DOE/PC/93066--T7

QUARTERLY TECHNICAL PROGRESS REPORT
(January-March, 1996)

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 1995)
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:	January 1, 1996 - March 31, 1996
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.

DISCLAIMER

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 0.67. Dr. D.B. Bukur of Texas A&M University has been developing Fischer-Tropsch catalysts which are active at a low H_2/CO ratio of 0.67. 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.

Mössbauer spectroscopy investigations were carried out on 13 iron-based catalysts during the period under review. The catalysts were taken from fixed bed reactors at the end of the tests. All the catalysts were mixed with glass beads. The glass beads were removed to a large extent by a hand held magnet. For each run, samples were taken from both top and bottom of the reactor to find out whether there are any differences between the two samples taken from different regions of the reactor. The catalysts with 24 parts of SiO_2 were reduced with H_2 at 250°C for 24h, and the catalysts with 16 parts of SiO_2 were reduced with H_2 at 240°C for 2h. All the test were carried out at 250°C, 200psig, 2.0nL(syngas)/g-cat/h with H_2/CO feed ratio of 0.67.

The compositions of the catalysts studied are given in table I. Three catalysts consisted of Ca in addition to Cu and K.

These samples were provided by Dr. D.B. Bukur.

RESULTS:

The phase distributions as determined from Mössbauer measurements are given in table I. All the used catalysts consisted of epsilon carbide, $Fe_{2.2}C$ and a superparamagnetic (spm) phase. The catalysts which contained 6% of Ca in addition to Cu and K, also exhibited the presence of magnetite, Fe_3O_4. The catalysts drawn from the top and bottom exhibited more or less the same relative amounts of different phases. The syngas conversion is low for those catalysts containing higher amounts of Ca (6%) in addition to Cu and K as can be seen from the table I. It is to be noted that only those catalysts containing Ca gave rise to the presence of magnetite, except the one containing smaller amount of (2%) Ca.

The low temperature measurements on one of the samples of the same kind carried out earlier showed that the spm phase found in that catalyst to be an oxide.

The formation of epsilon carbide in all these catalysts is consistent with earlier observation that whenever an iron based catalyst is reduced in H_2, one would usually get epsilon carbide.

Summary of Technical Progress:

During the period under review only the scheduled Task 2 was carried out.

Mössbauer spectroscopy measurements on 13 iron catalysts received from Dr. D.B. Bukur, Texas A&M University were carried out. The catalysts were subjected to Mössbauer measurements as received without any cleaning of any wax coating present on the surface of the catalysts. The glass beads were removed using a hand held magnet.

Table I

Sr#	Sample	CFFLS#	MK#	UK#	e'-Fe2.2C	Spm	Fe3O4	%Conv
1	FA-1525 Mixed 100Fe/3Cu/4K/2Ca/16SiO2	95-159	2171	UK95-013	54	46	---	72-69
2	FA-1605 Top 100Fe/3Cu/4K/16SiO2	95-160	2173	UK95-014	49	51	---	74-71
3	FA-1605 Bottom 100Fe/3Cu/4K/16SiO2	95-161	2175	UK95-015	50	50	---	
4	FB-1985 Top 100Fe/3Cu/5.3K/16SiO2	95-162	2177	UK95-016	53	47	---	80
5	FB-1985 Bottom 100Fe/3Cu/5.3K/16SiO2	95-163	2179	UK95-017	49	51	---	
6	FA-1705 Top 100Fe/5Cu/5K/6Ca/24SiO2	95-164	2181	UK95-018	43	35	22	31-38
7	FA-1705 Bottom 100Fe/5Cu/5K/6Ca/24SiO2	95-165	2183	UK95-019	26	41	33	
8	FA-1795 Top 100Fe/5Cu/6K/24SiO2	95-166	2185	UK95-020	34	66	---	70
9	FA-1795 Bottom 100Fe/5Cu/6K/24SiO2	95-167	2188	UK95-021	34	66	---	
10	FB-1715 Top 100Fe/5Cu/6K/24SiO2	95-168	2190	UK95-022	40	60	---	74-64
11	FB-1715 Bottom 100Fe/5Cu/6K/24SiO2	95-169	2192	UK95-023	42	58	---	
12	FB-1515 Top 100Fe/3Cu/4K/6Ca/16SiO2	95-170	2193	UK95-024	44	47	9	46-54
13	FB-1515 Bottom 100Fe/3Cu/4K/6Ca/16SiO2	95-171	2194	UK95-025	40	44	16	

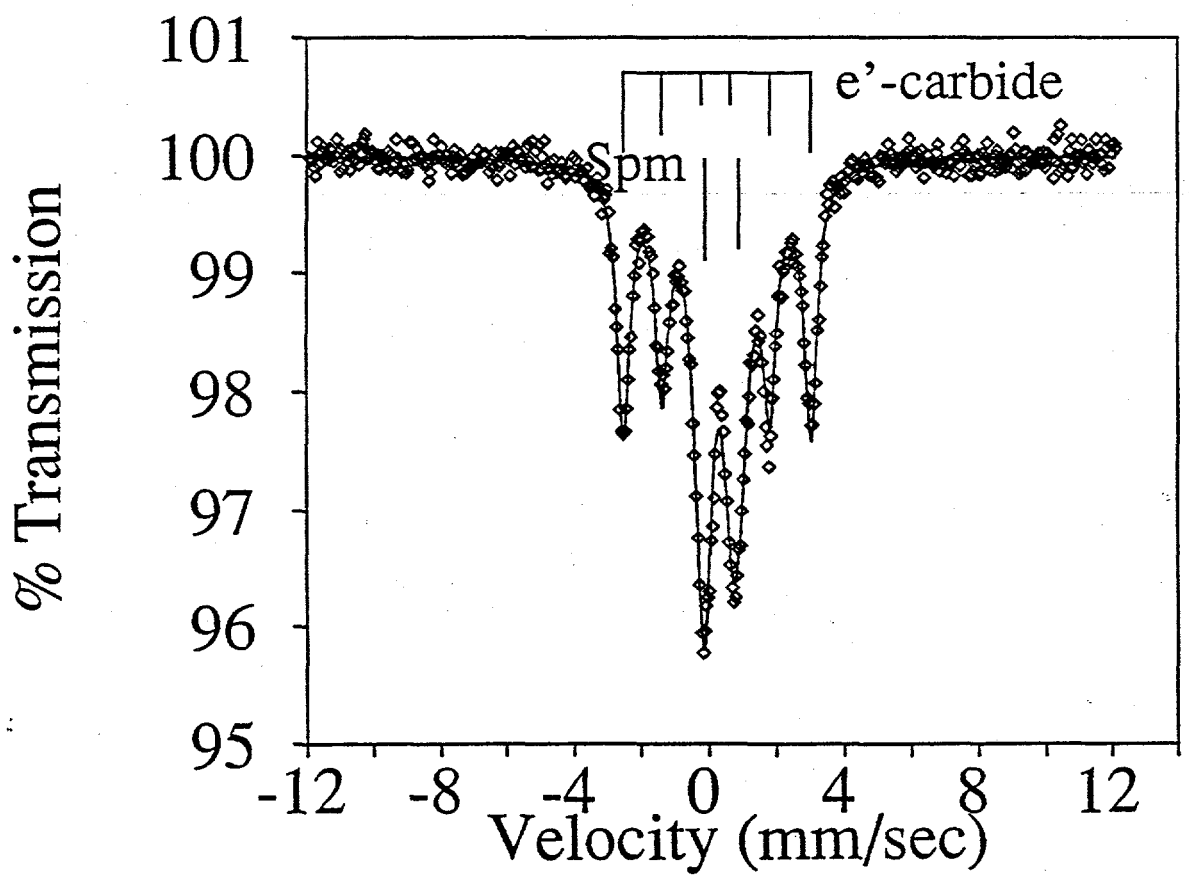
Mössbauer Analysis UK95-013

D.B.Bukur, Texas A&M University

FA-1525, Mixed, 100Fe/3Cu/4K/2Ca/16SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm. iron oxide		0.37	0.99	0.69	46
e'-Fe2.2C	171	0.25	0.02	0.46	54

Mössbauer run MK2171 on sample 95-159 at 293K



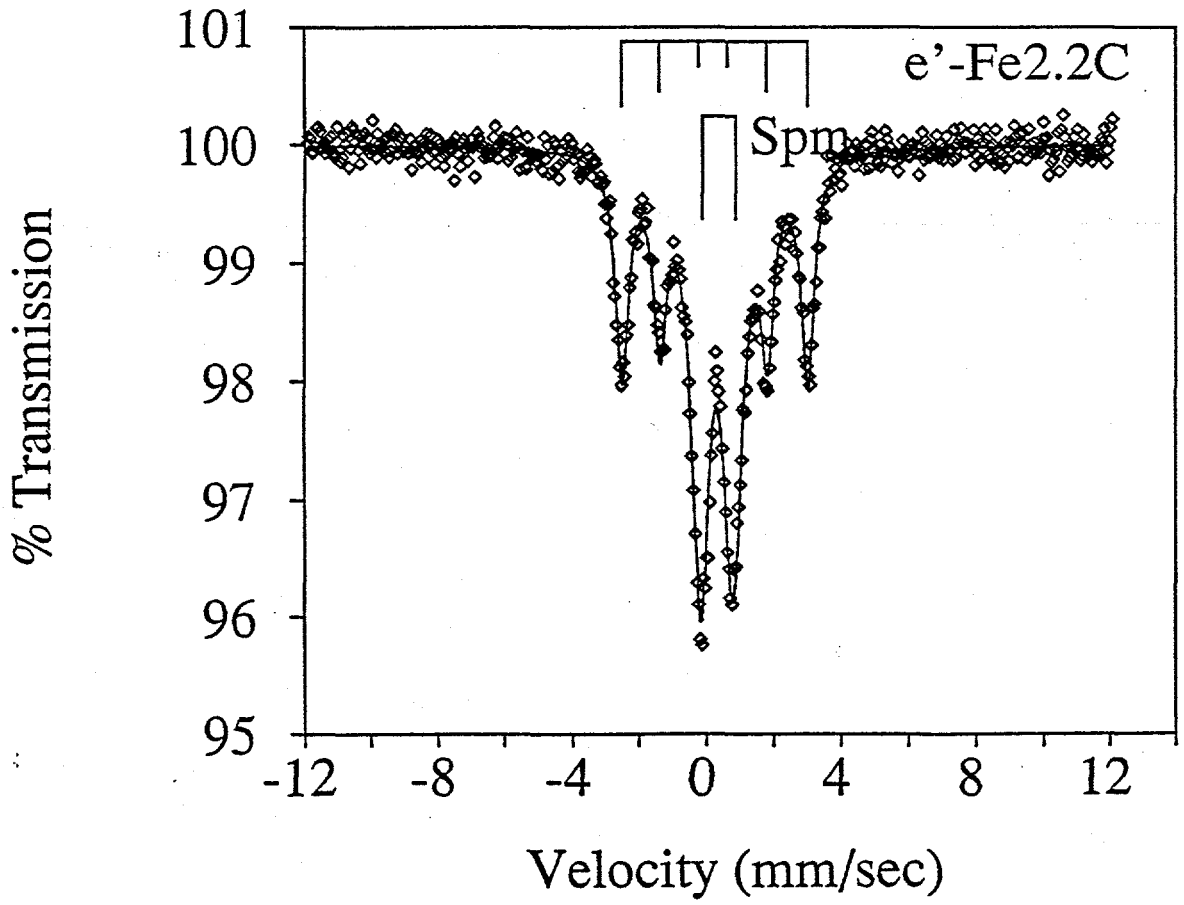
Mössbauer Analysis UK95-014

D.B.Bukur, Texas A&M University

FA-1605, Top, 100Fe/3Cu/4K/16SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm. iron oxide		0.36	1.01	0.67	51
e'-Fe2.2C	171	0.26	0.02	0.47	49

Mössbauer run MK2173 on sample 95-160 at 293K



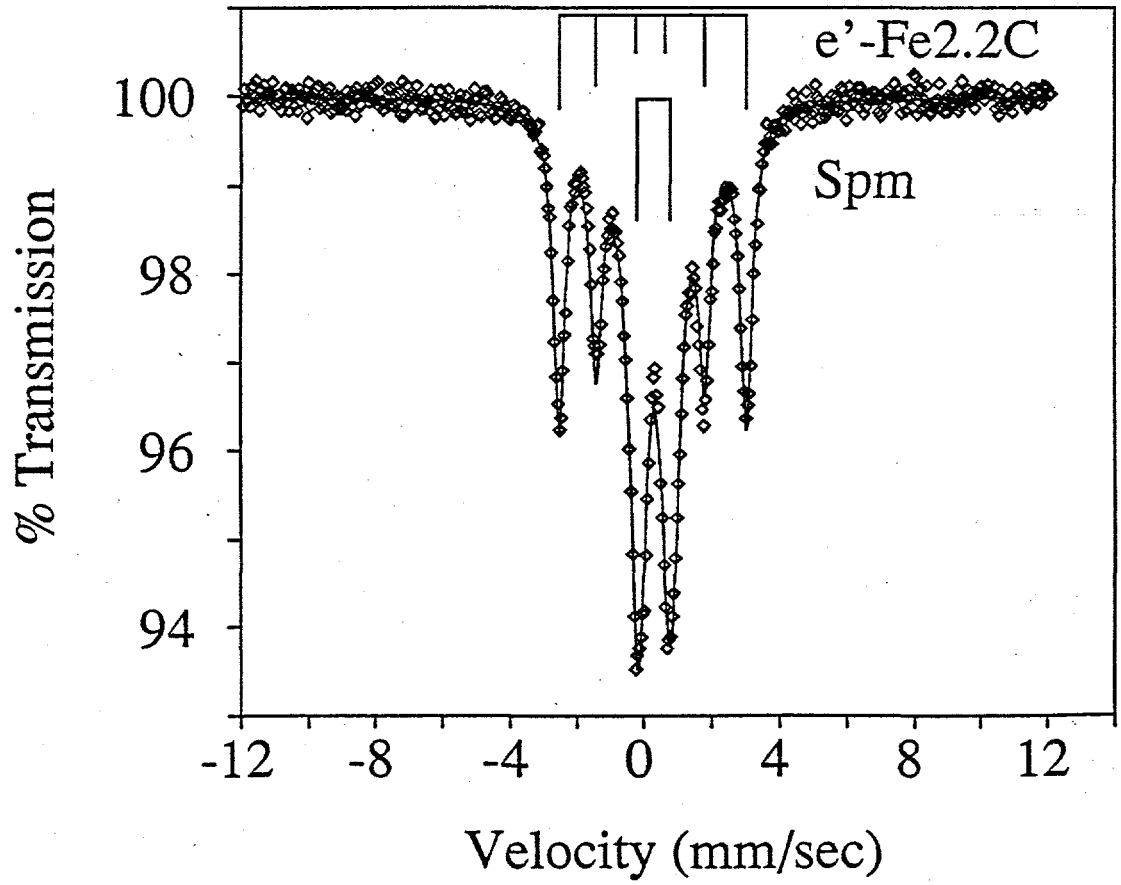
Mössbauer Analysis UK95-015

D.B.Bukur, Texas A&M University

FA-1605, Bottom, 100Fe/3Cu/4K/16SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm. iron oxide		0.35	0.98	0.66	50
e'-Fe2.2C	172	0.25	0.03	0.42	50

Mössbauer run MK2175 on sample 95-161 at 293K



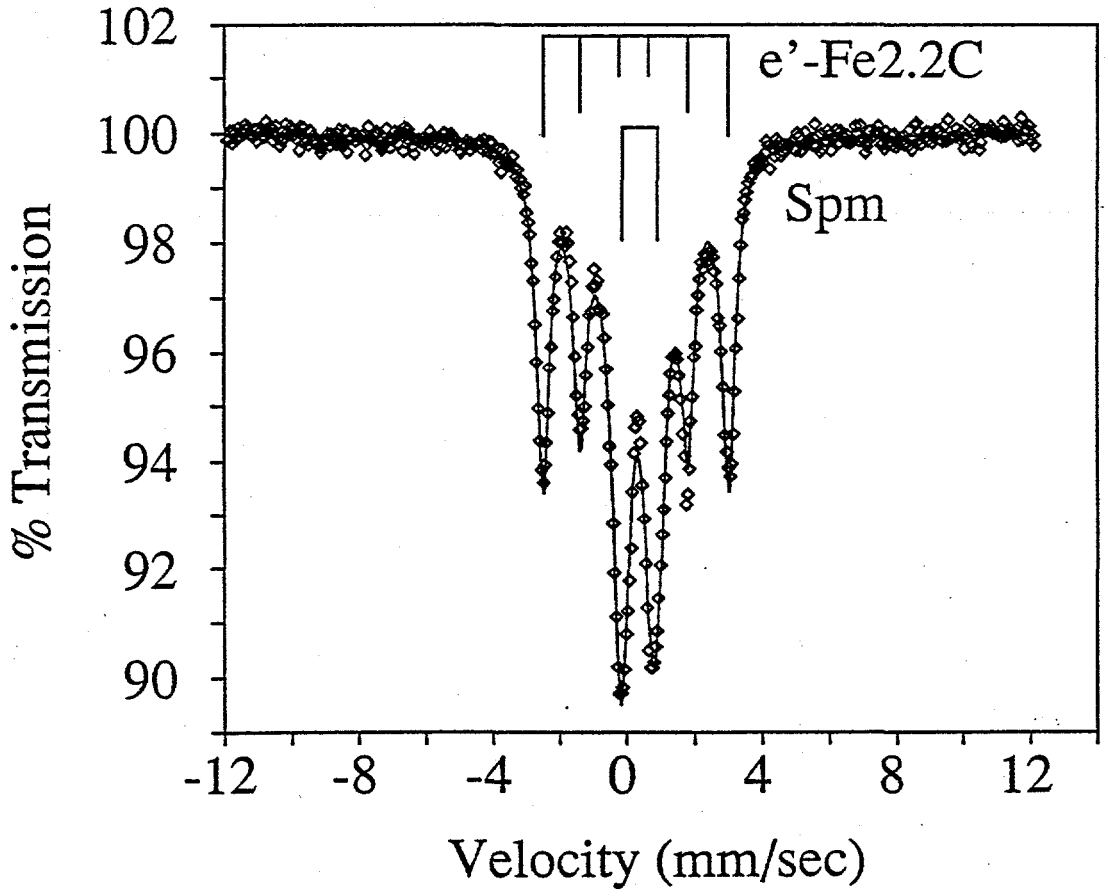
Mössbauer Analysis UK95-016

D.B.Bukur, Texas A&M University

FA-1985, Top, 100Fe/3Cu/5.3K/16SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm. iron oxide		0.36	1.02	0.70	47
e'-Fe2.2C	170	0.25	0.02	0.47	53

Mössbauer run MK2177 on sample 95-162 at 293K



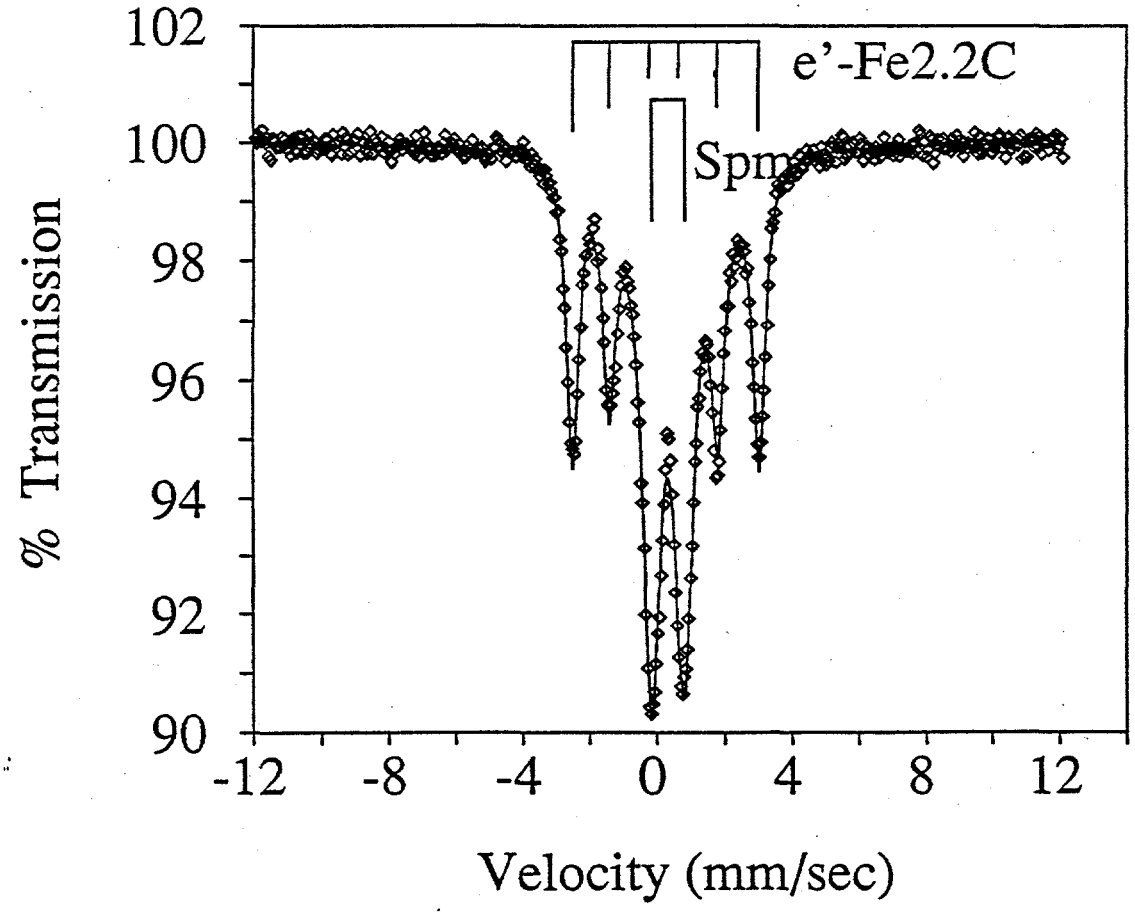
Mössbauer Analysis UK95-017

D.B.Bukur, Texas A&M University

FA-1985, Bottom, 100Fe/3Cu/5.3K/16SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.36	0.98	0.68	51
e'-Fe2.2C	171	0.25	0.03	0.46	49

Mössbauer run MK2179 on sample 95-163 at 293K



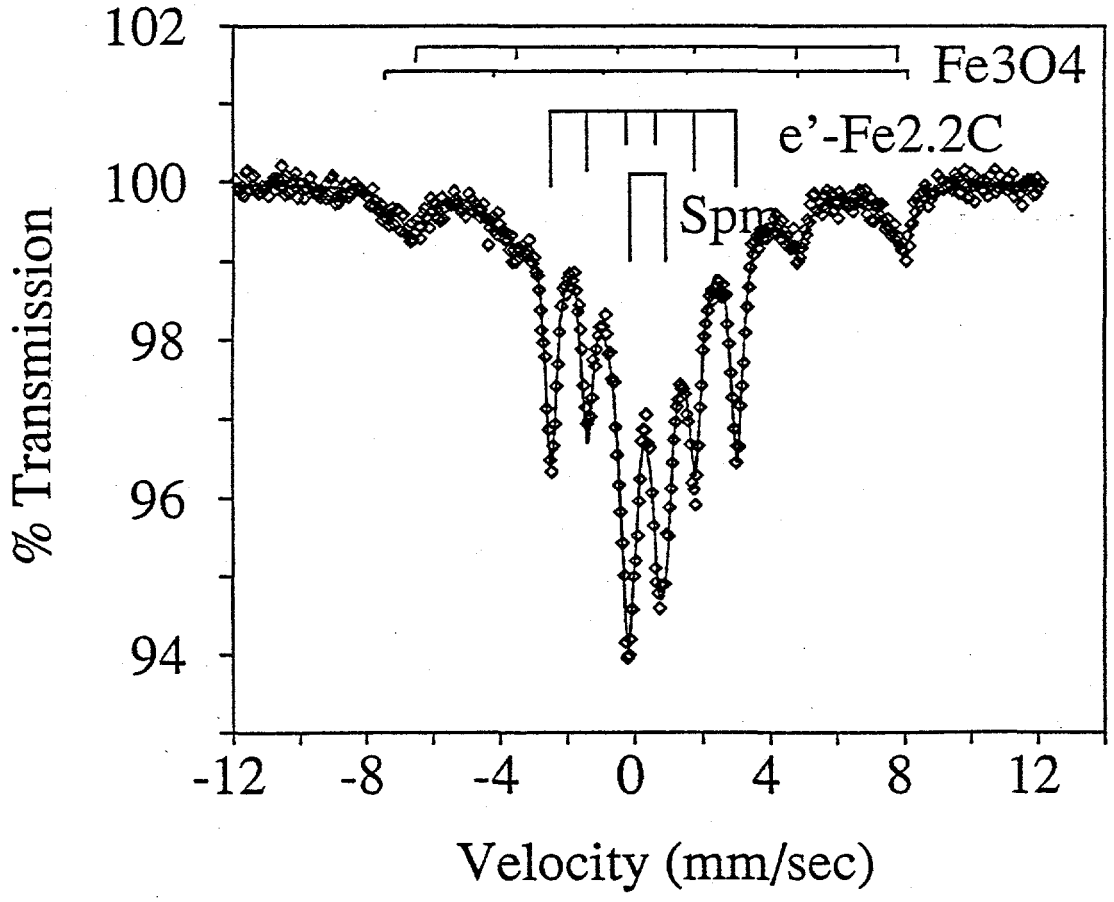
Mössbauer Analysis UK95-018

D.B.Bukur, Texas A&M University

FA-1705, Top, 100Fe/5Cu/5K/6Ca/24SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.36	1.04	0.71	35
e'-Fe2.2C	170	0.25	0.03	0.46	43
Fe3O4	482	0.32	0.00	0.37	3
Fe3O4	444	0.62	0.00	1.03	19

Mössbauer run MK2181 on sample 95-164 at 293K



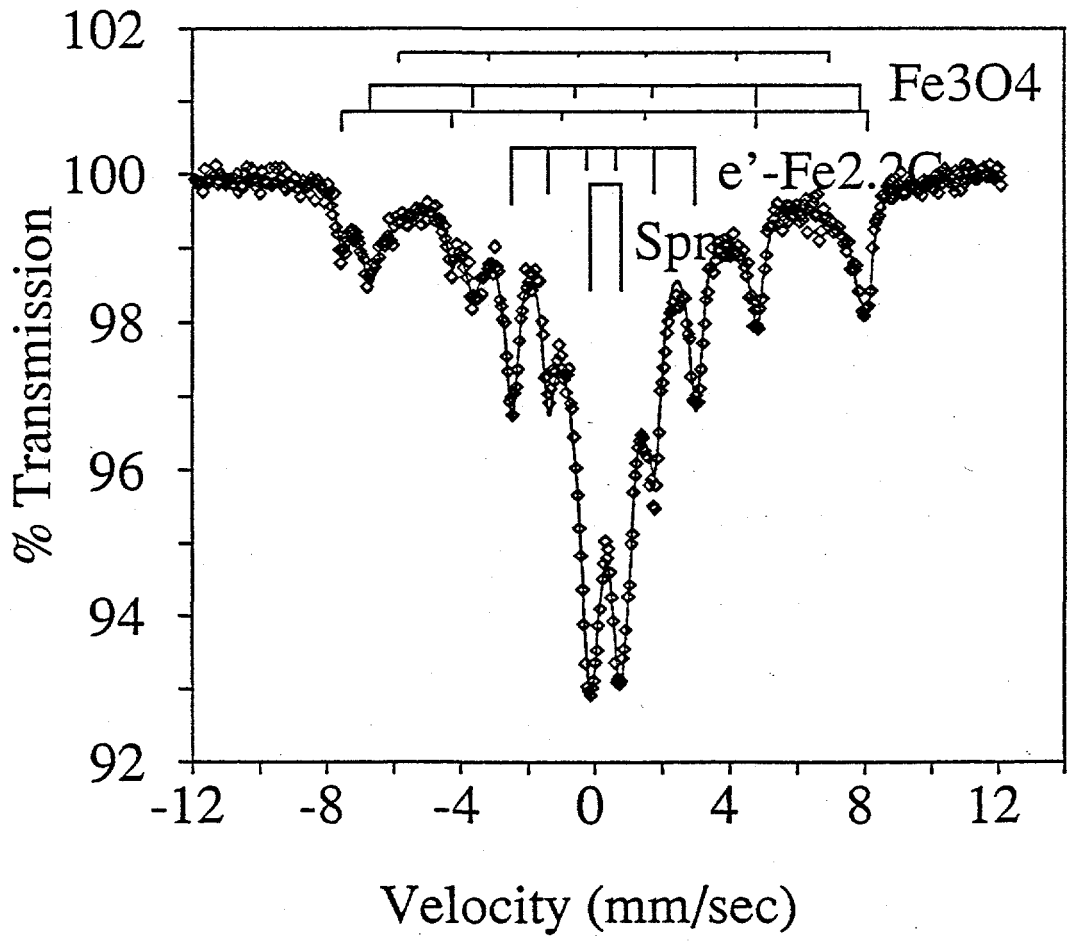
Mössbauer Analysis UK95-019

D.B.Bukur, Texas A&M University

FA-1705, Bottom, 100Fe/5Cu/5K/6Ca/24SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.37	0.93	0.84	41
e'-Fe2.2C	170	0.26	0.03	0.50	26
Fe3O4	486	0.29	0.00	0.31	5
Fe3O4	453	0.59	0.00	0.66	15
Fe3O4	396	0.54	0.01	1.45	13

Mössbauer run MK2183 on sample 95-165 at 293K



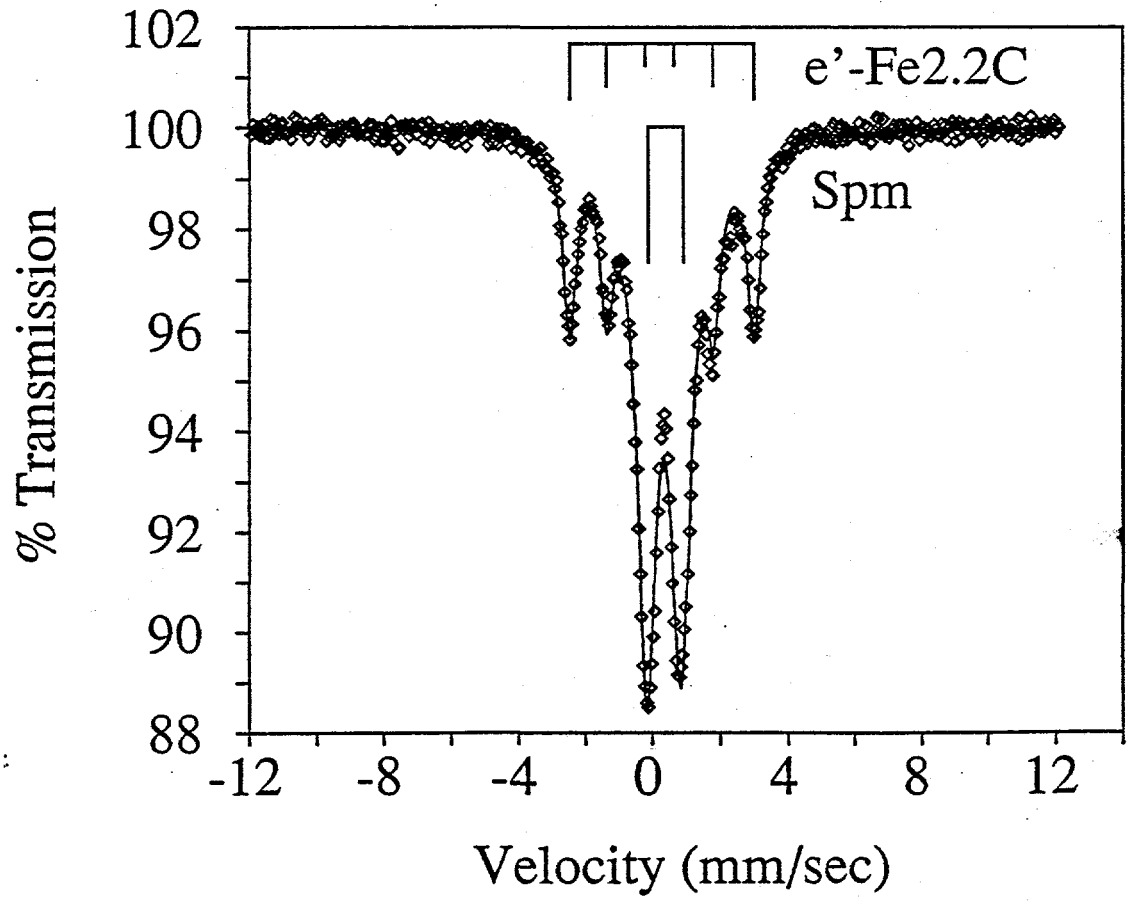
Mössbauer Analysis UK95-20

D.B.Bukur, Texas A&M University

FA-1795, Top, 100Fe/5Cu/6K/24SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.35	1.03	0.69	66
e'-Fe2.2C	169	0.26	0.02	0.48	34

Mössbauer run MK2185 on sample 95-166 at 293K



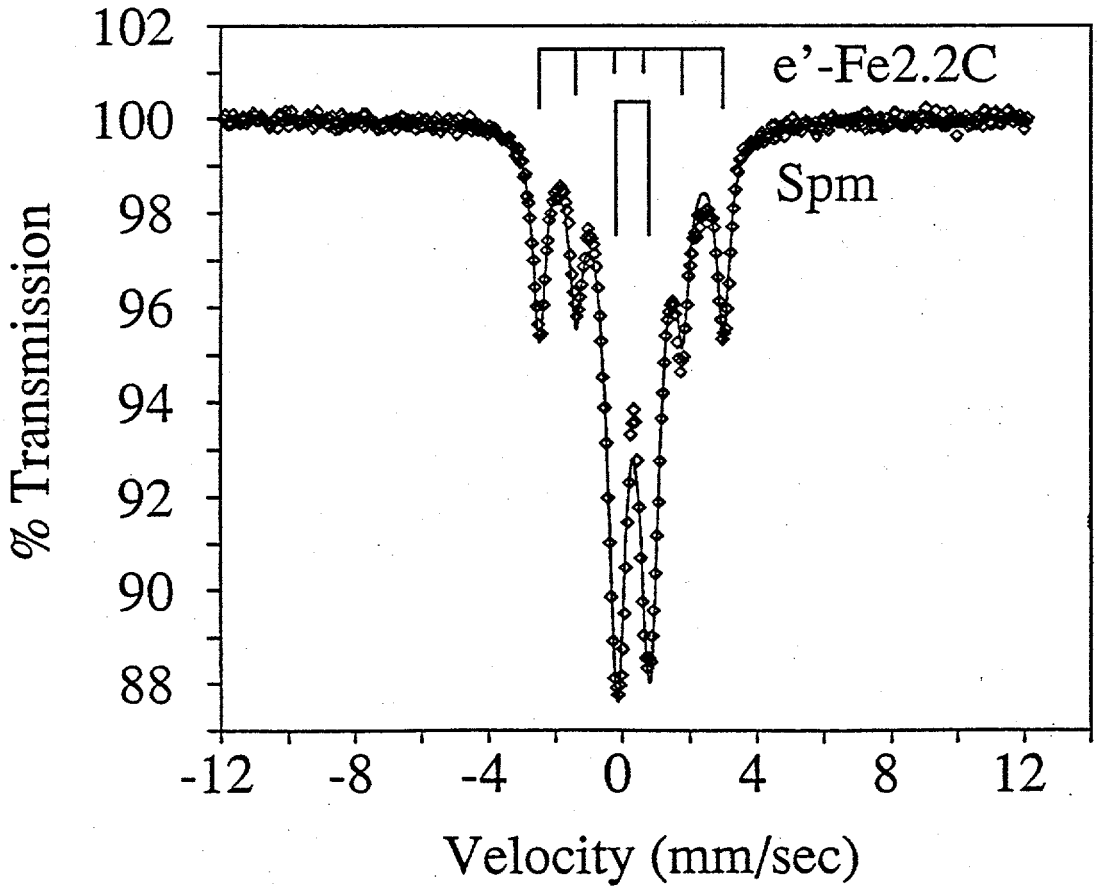
Mössbauer Analysis UK95-21

D.B.Bukur, Texas A&M University

FA-1795, Bottom, 100Fe/5Cu/6K/24SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.35	0.98	0.68	66
e'-Fe2.2C	170	0.26	0.03	0.46	34

Mössbauer run MK2188 on sample 95-167 at 293K



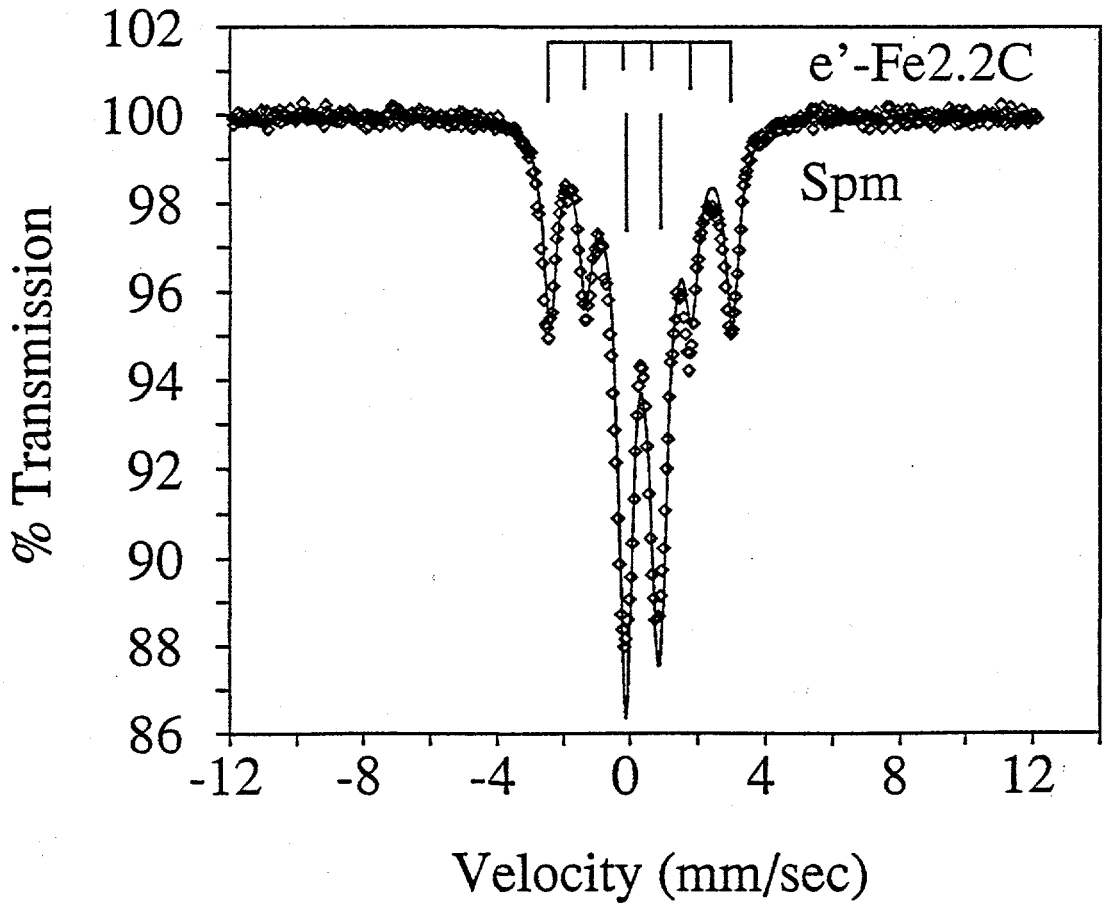
Mössbauer Analysis UK95-22

D.B.Bukur, Texas A&M University

FA-1715, Top, 100Fe/5Cu/6K/24SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.35	1.03	0.67	60
e'-Fe2.2C	169	0.25	0.02	0.49	40

Mössbauer run MK2190 on sample 95-168 at 293K



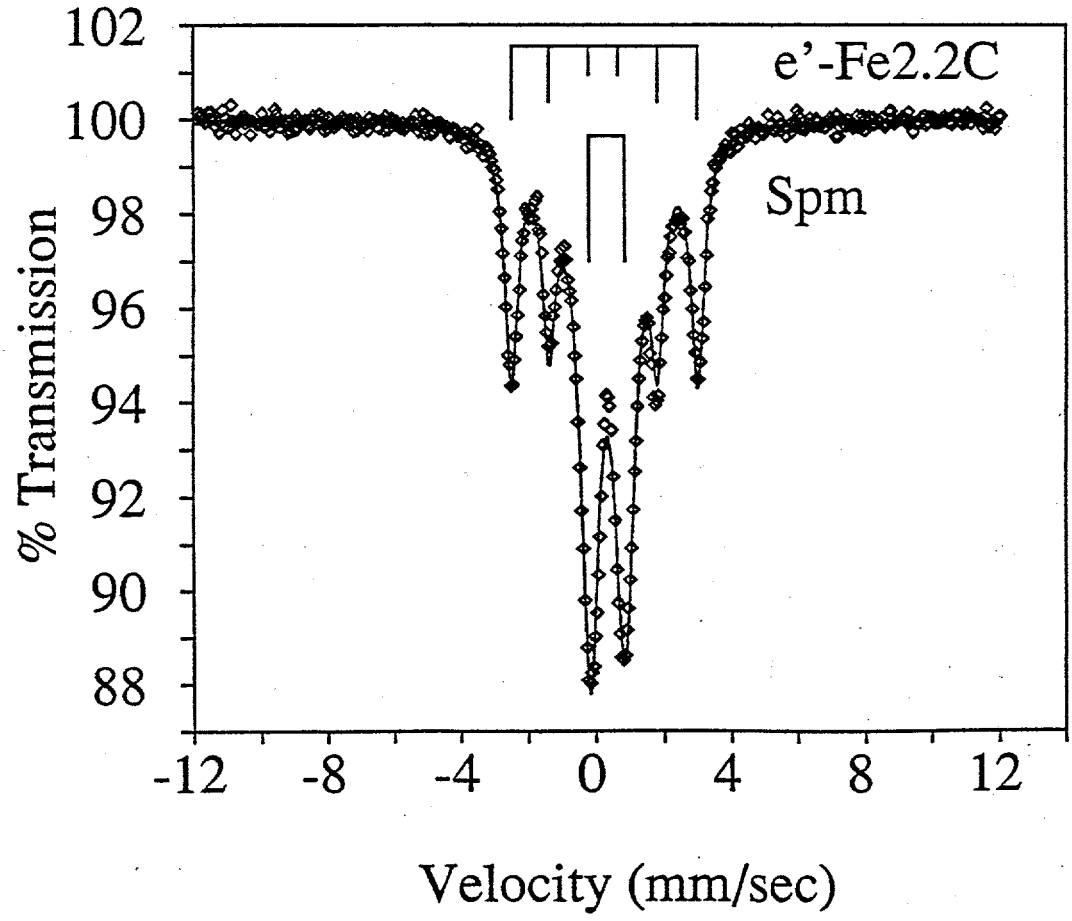
Mössbauer Analysis UK95-23

D.B.Bukur, Texas A&M University

FA-1715, Bottom, 100Fe/5Cu/6K/24SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.36	1.04	0.69	58
e'-Fe2.2C	170	0.25	0.02	0.47	42

Mössbauer run MK2192 on sample 95-169 at 293K



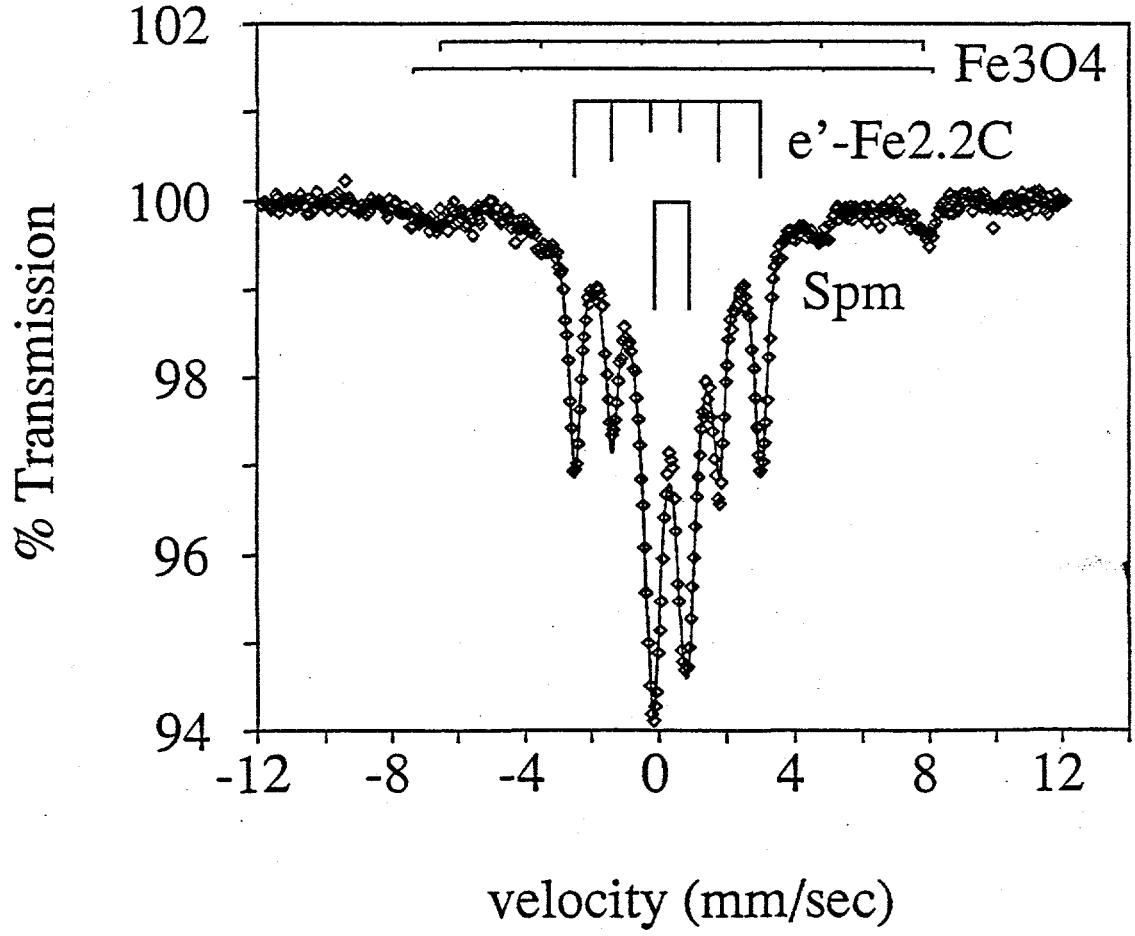
Mössbauer Analysis UK95-24

D.B.Bukur, Texas A&M University

FA-1515, Top, 100Fe/3Cu/4K/6Ca/16SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.36	1.03	0.69	47
e'-Fe2.2C	171	0.25	0.03	0.45	44
Fe3O4	480	0.33	0.00	0.30	2
Fe3O4	445	0.61	0.00	0.75	7

Mössbauer run MK2193 on sample 95-170 at 293K



Mössbauer Analysis UK95-25

D.B.Bukur, Texas A&M University

FA-1515, Bottom, 100Fe/3Cu/4K/6Ca/16SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.36	0.97	0.69	44
e'-Fe2.2C	170	0.25	0.03	0.45	40
Fe3O4	482	0.31	0.00	0.38	4
Fe3O4	443	0.59	0.00	0.88	12

Mössbauer run MK2194 on sample 95-171 at 293K