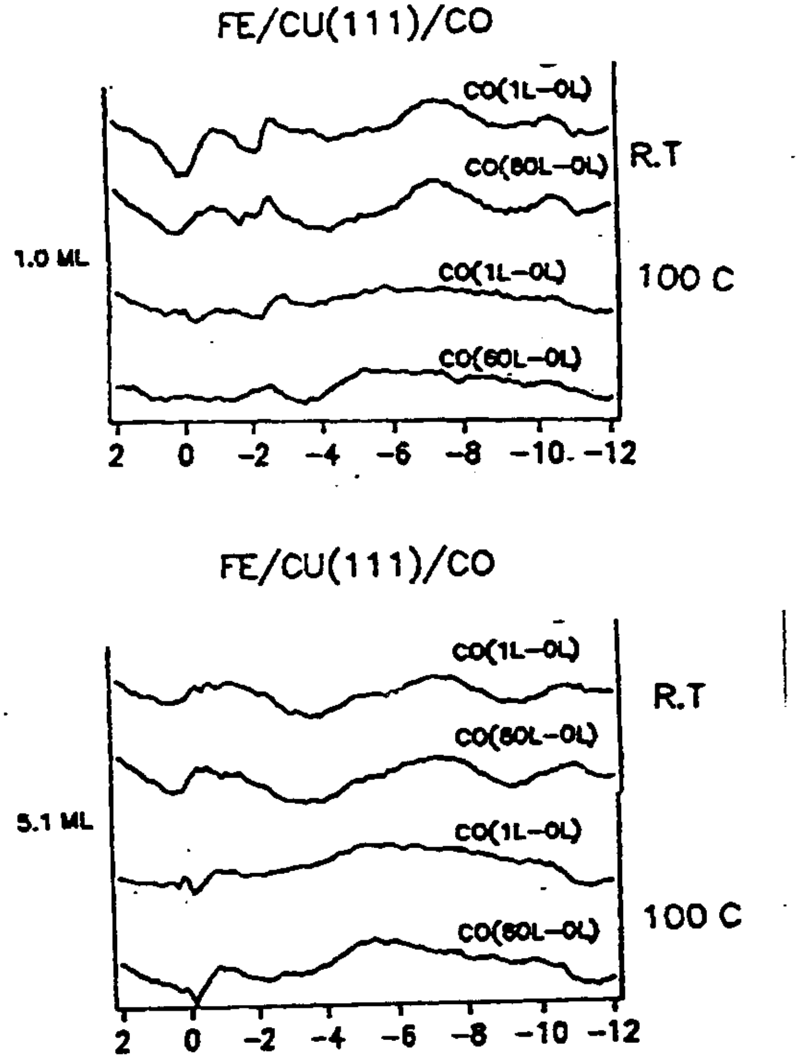
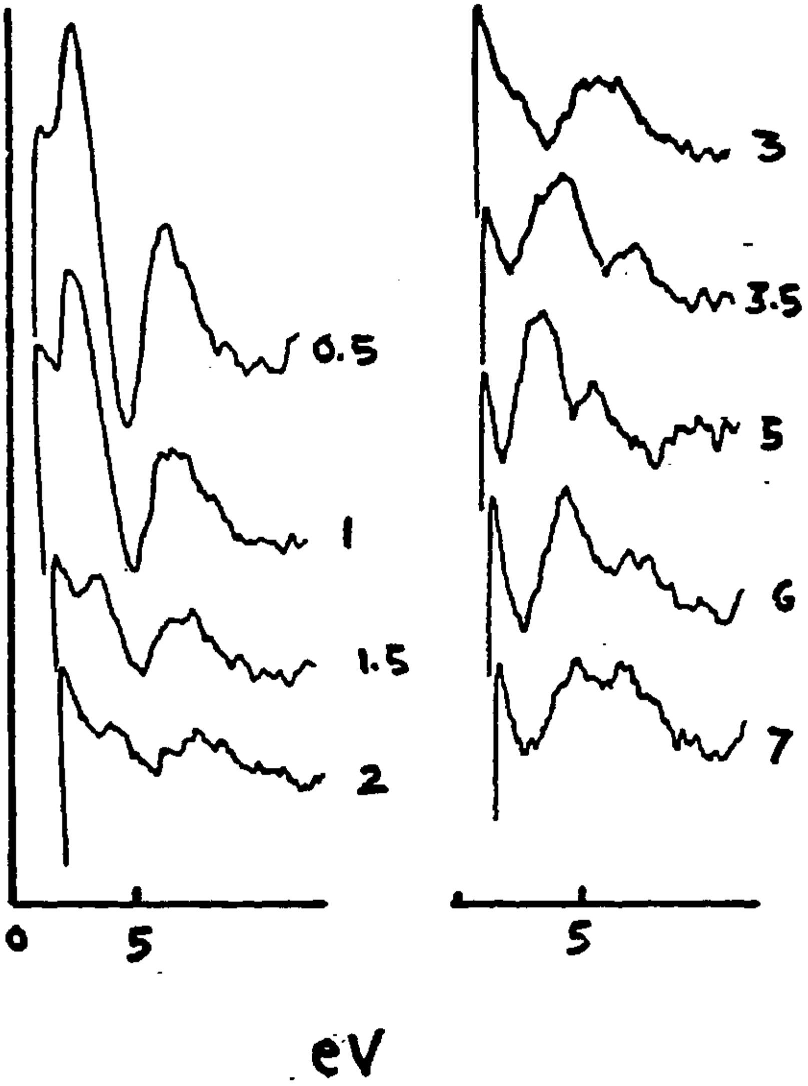

FE/CU(111)/CO
CO(1L-0L)
R.T
CO(60L-0L)
1.0 ML
CO(1L-0L)
100 C
CO(60L-0L)
2
0
-2
-4
-6
-8
-10
-12
FE/CU(111)/CO
CO(1L-0L)
R.T
CO(60L-0L)
5.1 ML
CO(1L-0L)
100 C
CO(60L-0L)
2
0
-2
-4
-6
-8
-10
-12

Figure 4



Ep = 50 eV   Fe /Cu (110)

Fig. 5

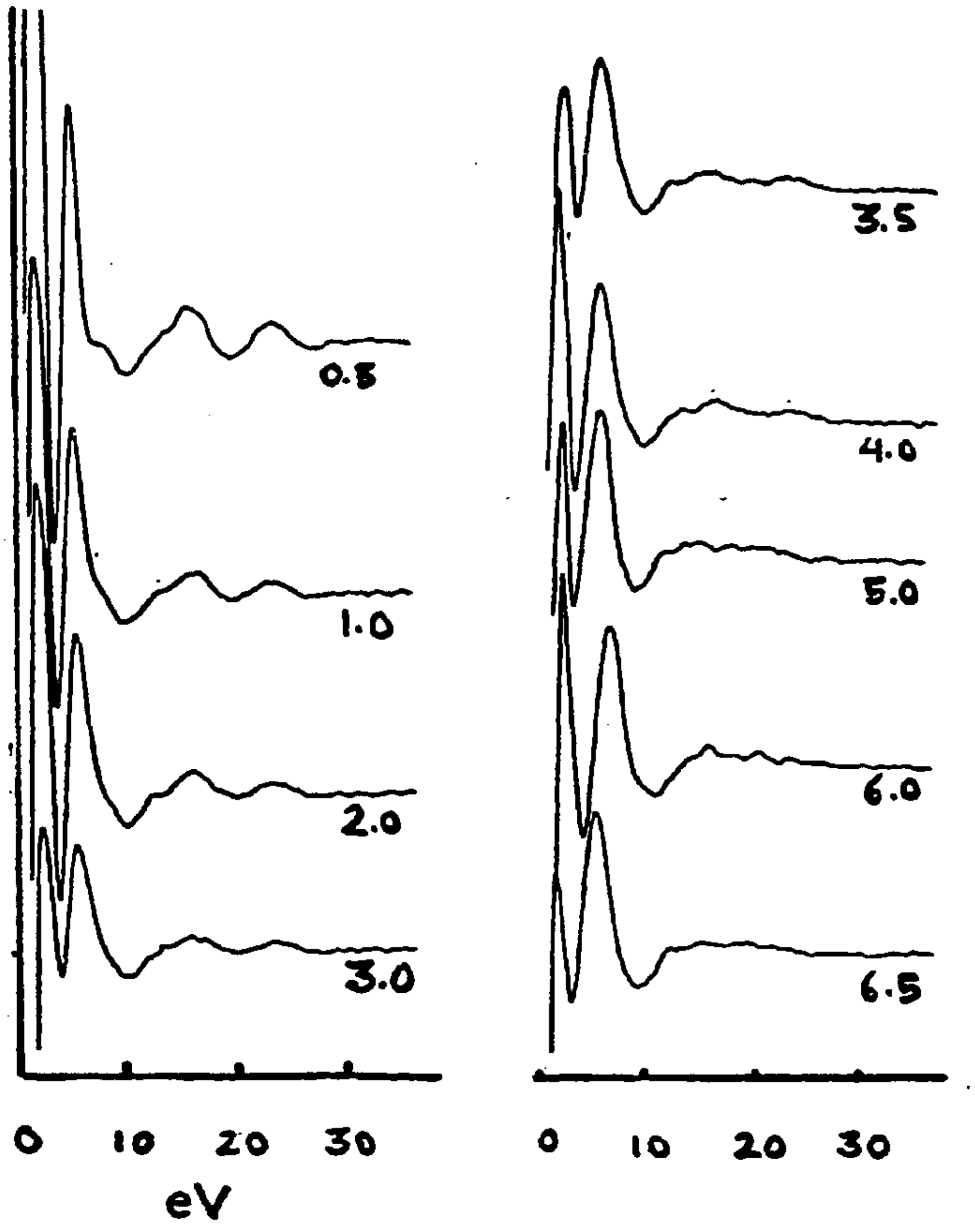
EEL SPECTRA BEFORE AND AFTER FISCHER-TROPSCH REACTIONS:

Fe on Cu(110):

Figures 5 and 6 show the EEL spectra for primary energies of 50 and 150 eV for various iron coverages. The spectra were taken after performing Fischer-Tropsch reactions. In Figure 5 the intensity of peaks 4.2 and 7.4 eV show a reduction as a function of coverage and disappear after 3.5 ML of Fe. Two new peaks appear at 5.5 eV and 8.3 eV, these two peaks are identified as belonging to iron carbides. Their intensity increases with the amount of coverage (3.5 - 6.0 ML Fe) and begins to decrease at 7.0 ML Fe. It is noted that bcc iron is formed at about 7 ML Fe coverage. A similar trend is observed for the EEL specra measured using 150 eV primary energy.

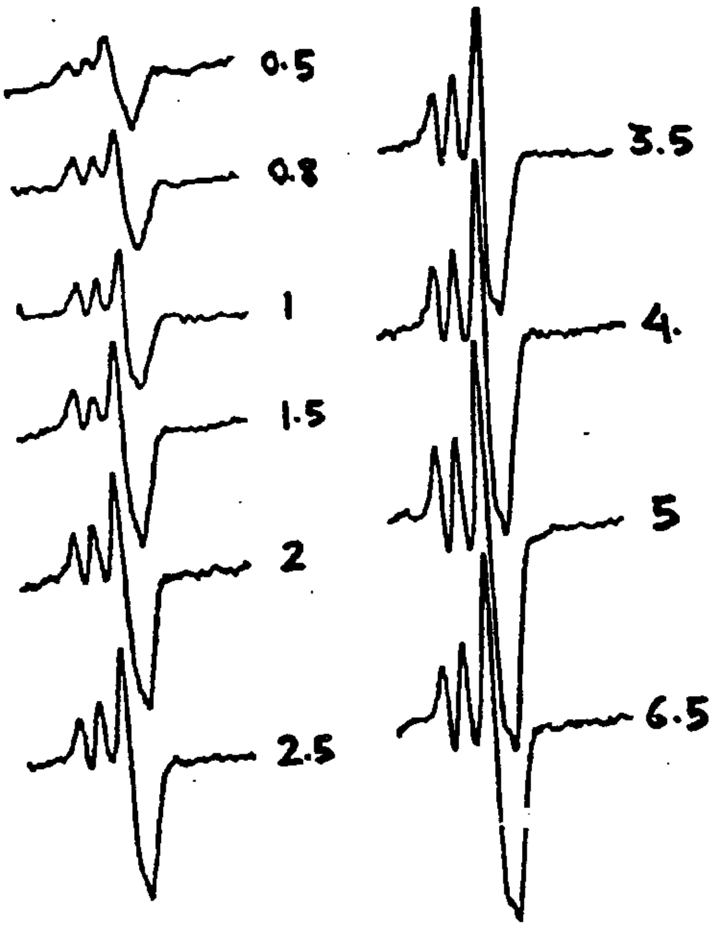
We also performed an Auger study of the carbon after F-T reaction. Figure 6 shows the C-Auger spectra after reaction as a function of iron coverage. For low coverage we observed the presence ofa carbon rich compound, not fully carbidic not totally graphic. At about 3.5 ML Fe there is a change in the Auger spectra that can be understood as formation of an iron carbide.

We also measure the core ionization losses of iron due to the 3p - 3d empty site transitions. The spin orbit interaction produces a splitting of the 3p orbitals into $3p_{1/2}$ and $3p_{3/2}$. The peak position and splitting before and after reaction are given in Table I.



$E_p = 150$ eV Fe/Cu(110)

Fig 6



Carbon Auger Fe / Cu(110)

Fig. 7

TABLE I

ML	Before Reaction			After Reaction		
Fe	M_3	M_2	Splitting	M_3	M_2	Splitting
0.5	54	56.5	2.5	54.5	---	---
1.0	54.1	56.4	2.3	54.2	57.5	3.3
2.0	53.8	56.2	2.4	53.8	57.7	3.9
3.5	53.4	55.7	2.3	54.2	57.6	3.4
6.5	53.7	56.3	2.6	53.6	56.8	3.2

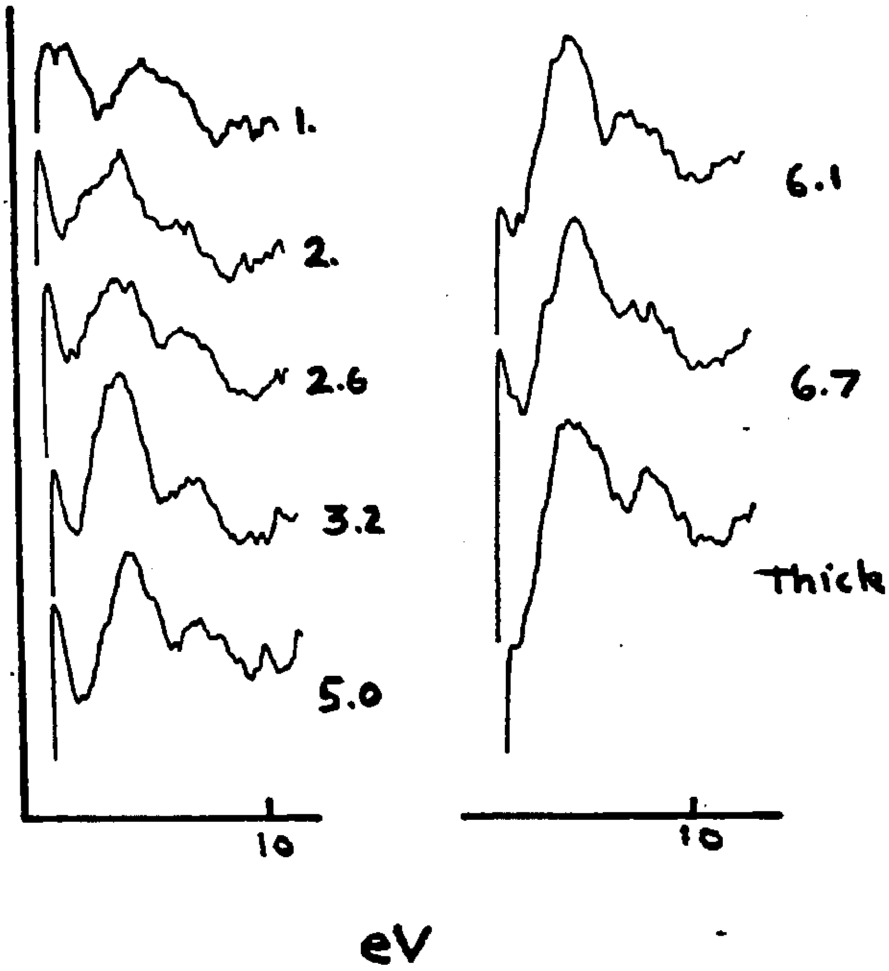
After the F-T reaction the energy of the M_3 transition remains about the same but the energy of M_2 increases. There is a change in the spin-orbit splitting of about 1 eV. It is noted that the intensity of the M_2 transition is reduced more than the intensity of M_3.

Fe/Cu(111):

Figure 8 shows the EEL spectra for iron at various coverages on Cu(111) after F-T reaction. We observe that at low coverage the intensities of the peaks at 3.2, 4.2 and 7.2 eV are reduced when compared to the spectra prior to the reaction. At 2.0 ML coverage, the peak at 7.2 eV disappears and two new losses appear at 6.1 and 8.2 eV. When the iron thickness is more than 2 ML, the peak at 6.1 eV increases in intensity and shifts to lower energies until it reaches 5.5 eV for a thick iron film (bcc). The peak at 8.2 eV also increases in intensity as a function of iron thickness. Figure 9 shows the EEL spectra for a primary energy of 150 eV. There are similarities to the results obtained with a primary energy of 50 eV. At high coverage (75 ML) the peak at 7.7 eV increases and it is identified as due to carbidic carbon.

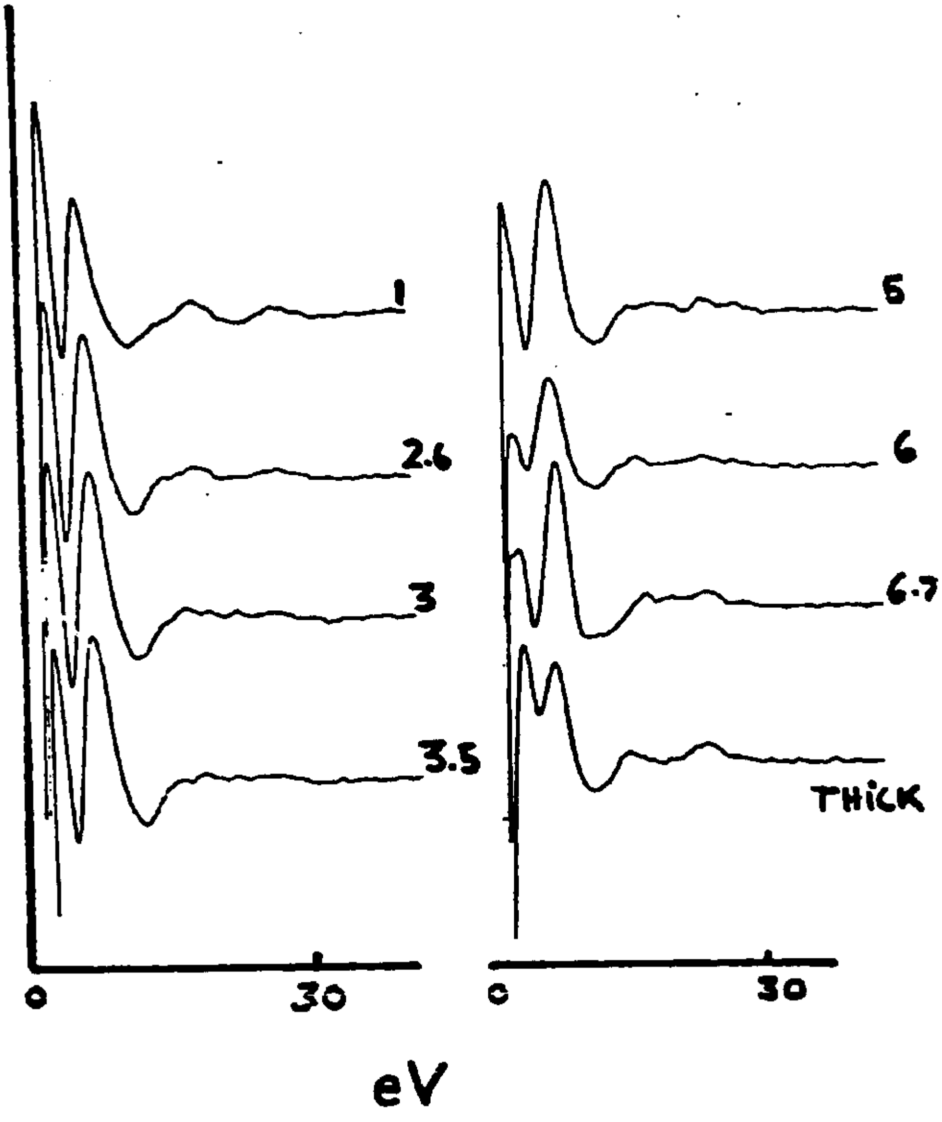
Figure 10 shows the Auger spectra as a function of iron coverage after F-T reaction. These spectra are similar to the ones obtained for Fe on Cu(110). We interpret the results as formation of non-carbidic carbon for low coverage and subsequent growth of a well defined carbide for higher coverages. Bcc iron is evident in the EELs and Auger spectra after 5 ML.

The core ionization losses were also measured for Fe on Cu(111) and the results are given in Table II.



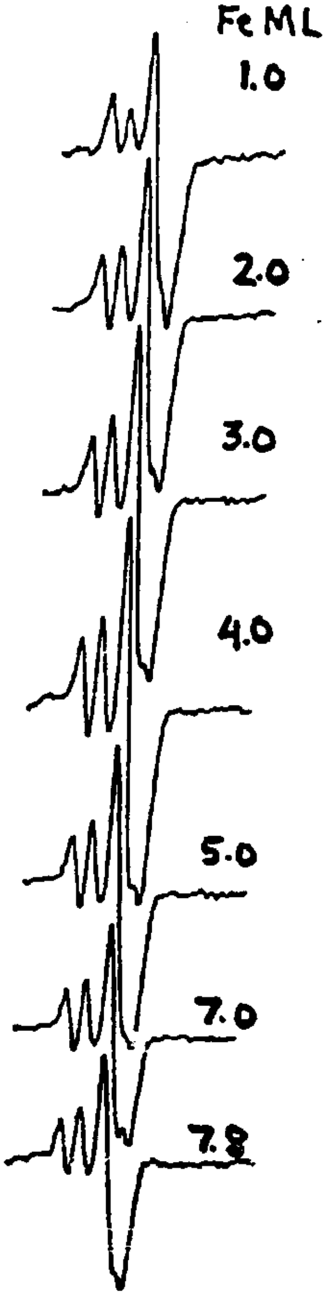
$E_p = 50$ eV   Fe /Cu(111)

Fig. 8



E_p = 150 eV Fe /Cu(111)

Fig. 9



Carbon Auger Fe / Cu(111)

Fig. 10

TABLE II

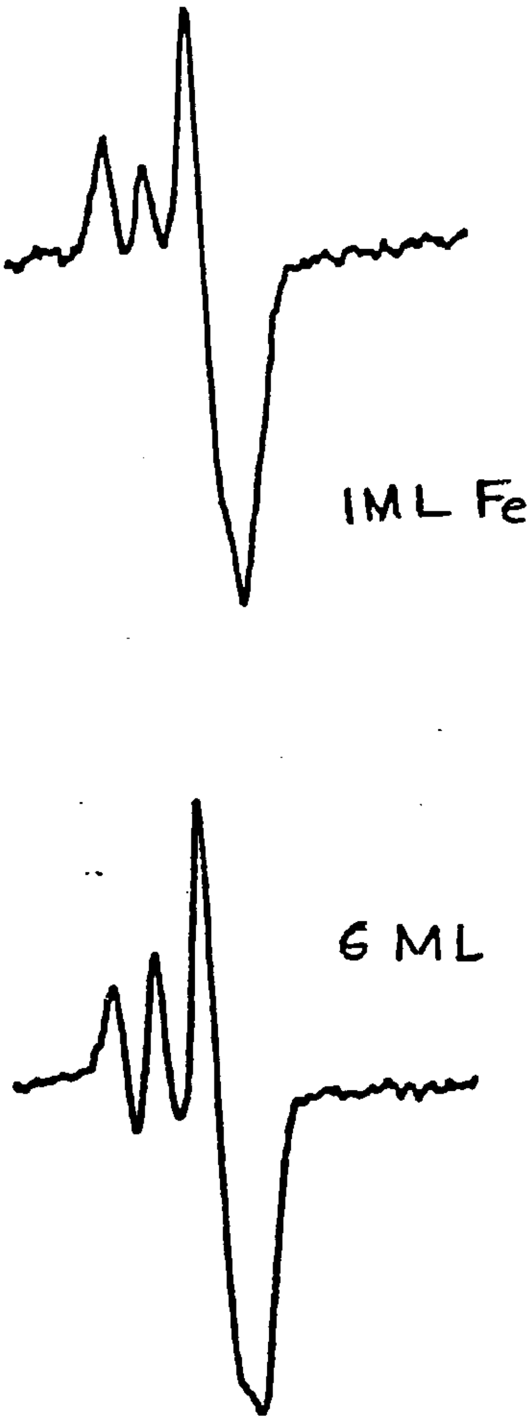
	Before Reaction			After Reaction		
ML	M_3	M_2	ΔM_{23}	M_3	M_2	ΔM_{32}
1.3	53.1	55.2	2.1	—	—	—
2.1	53.4	55.9	2.5	53.5	56.5	3.0
2.6	53.5	55.6	2.1	53.7	55.9	2.2
3.2	53.9	55.7	1.8	53.3	56.1	2.8
5.0	53.2	55.8	2.6	54.3	57.6	3.3
6.1	53.2	55.8	2.6	53.7	56.6	2.9
Thick	53.7	56.5	2.8	53.7	57.2	3.5

After the F-T reaction the M_2 peak is reduced and slightly shifted in energy. By contrast M_3 remained nearly the same in both intensity and position. The bonding of the carbon to iron has great influence on the availability of 3d empty states as well as in the energy position of the levels.

EFFECT OF SULFUR ON THE FORMATION OF CARBIDES ON Fe/Cu

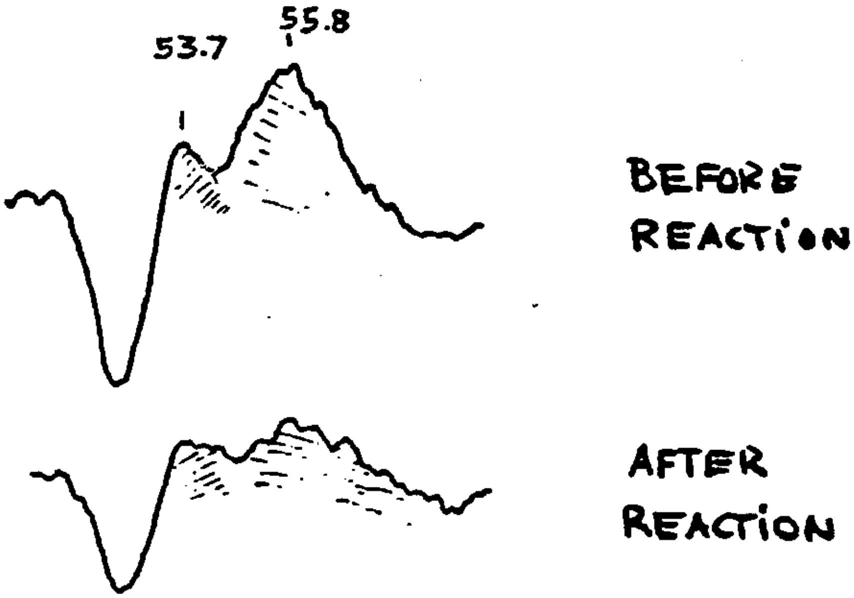
Fcc iron epitaxially grown on Cu was exposed under UHV to small amounts of sulfur. The sulfur exposures were from 0.05 to 0.2 of a ML, the coverage was determined by Auger spectroscopy. The Fischer-Tropsch reactions were performed after the exposures. Figure 11 shows the Auger spectra of carbon for Fe on Cu(100) after F-T reaction with about 0.1 ML of sulfur. The top spectrum is characteristic of fcc iron low coverege, the carbon Auguer spectrum is almost identical to the one obtained without sulfur. The second Auger spectra is for a thicker film, in this case the sulfur coverage was 0.1 ML. One observes that the carbon Auger spectrum is typical of a carbide.

We found that the core ionization losses are the most sensitive towards changes in the surface states after F-T reactions. Figure 12 shows the spectrum for the 3p - 3d (empty states) transitions for a 6 ML fcc Fe on Cu(100). The spectra are before and after reaction. One observes the increase in the spin-orbit splitting and the pronounced decrease in the intensity of the M_2 transition. It is noted that the sulfur coverage is 0.1 ML. The spectra are very similar to that observed for the clean iron on copper. The observed decrease in the M_2 intensity is associated with the donation ofan electron to the 3d empty states due to the bonding of C-Fe. This bonding is not affected by the presence of sulfur. Similiar results were obtained for the other crystal orientations.



CARBON AUGER
Fig. 11

6 ML Fe fcc



0.1 ML S

$3p_{1/2, 3/2} \longrightarrow 3d$

Fig. 12

In order to understand these intriguing results, we performed a temperature and time dependent study of iron epitaxially grown on Cu. We observed that segregation of Cu to the surface occurs for Cu(111) above 100°C, for Cu(100) the segregation occurs above 200°C and for Cu(110) above 250°C; the segregation is a strong function of time. The latter observations suggest that the absence of a poisoning effect of sulfur on the iron fcc surface can be attributed to the presence of copper on the surface. The Cu does not fully cover the surface but there are enough atoms present to absorb the sulfur and allow the fcc iron to dissociate CO. However, we cannot exclude the possibility that fcc iron has significant differences with bcc iron, which modifies its chemical reactivity towards sulfur. This specific point needs further investigation in order to establish the true catalytic properties of the new phase of iron.

SUMMARY OF THE RESULTS

1. Fcc iron can be prepared on Cu at room temperatue. It is found that fcc iron is viable at high temperatures.

3. The theoretically determined density of states of fcc iron is very different from bcc iron, indicating very different chemical reactivity.

3. Fcc iron dissociates CO.

4. The state of the system for fcc iron deposited on copper at elevated temperatures differs strongly from that at room temperature implying unusual catalytic activity at operating temperatures.

5. Up to 0.2 ML of sulfur does not produce any significant changes in CO dissociation and carboization of fcc iron.

6. We observed that there is partial segregation of Cu to the iron surfaces at high temperatures.

PUBLICATIONS

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2. Electronic and Crystallographic Structure of Iron Films Epitaxially Grown on Cu Single Crystals, P.A. Montano, y.C. Lee, J. Marcano and H. Min, MRS, Proceedings Layered Structures and Epitaxy (1986).

3. Practical Method for Highly Accurate Large-Scale Surface Calculations, G.W. Fernando, B.R. Cooper, M.V. Ramana, H. Krakauer, and C.Q. Ma, Physical Review Letters 56, 2299 (1986).

4. Surface Electronic Behavior of fcc Iron on Copper, G.W. Fernando, Y.C. Lee, P.A. Montano, B.R. Cooper, E.R. Moog, H.M. Naik and S.D. Bader, J. of the Vacuum Society A5(4), 882 (1987).

5. LEED Measurements of Fe Epitaxially Grown on Cu(100), Y. Darici, H. Min, J. Marcano, and P.A. Montano, Surface Science 187, 477 (1987).

6. Two Magnetically Different Closely Lying States of fcc Iron Grown on Copper (100), P.A. Montano, G.W. Fernando, B.R. Cooper, E.R. Moog, H.M. Naik, S.D. Bader, Y.C. Lee, Y.N. Darici, H. Min, and J. Marcano, Phys. Rev. Lett. 59, 1041 (1987).

7. LEED Measurements of One Monolayer of Iron Epitaxially Grown on Cu(111), Y. Darici, J. Marcano, H. Min and P.A. Montano. To appear in Surface Science.

8. Theory of Electronic Structure and Magnetic Behavior of fcc Iron Grown on Cu(001), G.W. Fernando and B.R. Cooper, to appear in Physical Review B.