytic role is iron epitaxially grown on Cu single crystals. It has been observed that iron grows epitaxially on Cu(100) forming an fcc lattice [7]. It is noted that the γ-iron has a lattice constant of 3.588 A at room temperature, closer to that of bulk Cu, 3.61 A, than that of bulk nickel (3.52 A).

In this paper we report the results of LEED, UPS and EEL measurements on iron epitaxially grown on Cu single crystal surfaces. LEED was used to determine the geometry of the deposited layers and Auger spectroscopy to determine the surface composition and cleanliness of the surface before and after deposition.

EXPERIMENTAL

The experiments were performed in a UHV system with pressures around 10^{-10} Torr. The system was provided with a 4-grid LEED optics and a CMA. He I (21.2 eV) was used as the excitation source for the UPS measurements (angular integrated). The EELS measurements were performed using the second derivative method. A modulation voltage of 1 eV was applied to the CMA. The iron metal was evaporated from an alumina crucible. High purity single crystals of Cu(100), Cu(110) and Cu(111) were used for the measurements. The crystals were aligned using vonLaue X-ray back diffraction techniques. Mechanical polishing followed by chemical etching produced a clean surface with a bright mirror finish. In vacuum, the crystals were cleaned by alternate cycles of argon ion sputtering and heating until no surface impurities were detected. Finally, annealing at 450°C for 5 min. produced a clean surface which gave sharp LEED spots. The iron deposition was monitored by measuring the growth of the 651 eV iron Auger peak and the reduction of the 920 eV copper peak. The deposition was monitored as a function of time and the coverage determined using the mean free path for

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1

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electrons of 920 eV, the thickness was corrected for the acceptance angle
(42.3°) of the CMA. The auger measurements suggest that iron grows ap-
proximately layer-by-layer in Cu(100) and Cu(110), the study is in progress
for the Cu(111) face. For long deposition time the presence of carbon and
oxygen contaminants was observed.

RESULTS AND DISCUSSION

LEED

It was used to monitor the order of the deposited films. Deposition
was performed with the substrate at room temperature. The growth on the
Cu(100) is epitaxial, up to about 17 layers. Iron grows in its non mag-
netic γ -phase; for more than 17 layers there is evidence of bcc iron [8].
For the Cu(110) the epitaxial growth seems to occur up to a few layers
(less than 10). LEED intensity-versus-energy curves were obtained by using
a spot photometer to measure the intensity of the spots on the screen. The
recorded intensity was directly converted to digital form and stored in a
microcomputer for further processing. Figure 1 shows the LEED spectra for
the (00) spot with $\Theta = 5.0° \pm 0.1°$ and $\phi = 26° \pm 1°$, the top figure is for
1 ML coverage and the bottom one for 4 ML on Cu(100). The intensity vs.
temperature were monitored for the (00) spot. A simple Debye model was used
to analyze the temperature dependence of the intensities, for 1 ML the
temperature range was between room temperature and 400°C; a $\Theta_D = 267°$ was
found for the 94 eV peak and 380° for the 270 eV. The former is more re-
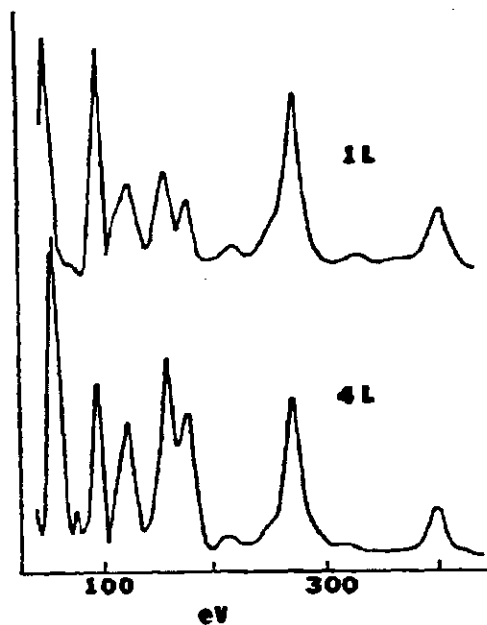presentative of the surface Debye temperature of the iron monolayer. It is

Figure 1. LEED intensity vs. energy
curves (00) for 1 L and 4 L of iron
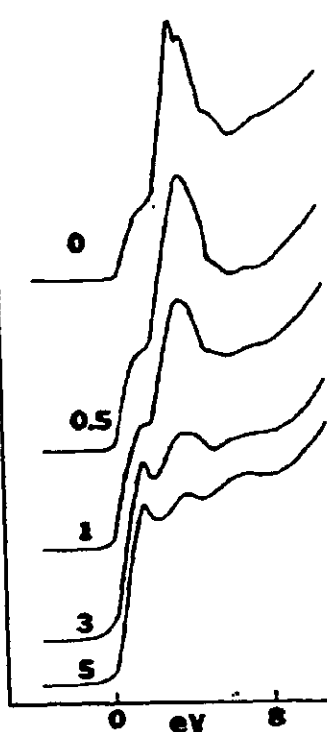on Cu(100). $\Theta = 5.0°$ and $\phi = 26°$

Figure 2. EDC for iron on Cu(100),
the numbers indicate the number of
layers of iron on Cu(100).

noted that there is evidence of iron loss at the surface, this loss seems to occur by diffusion inside Cu (or the equivalent effect Cu surface seg-gregation). For 4 ML this effect is more pronounced and considerable re-duction in the coverage is observed. For a 4 ML coverage of Cu(100) the Debye temperature between RT and 200°C was determined to be 310° for the 94 eV peak and 389° for the 270 eV peak. This is indicative of a stronger binding of iron to iron as compared to the iron-copper interface, not an unexpected result. A full dynamical analysis of the intensity versus energy curves for the (00), (10), (11), (20) and symmetry related spots is present-ly in progress. Preliminary results indicate the presence of small surface relaxation for iron on Cu(100).

UPS

Ultraviolet photoelectron spectroscopy (UPS) was used to follow the changes in the electronic structure for iron epitaxially deposited on Cu(100). Figure 2 shows the electron distribution curves (EDC) obtained using HeI (21.2 eV) radiation as a source of photons. The top spectrum in figure 1 shows the typical EDC spectrum of metallic Cu on a smooth back-ground of secondary emission due to inelastically scattered electrons. The pure Cu(100) EDC spectrum is in good agreement with the one observed by Binn and Norris [9]. Four easily identifiable peaks are observed at around -0.7, -2.6, -3.1 and -4.6 eV. As the iron coverage increases the resolvable peaks at -2.6 and -3.1 eVs become one broad asymmetric peak, which disap-pears for higher coverages. In going from pure Cu(100) to pure fcc Fe a prominent peak at -1.5 eV appears with a secondary peak around -3.4 eV. For coverages up to 5 ML the EDC does not show the presence of large amounts of oxygen on the surface, which is characterized by the appearance of a peak around -6 eV [10]. For higher iron coverages and up to about 15 ML one can detect the presence of oxygen on the surface; however, the iron substrate remains in the fcc structure. It is noted that the EDC curves for Cu(100) and fcc iron are in good agreement with theoretical calcula-tions by Fernando and Cooper [11]. The EDC for fcc iron on Cu(100) is re-markably different from that observed for bcc iron, which shows a prominent maximum at -0.5 eV and a weaker one at -2.4 eV below E_F [10, 12, 13]. Such a difference in the electron density of states between iron fcc and bcc should be reflected in their respective surface reactivities. Consequently one expects very different catalytic properties for the two surfaces.

Electron Energy Loss Measurements

The EEL spectra of the Cu(100), Cu(110) and Cu(111) surfaces show features which are common to all the faces. Figures 3 and 4 show the EEL spectra for Cu(111) and Cu(110) for primary energies of 300, 150 and 50 eV, the spectra are very similar to those reported for Cu(100) [5]. EEL peak positions and relative intensities remain the same for the three crystal-lographic faces of Cu. Peaks a and c have been attributed to interband transitions. Peak d can be identified as a surface plasmon, peak e is a volume plasmon after Powell's investigation [14]. Peak f has been iden-tified as an interband transition or multiple losses. However, recent EEL measurements [15] indicate that the assignment of f to an interband transition is more plausible. The EEL spectra obtained with E_p = 150 eV for iron deposited on Cu(111) are shown in Figure 5. One observes that with iron coverage there is a decrease in the relative intensity of peak a, peak f is almost totally suppressed by 2 ML of iron on Cu(111). Similar results are obtained for the other crystallographic faces of Cu. The EEL spectra for iron on Cu(100), Cu(110) and Cu(111) are shown in Figures 6, 7, and 8 for a primary energy of E_p = 50 eV, at such energy the spectra are
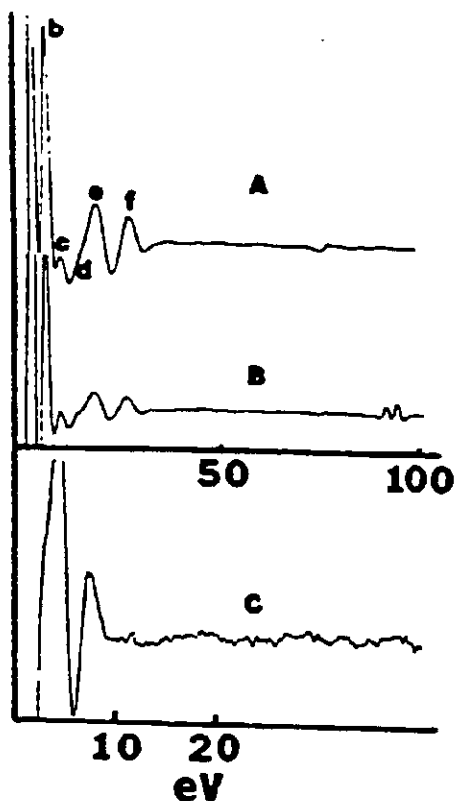
Figure 3. EEL spectra for Cu(110)
A) E_p=300 eV, B) E_p=150 eV, and
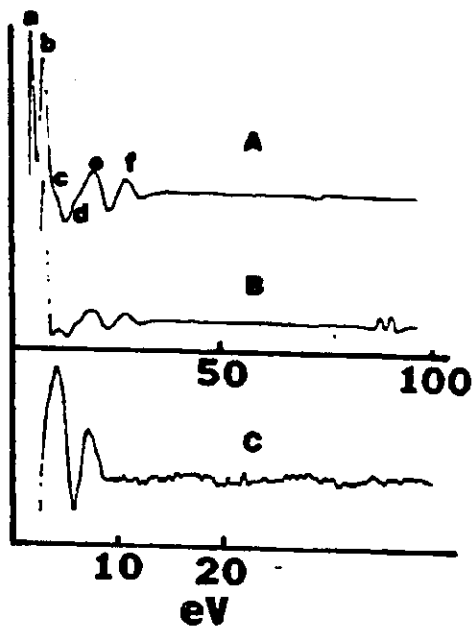C) E_p=50 eV.

Figure 4. EEL spectra for Cu(111)
A) E_p=300 eV, B) E_p=150 eV, and
C) E_p=50 eV

more sensitive to the surface layers. One can observe great similarities in the EEL spectra for the iron covered sample, independent of the crystal orientation of the substrate, except perhaps for slight shifts in energies and peak intensities. For the low coverages, less than 4 ML, none of the spectra resemble that of bcc iron. For larger coverages and depending on the orientation of the substrate, bcc iron starts to appear, mainly by formation of α-Fe islands, detected by rapid deterioration of the LEED patterns. For the Cu(111) surface substrate, the EEL peaks from 15 to 26 eV appear at an earlies stage of iron coverage. The experimental results indicate that iron epitaxially grown on Cu(111) starts to show a conversion to α-Fe (bcc) after the formation of 4 to 5 ML. This result is in good agreement with Gradmann and Tillmanns' observations [16]. Furthermore, along the Cu(110) direction the epitaxial growth occurs up to a few layers, with the formation of α-Fe at an earlier stage than for Cu(100).
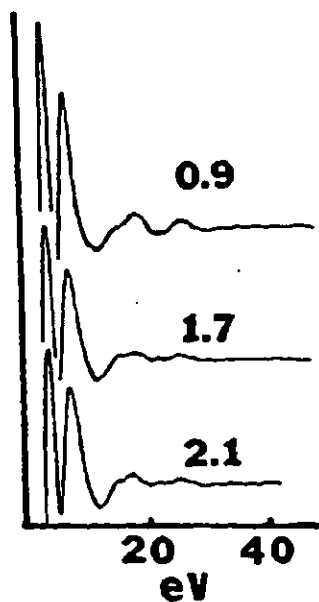
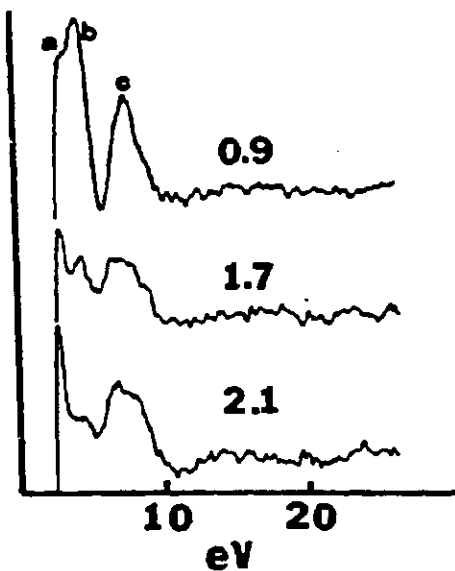**Figure 5. EEL spectra for 3 different iron coverages on Cu(111) E_p=150 eV**

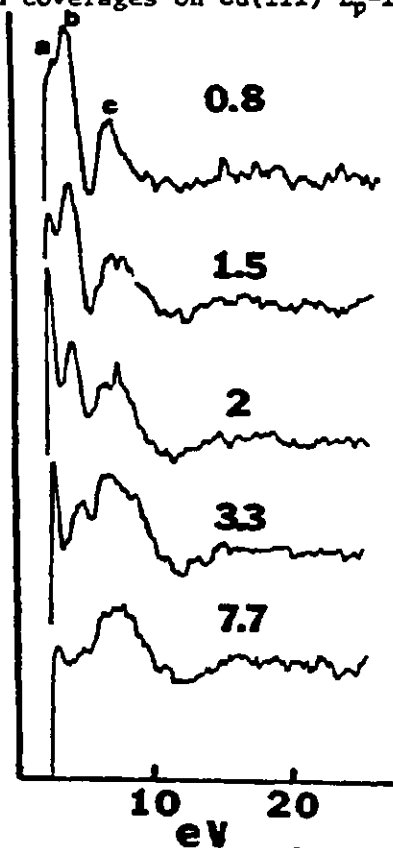**Figure 7. EEL spectra for various iron coverages on Cu(111) E_n=50 eV**

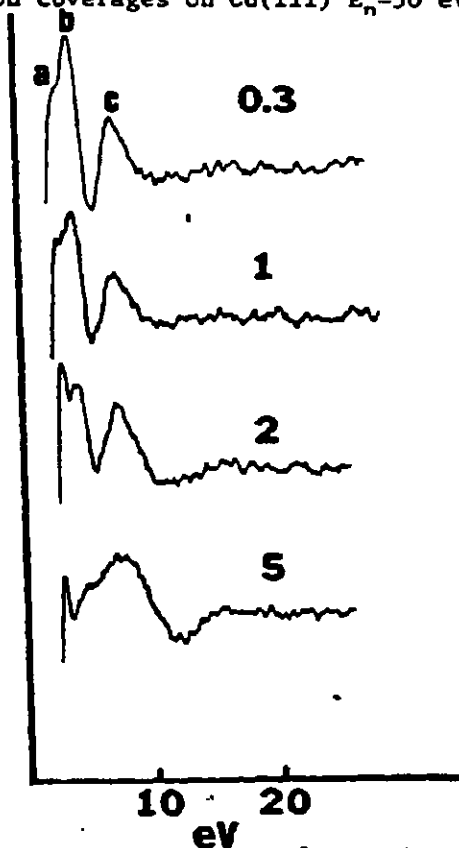**Figure 6. EEL spectra for various iron coverages on Cu(100) E_p=50 eV**

Figure 8. EEL spectra for various iron coverages on Cu(110) E_p=50 eV

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9. UPS AND EEL STUDY OF THE REACTION OF CO

AND H_2 WITH FCC IRON ON CU

ABSTRACT

We prepared iron on copper substrates by epitaxial growth with the iron growth epitaxially forming an fcc lattice. We used three different crystallographic faces of copper as substrates, Cu(100), Cu(111), and Cu(110). The samples were characterized by LEED, and Auger, the electronic structure was investigated using UPS and EELS.
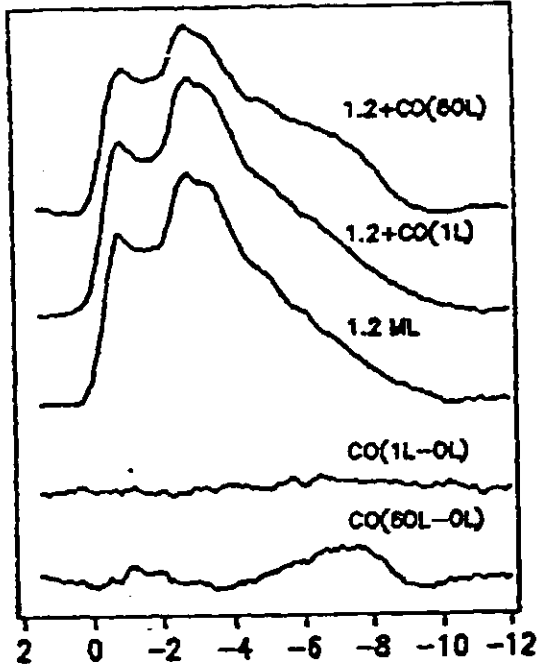
The main apparatus used in our experiments was an UHV chamber with a base pressure of 10^{-10} torr. The chamber has a CMA, an ion gun and residual gas analyzer. Attached to the major analytical chamber was a reaction cell employed for preparing the samples and performing the reactions. A second UHV system was used for the LEED, UPS and Auger measurements. High purity copper single crystals were used as substrates. The suface impurities of the substrate were eliminated by ion splitting and annealing. The iron was deposited from a specially designed Knudsen cell. The thickness of the sample was determined by Auger spectroscopy using the Cu 62eV and Fe 47eV Auger transitions for low coverage and the 920eV(Cu) and 651 eV (Fe) for high metal coverages. High purity gases were employed for all the reactions. The Fischer-Tropsch reactions were performed for a CO/H_2 ratio of 1, at 250°C for 5 minutes (pressure in the cell was 10^{-3} torr). The LEED optics was employed to determine the diffractive patterns for various iron coverages. The UPS measurements were performed using a 4-grid retarding field analyzer, HeI (21.2eV). UV radiation was used as a source. The EEL measurements were performed using primary energies of 50, 150 and 300 eV at normal incidence. The spectra were taken using the lock-in differentiation technique taking the negative of the second derivative $(-d^2N/dE^2)$ mode. A modulation voltage of 1 eV was used in the EEL measurements.
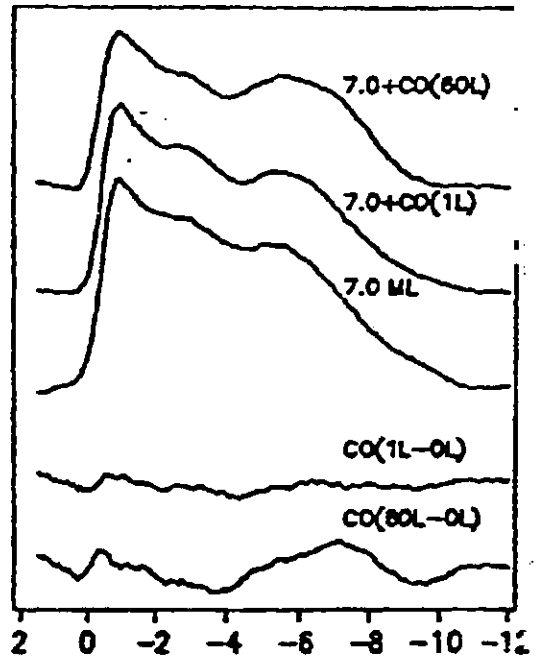
UPS STUDY OF THE REACTION OF CO WITH FCC IRON ON COPPER

Figure 1 shows the UPS spectra for different coverages of iron on Cu(100) after exposures to CO. The exposures used were 1L and 60L (1L=10^{-6} Torr/sec). The bottom of the figure shows the spectra after subtracting the background for the unexposed sample. For low iron coverage the ED curves indicate that CO is molecularly absorbed on the surface, however for 7ML of iron there is evidence that after 60L exposure to CO there is at least partial dissociation of CO. One observes the appearance of an oxygen 2p peak around 5.5eV and carbon 2p around 2eV. For iron epitaxially grown on Cu(111) the reactions with CO were studied at RT and 100°C. It is noted that along this axis the interplanar spacing is larger than along the Cu(100) or Cu(110) surfaces. Figure 2 shows the UPS spectra for chemisorption of CO on Fe for various coverages of iron, where the sample was at RT. Figure 3 shows the spectra when the exposures were performed at 100°C. The results of such measurements are more clearly illustrated in Figures 4 and 5, where the background of the unexposed sample has been subtracted. One observes immediately that at 100°C CO is totally dissociated on the surface, with such exposure to hydrogen. There is almost complete removal of carbon, with a small layer of oxide formed on the surface.

FE/CU(100)/CO AT R.T

1.2+CO(60L)

1.2+CO(1L)

1.2 ML

CO(1L-0L)

CO(60L-0L)

2   0   -2   -4   -6   -8   -10 -12

FE/CU(100)/CO AT R.T

7.0+CO(60L)

7.0+CO(1L)

7.0 ML

CO(1L-0L)

CO(60L-0L)

2   0   -2   -4   -6   -8   -10 -12

FE/CU(100)/CO AT R.T

3.8+CO(60L)

3.8+CO(1L)
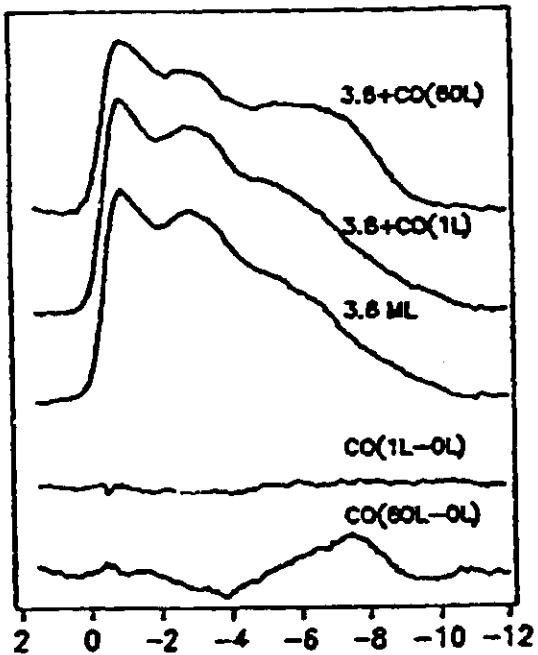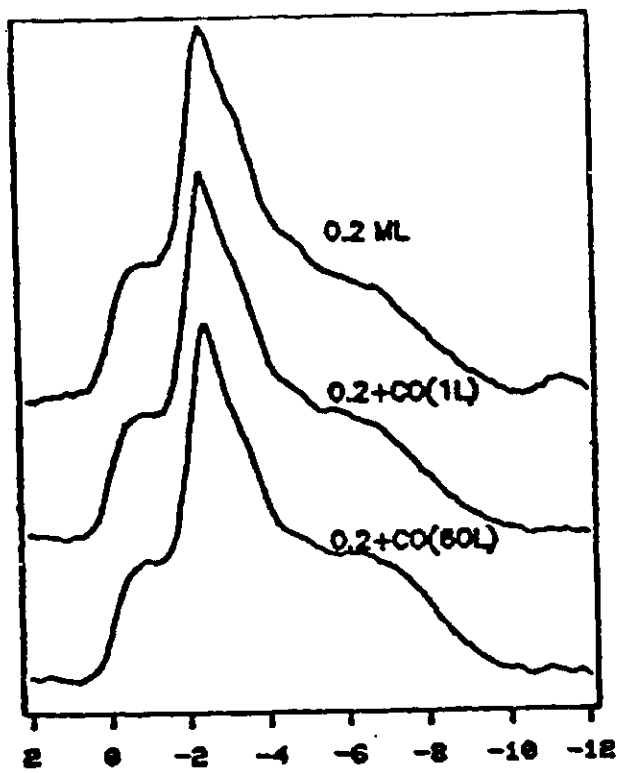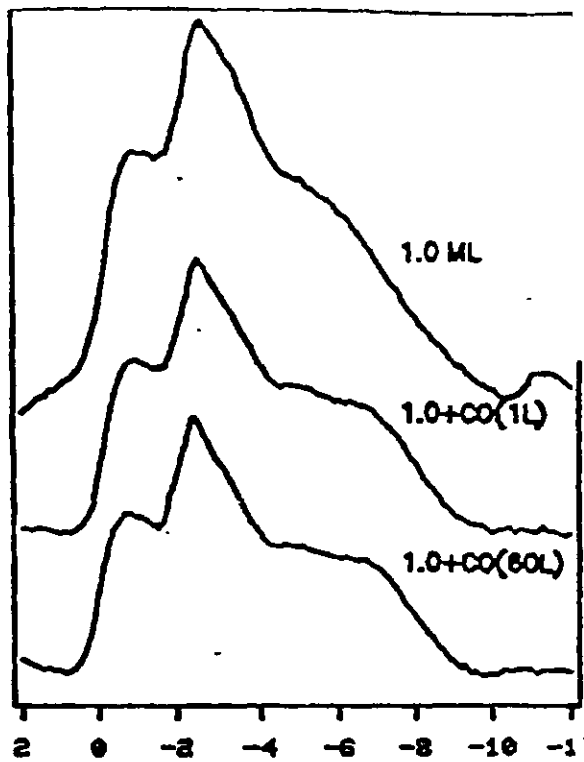
3.8 ML

CO(1L-0L)

CO(60L-0L)

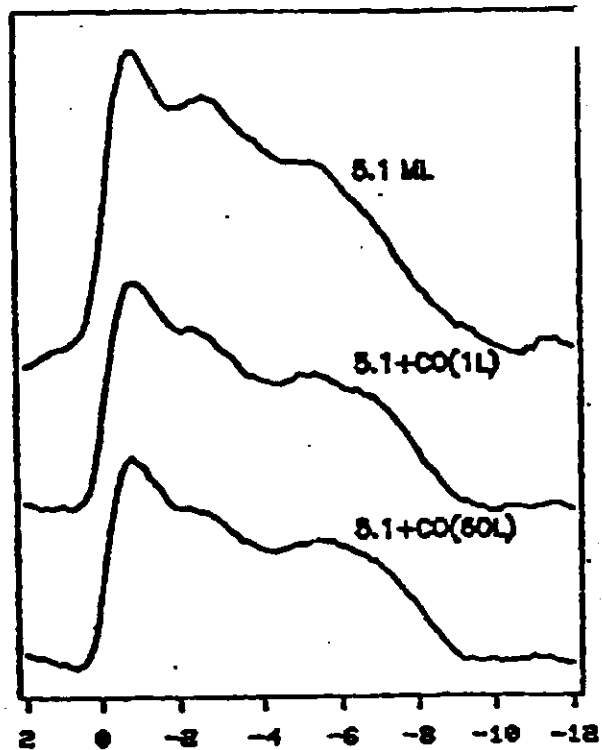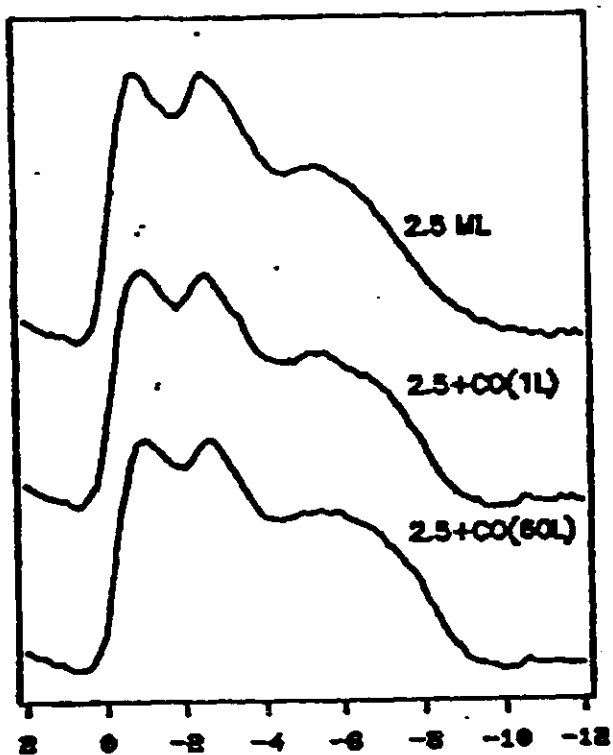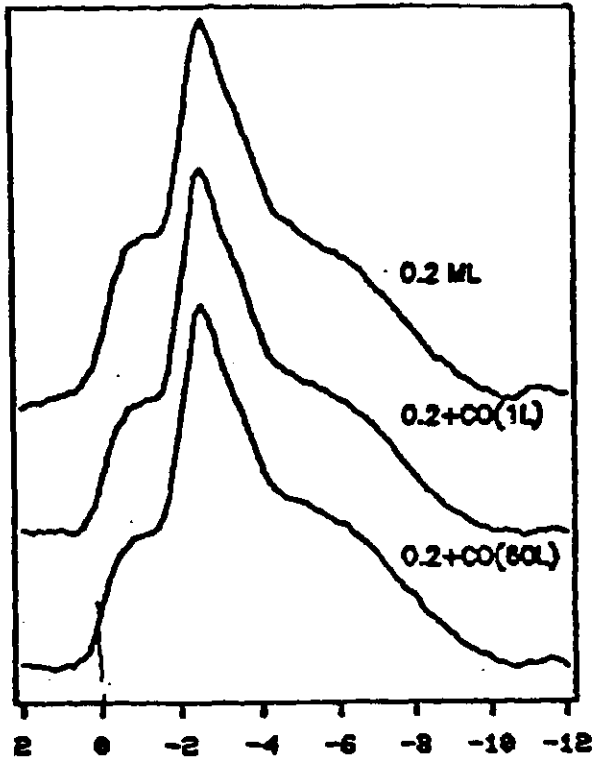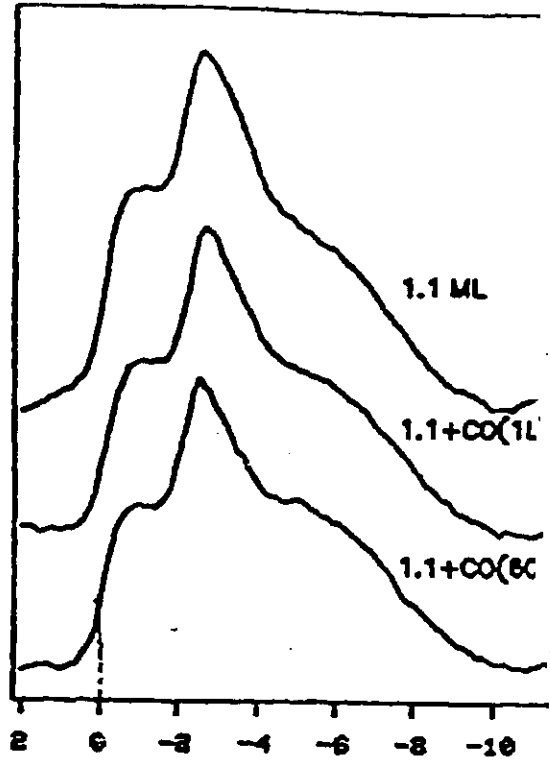2   0   -2   -4   -6   -8   -10 -12

Fig 1

FE/CU(111)/CO AT R.T
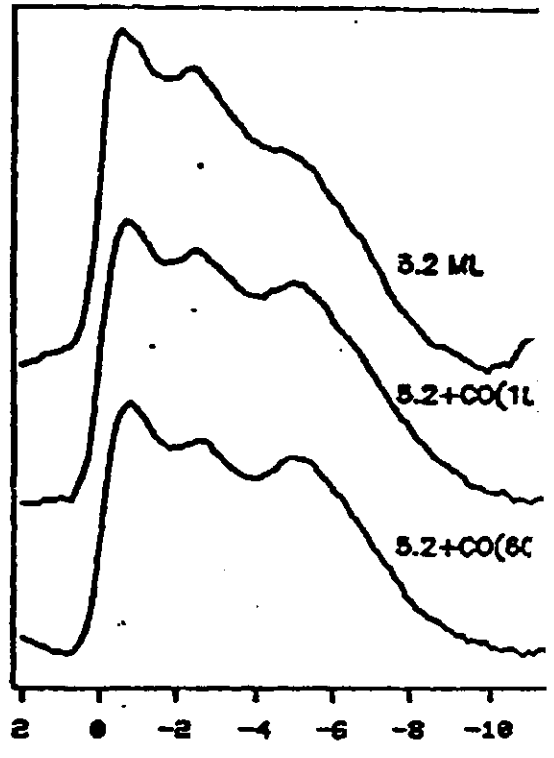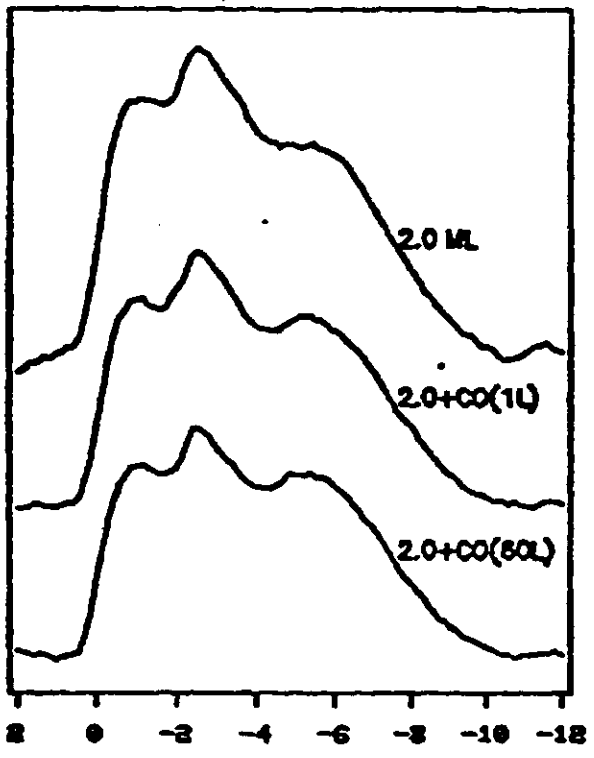
FE/CU(111)/CO AT R.T

FiG 2

FE/CU(111)/CO AT 100C

FE/CU(111)/CO AT 100C

Fig 3