Final

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QUARTERLY TECHNICAL PROGRESS REPORT

(Oct.-Dec, 1994)

CONTRACT TITLE:	MÖSSBAUER SPECTROSCOPY STUDIES OF IRON-CATALYSTS USED IN FISCHER-TROPSCH (FT) PROCESSES
CONTRACT NUMBER:	DE-AC22-93PC93066 University of Kentucky, Lexington, KY
CONTRACT DATE:	Jan 12, 1994
ANTICIPATED COMPLETION DATE:	Jan 11, 1997
GOVERNMENT AWARD:	$ 64679.00 (for 1994)
PROGRAM MANAGER:	Dr. Gary J. Stiegel U.S. DOE, PETC, Pittsburgh
PRINCIPAL INVESTIGATORS:	Prof. Gerald P. Huffman, (PI) Dr. K.R.P.M.Rao, (Co-PI)
CONTRACTING OFFICER'S REPRESENTATIVE (COR):	Dr. Richard T. Tischer U.S. DOE, PETC, Pittsburgh
REPORTING PERIOD:	October 1, 1994 - December 31, 1994
OBJECTIVES:	To carry out Mössbauer spectroscopy study of Iron-based catalysts used in FT synthesis to identify iron phases present and correlate with water gas shift and FT activities.

MÖSSBAUER SPECTROSCOPY STUDIES:

The U.S. Department of energy has currently a program to develop Fischer-Tropsch catalysts which are active at low H_2/CO ratio of 0.7. R.J.Gormley, Dr.Burt Davis and Dr. D.B.Bukur have been developing Fischer-Tropsch catalysts which are active at a low H_2/CO ratio. It is of interest to find out any relationships that may exist between the iron phases that are produced during activation and FT synthesis and the activity of the catalysts.

EXECUTIVE SUMMARY

Mössbauer spectroscopy investigations on 6 iron-based catalysts and analysis of the XAFS mesurements done earlier on 23 catalysts , were carried out during the period under review.

A set of 4 catalysts subjected to CO pretreatment and Fischer-Tropsch synthesis were sent by Robert J. Gormley, PETC, Dept. of Energy, to understand the effect of reduction on the iron phases formed.

A catalyst activated in CO and subjected to Fischer-Tropsch synthesis and extracted directly in to an "O" ring sealed Mössbauer absorber holder under argone atmosphere and another catalyst from the same run but exposed to air were sent by Dr.Burt Davis, CAER, Univ. of Kentucky, for identifying the iron phases present and to monitor the differences, if any, between two catalysts.

Mössbauer results:

The Mössbauer investigations of the four catalyst samples from Gormley indicate that the activation was not complete during pretreatment period in these samples as seen by the increase of the chi-carbide with TOS. The ($CO+H_2$) conversion relatively decreases with increase in the carbide content. Taking into account the Mössbauer results obtained earlier on other iron catalysts, the growth rate of chi-carbide during CO pretreatment appears to give a clue as to how good is the catalyst. Rapid formation of chi-carbide during pretreatment might indicate that the surface is clean and congenial for good FT synthesis. On the otherhand, sluggish formation of chi-carbide during pretreatment and its further development during FT synthesis may be an indication of a surface which does not support good FT synthesis. This inference has to be further investigated and confirmed.

The catalyst which was collected in argone and the one exposed to air were found to be similar in composition of iron phases and contain about 67% of gamma- Fe_2O_3, 22% of chi-Fe_5C_2 and the remaining in the form of superparamagnetic oxide. This indicates that in the case of used catalyst samples exposure to air does not alter the composition.

XAFS results:

The reduction behaviour of UCI 118-78 (61.5Fe/8.8Cu/0.04K , all wt.%) and the DOE catlyst MB6ABC (65.8Fe/2.9Cu/0.3K, all wt.%) was found to be different. The UCI catalyst was reduced better than the DOE catalyst under CO activation as indicated by the 62% of carbide formed in the former catalyst as compared to the 55% carbide formed in the latter catalyst under similar CO reduction. The XAFS measurements were carried out on these and other iron catalyst to identify the chemical state of copper. Thecatalysts were not subject to any kind of pretreatment prior to the XAFS measurements. It was found from XAFS measurements that the copper was in metallic form in the UCI catalyst and in oxide form in the DOE catalyst indicating that the UCI catalyst gets reduced better than the DOE catalyst consistant with the relative amounts of carbides found in these catalysts.

The XAFS results of the other catalysts indicate that the copper is in the oxide form in some catalysts and Cu-Fe alloy form in other catalysts.

SUMMARY OF TECHNICAL PROGRESS:

During the period under review only the scheduled Task 2 and Task VI were carried out.

The following iron catalyst samples were received from R.J. Gormyey:

(1)	CW-S3-11-D	TOS= 84 hrs	
(2)	CW-S3-11-J	TOS=235 hrs	
(3)	CW-S3-11-M	TOS=305 hrs	
(4)	S3-11-END	TOS=329 hrs :	Same as CW-S3-11-M except that the hot wax was removed and the sample was cooled.

The catalyst used in these FT runs: UCI 1185-149 (2nd)
(57.2Fe/9.3Cu/0.05K-all weight percentages)

The activation was done in CO at 270°C, 175psig, 1.4nL CO/g-Fe hr for 22hrs.

The FT synthesis was carried out with Allied-Signal heavy wax at 10% loading of the catalyst, 270°C,175 psig, 2.4 nl syngas/g-Fe hr at 1000rpm.

The catalysts were subjected to Mössbauer measurements as received without a cleaning of any wax coating present.

The Mössbauer results are given in Table I and the spectra are enclosed.

Table I

MÖSSBAUER ANALYSIS
Samples from Robert J. Gormley, PETC/DOE

Sample@	χ-Fe_5C_2	Fe_3O_4	Spm phase	% (H2+CO) conversion*
CW-S3-11-D	41	36	23	84
CW-S3-11-J	60	30	10	67.7
CW-S3-11-M	68	27	5	51.2
S3-11-END	58	32	10	51.2

@ The catalyst used in these FT runs: UCI 1185-149 (2nd)
(57.2Fe/9.3Cu/0.05K-all weight percentages)

* The FT synthesis was carried out at PETC with Allied-Signal heavy wax at 10% loading of the catalyst, 270°C,175 psig, 2.4 nl syngas/g-Fe hr at 1000rpm.

* The activation was done in CO at 270°C, 175psig, 1.4nL CO/g-Fe hr for 22hrs.

The following two catalysts were received from Dr. Burt Davis, CAER

	Sample	Composition
(1)	LGX-164A	Si/(Si+Fe = 0.044 atomic % K/(K+Fe) = 0.030 atomic %

CO pretreated at 270°C,275psig,2.0nL/hr-g(Fe), for 24hrs.
Subjected to FT synthesis at 230°C, 175psig,3.4nL/hr-g(Fe)

The catalyst was collected into an "O" ring sealed Mössbauer absorber holder in argone atmosphere.

(2) Same as above except that the catalysts was exposed to air and then transfered to a Mössbauer absorber holder.

The catalysts were subjected to Mössbauer measurements as received without cleaning of any wax coating present.

The ($CO+H_2$) conversion of the above two catalysts was low at about 30%.

The Mössbauer spectra of the catalyst collected in argone and the one exposed to air are very similar. The spectra are enclosed and the results are given in Table II.

Table II

Sample[@]	χ-Fe_5C_2	Gamma-Fe_2O_3	Spm phase	% (H2+CO) conversion[*]
LGX-164A	22	67	11	30

@ CO pretreated at 270°C,275psig,2.0nL/hr-g(Fe), for 24hrs.
* Subjected to FT synthesis at 230°C, 175psig,3.4nL/hr-g(Fe)

The quantity of the catalyst,LGX-164A collected in argone is not sufficient to give a good Mössbauer spectrum with enough statistics for fitting, although it is clear from the spectrum that it is very similar to the spectrum of the sample exposed to air. Hence only raw Mössbauer spectrum of the LGX-164A collected in argone is enclosed for comparison with the spectrum of the sample exposed to air.

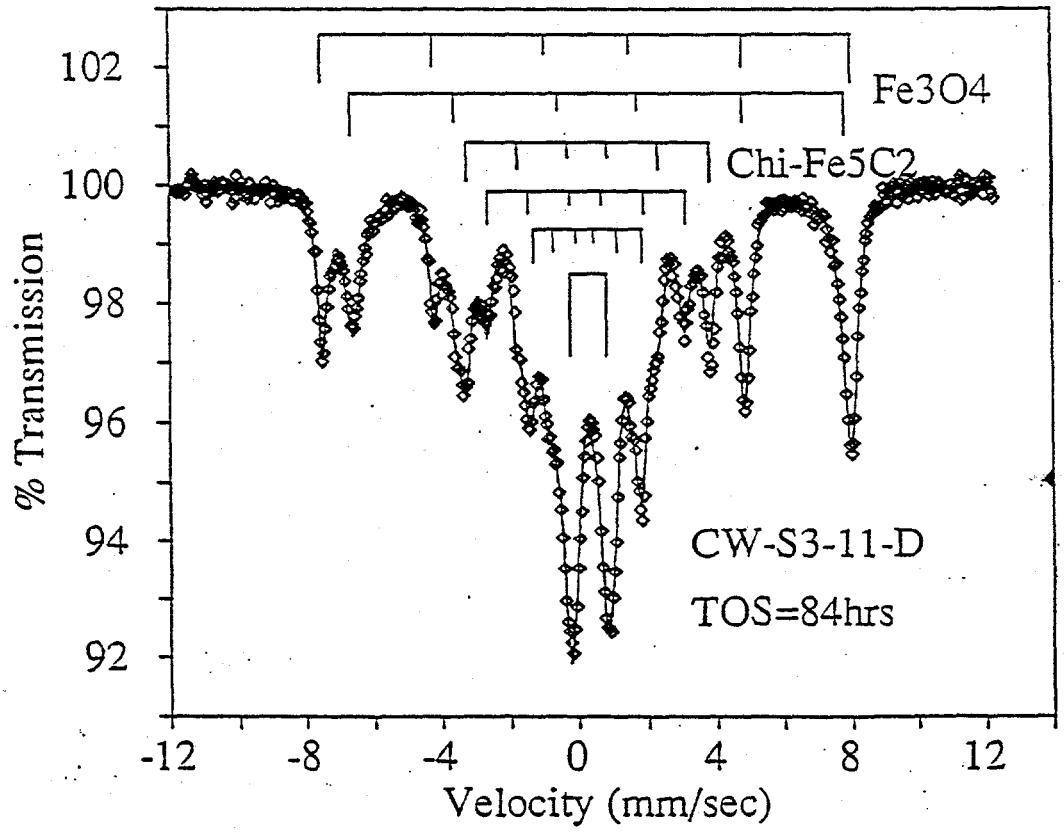
Mössbauer Analysis UK95-006

CW-S3-11-D, TOS=84hrs

R.J.Gormley, PETC

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm-phase		0.33	1.03	0.59	23
Fe3O4	482	0.29	-0.02	0.35	15
Fe3O4	449	0.63	-0.01	0.55	21
Chi-Fe5C2	220	0.27	0.00	0.41	15
Chi-Fe5C2	179	0.20	0.01	0.41	12
Chi-Fe5C2	97	0.19	0.04	0.46	14

Mössbauer run MK1956 on sample 1270 at 300K



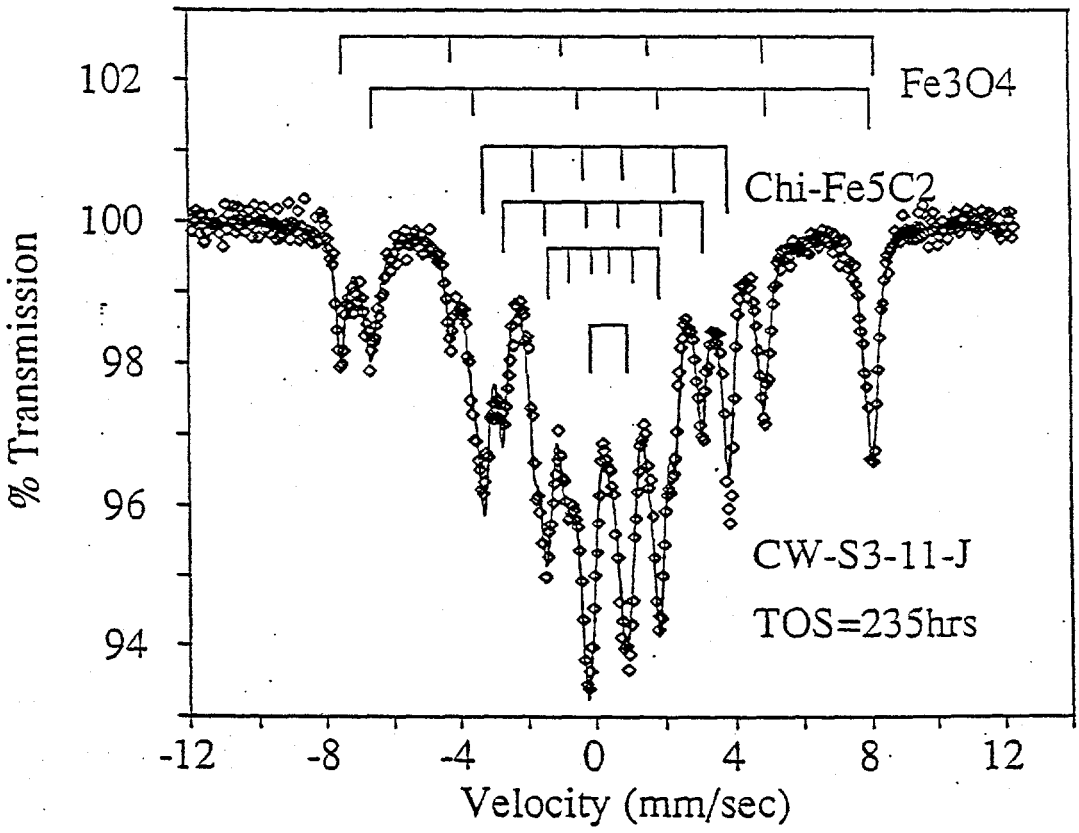
Mössbauer Analysis UK95-005

CW-S3-11-J, TOS=235hrs

R.J.Gormley, PETC

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm-phase		0.37	1.02	0.49	10
Fe3O4	484	0.29	-0.01	0.34	11
Fe3O4	452	0.65	0.00	0.54	19
Chi-Fe5C2	220	0.27	0.01	0.40	24
Chi-Fe5C2	180	0.18	0.00	0.37	16
Chi-Fe5C2	98	0.17	0.04	0.45	20

Mössbauer run MK1957 on sample 1271 at 300K



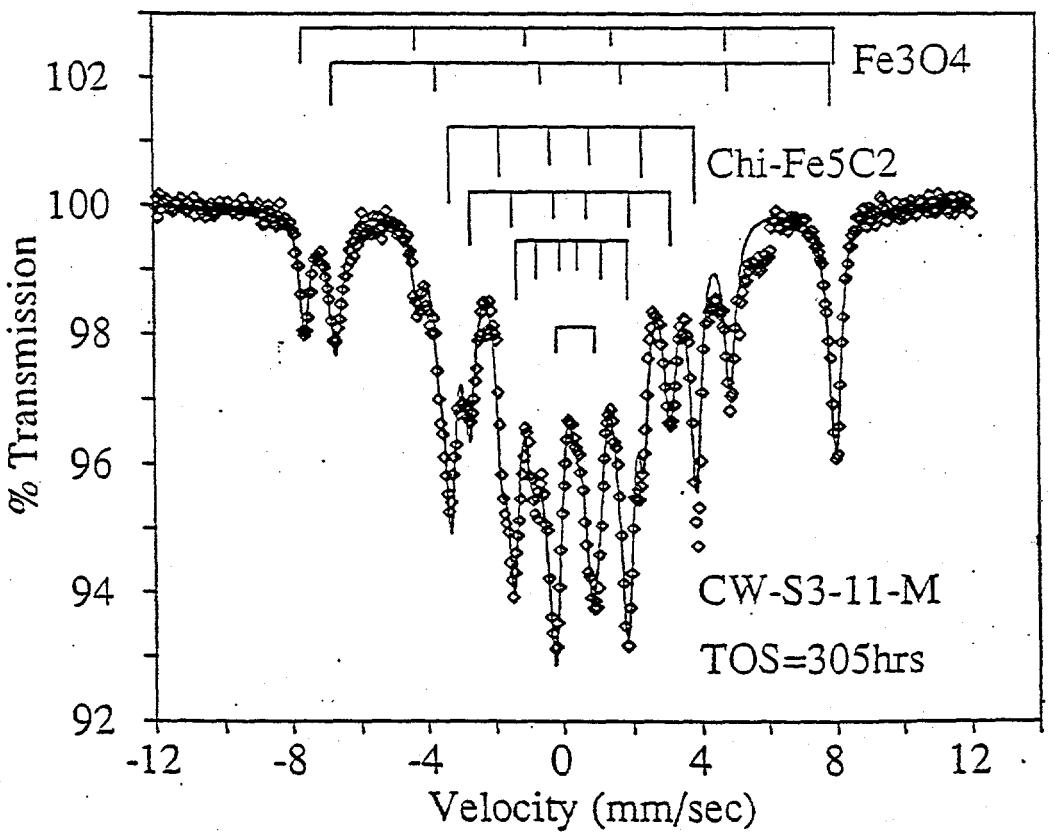
Mössbauer Analysis UK95-004

CW-S3-11-M, TOS=305hrs

R.J.Gormley, PETC

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm-phase		0.32	1.08	0.52	5
Fe3O4	486	0.26	-0.03	0.34	11
Fe3O4	455	0.63	-0.01	0.44	16
Chi-Fe5C2	222	0.27	0.01	0.38	26
Chi-Fe5C2	182	0.20	-0.01	0.43	20
Chi-Fe5C2	99	16.00	0.04	0.43	22

Mössbauer run MK1959 on sample 1272 at 300K



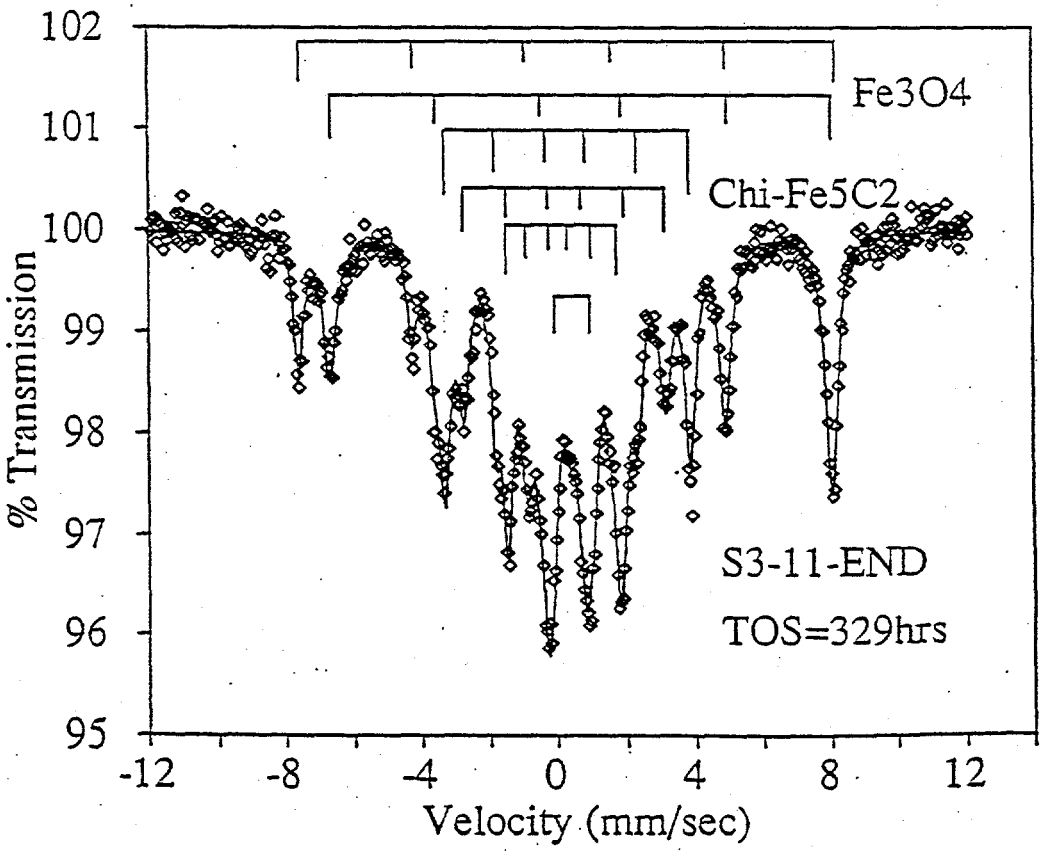
Mössbauer Analysis UK95-003

S3-11-END,TOS=329hrs

R.J.Gormley, PETC

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm-phase		0.33	1.00	0.62	10
Fe3O4	487	0.26	-0.02	0.34	13
Fe3O4	455	0.64	-0.01	0.45	19
Chi-Fe5C2	222	0.27	0.01	0.37	22
Chi-Fe5C2	183	0.21	-0.02	0.43	18
Chi-Fe5C2	100	0.14	0.04	0.38	18

Mössbauer run MK1960 on sample 1273 at 300K



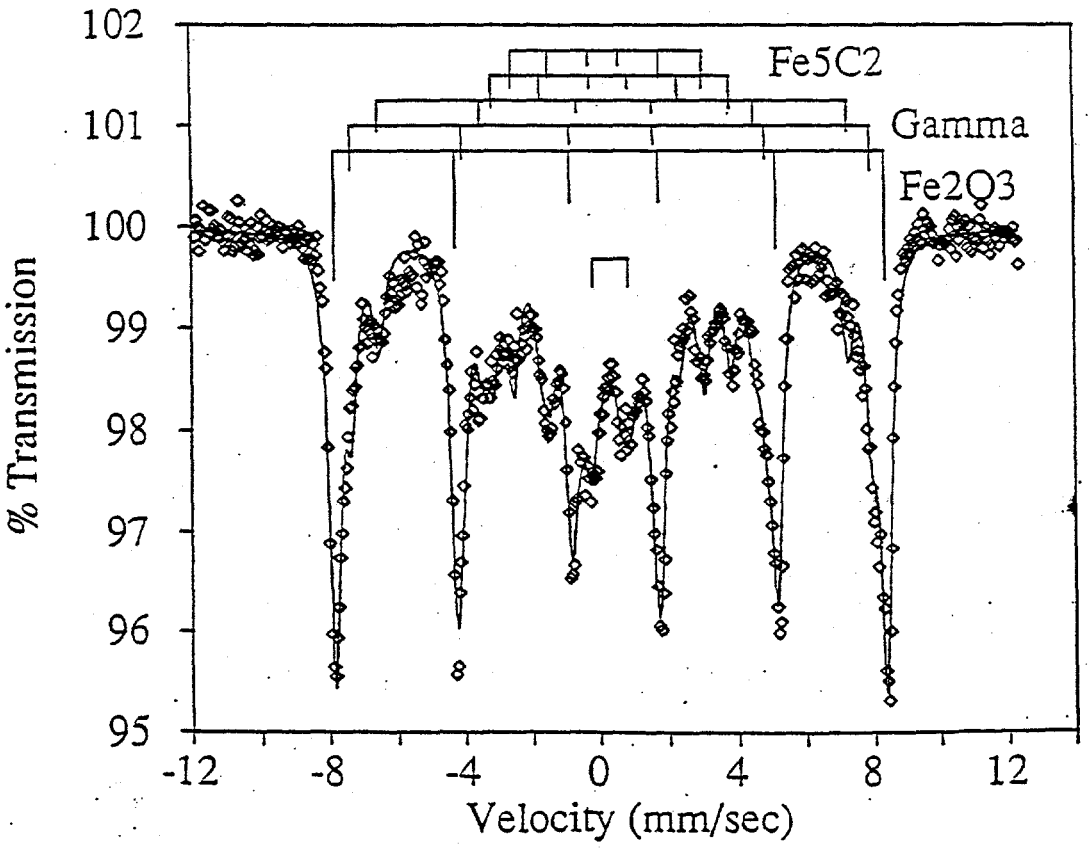
Mössbauer Analysis UK95-002

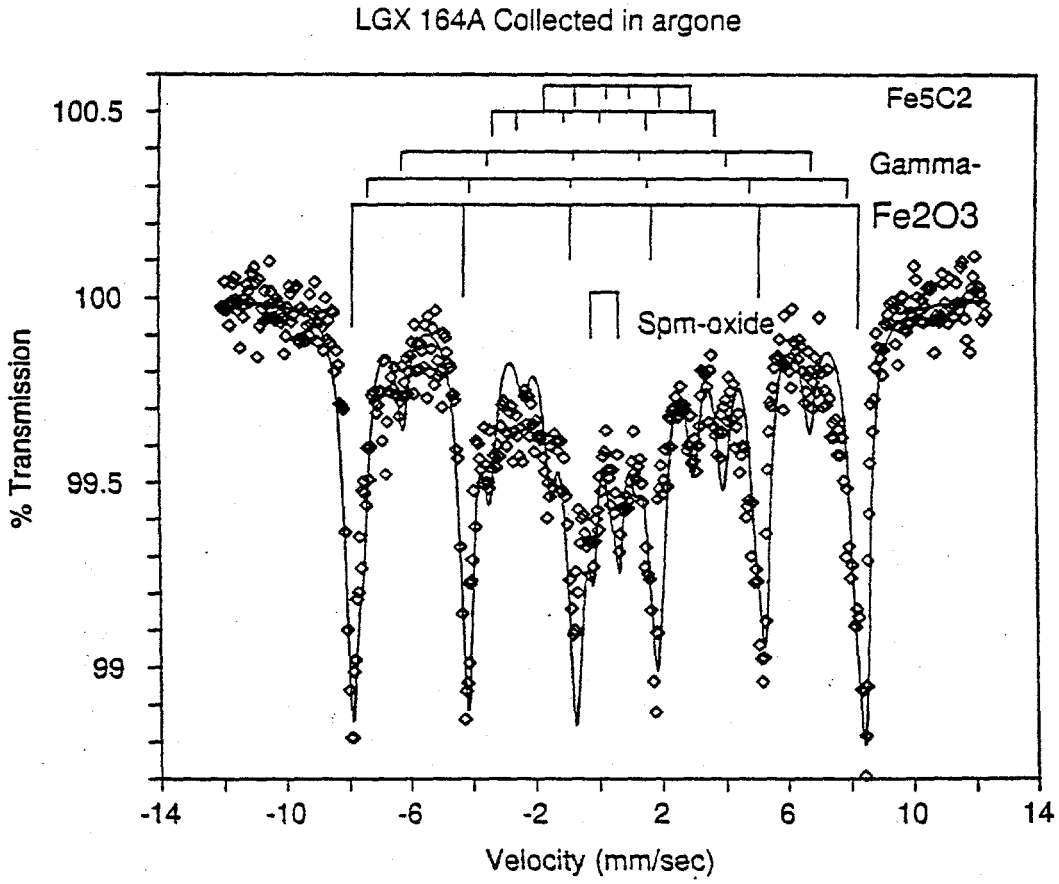
LXG-164A Exposed to air

Dr. Burt Davis, CAER, UK.

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Gamma-Fe2O3	502	0.36	-0.01	0.40	43
Gamma-Fe2O3	474	0.36	-0.50	0.40	14
Gamma-Fe2O3	429	0.45	-0.07	0.40	10
Chi-Fe5C2	216	0.34	0.00	0.40	10
Chi-Fe5C2	173	0.22	0.04	0.40	12
Spm. oxide		0.36	1.02	1.08	11

Mössbauer run MK1967 on sample 1291 at 293K




LGX 164A Collected in argone
Fe5C2
Gamma-
Fe2O3
Spm-oxide
100.5
100
99.5
99
% Transmission
-14
-10
-6
-2
2
6
10
14
Velocity (mm/sec)