FINAL

DOE/PC/93066--T1

QUARTERLY TECHNICAL PROGRESS REPORT
(January-March, 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
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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:	Jan 12,1994-April 11, 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.

Summary of Technical Progress:

(1) Mössbauer Spectroscopy Studies:

Mössbauer spectroscopy measurements of the following iron FT catalysts, received from (a) R.J. Gormley, PETC, DOE and (b) from Prof.D.B.Bukur, Texas A & M University, College Station, TX. were carried out.

(a) Iron Catalysts received from R.J. Gormley:

Sr. No.	CFFLS#	MK#(Run No)	Sample description
1.	1148	1747	UCI 1185-78, as prepared catalyst $87.9\%Fe_2O_3/11.1\%CuO/0.052\%K_2O$
2.	1151	1749	S3-03 END UCI-1185-78, used catalyst $87.9\%Fe_2O_3/11.1\%CuO/0.052\%K_2O$
3.	1149	1745	MB6C-FECUKCAL-1-79, as prepared catalyst 65.8%Fe/2.9%Cu/0.3%K (DOE)
4.	1152	1750	S1-110 END, Black cat at bottom Catalyst: MB6ABC-1-81 (DOE)
5.	1150	1743	FH09-FECOCUKCA-1-101, as prepared catalyst
		(300K)	55.2%Fe/4.8%Co/3.1%Cu/0.3%K (DOE)
6.	1150	1753	FH09-FECOCUKCA-1-101, as prepared catalyst
		(14.0K)	55.2%Fe/4.8%Co/3.1%Cu/0.3%K (DOE)
7.	1153	1748	S1-108 END homogeneous (DOE) Catalyst: FH09-FECOCUKCA-1-101 55.2%Fe/4.8%Co/3.1%Cu/0.3%K

The results of analysis of the Mössbauer spectra recorded for the above catalysts are given in Table I.

The fresh UCI 1185-78 catalyst consisted of hematite, α-Fe_2O_3. The two DOE as prepared catalysts consisted of a mixture of α-Fe_2O_3 and a superparamagnetic (spm) phase. Low temperature measurements were carried out on one of them at 14.0K to identify the spm phase. The low temperature spectrum revealed that the spm phase seen at the room temperature to be also α-Fe_2O_3. A comparison of the spm spectrum observed at roon temperature with theoretical Mössbauer relaxation spectra indicates that the spm phase corresponds to a particle size distribution of about 80Å.

The Mössbauer spectra of the catalysts subjected to FT synthesis revealed the presence of substantial amounts of carbides besides a spm phase and magnetite in two of the catalysts. The catalysts were pretreated in CO at about 270-280°C for 24 hrs. The CO pretreatment is known to convert the catalysts into carbides and the FT synthesis into a mixture of magnetite and carbides. It is desirable to characterize the CO reduced catalysts to understand the conversion of the catalysts during the reduction process. The spm phase could be fine particles of an oxide or an iron carbide. Low temperature Mössbauer measurements for the FT run sample will be carried out to identify the spm phase.

It is observed that the UCI 1185-78 catalyst gave rise to much higher carbide formation as compared to the DOE catalyst, MB6ABC (S1-110 END). The copper contents of these catalysts differ appreciably. The UCI catalyst contains three times as much copper as in the MB6ABC (S1-110 END) catalyst. Copper is known to help reduction of the catalysts. It is of interest to investigate whether copper is responsible for higher amounts of carbides in the UCI catalyst.

Co substitution in magnetite is known to lower the reduction temperature. The carbide content in the catalyst containing Co (S1-108 END) is 75%. It may be of interest to investigate whether Co is responsible for the higher amounts of carbides present in this catalyst.

(b) Iron-catalysts (reduced) received from Prof. D.B. Bukur:
(w/o separation from glass beads)

Sr. No	CFFLS#	MK#(Run No)	Sample description
1	1090	1757	FB-1903 TOP , Ruhrchemie
2	1091	1760	FB-1903 BOT, Ruhrchemie
3	1092	1770	FA-2073 TOP, Ruhrchemie
4	1093	1761	FA-2073 BOT, Ruhrchemie

5	1094	1769	FA-2153 TOP 100Fe/0.3Cu/0.8K
6	1095	1767	FA-2153 BOT TOM 100Fe/0.3Cu/0.8K
7	1096	1763	FA-2223 TOP 100Fe/0.3Cu/0.8K
8	1097	1768	FA-2223 BOT TOM 100Fe/0.3Cu/0.8K

The results of analysis of the Mössbauer spectra recorded for the above catalysts are given in Table II.

Two of the Ruhrchemie (**100Fe/5.0Cu/4.2K/25SiO_2**) catalysts, were reduced in CO at 280°C for 24hrs. It is observed that the CO reducition gave rise to the formation of about 50% of Chi-carbide (Fe_5C_2) and an equal amout of superparamagnetic phase. The other two Ruhrchemie catalysts were reduced in H_2 atmosphere at 280°C for 8hrs. These catalysts were reduced to a small extent to iron metal (8%) and the remaining catalyst exhibited a superparamagnetic phase.

Two of the catalysts of composition **100Fe/0.3Cu/0.8K** which were reduced in CO consisted of Chi-carbide (Fe_5C_2), superparamgnetic phase and magnetite. On the other hand the two other catalyst of the same composion but subjected to reduction in H_2 atmosphere consisted of essentially iron metal, epsilon carbide (Fe_2C), and magnetite (Fe_3O_4).

The superparamagnetic phase observed in the above catalysts is characteristic of iron particles of less than about 80Å diameter. The spm phase could be an iron-oxide or a carbide. Low temperature will be carried out to ascertain the nature of the spm phase.

Formation of iron-carbides is expected whenever an iron catalyst is pretreated in CO atmosphere. On the other hand pretreatment in H_2 atmosphere is expected to reduced the catalyst to iron-metal. In general, the results observed are consistant with the above expectations. However, the Ruhrchemie catalyst is seen to get reduced to the metallic iron to a lesser extent as compared to the catalyst, **100Fe/0.3Cu/0.8K**. Since the amount of reduced iron metal present in a catalyst may have a bearing on the Fischer-Tropsch activity, it is desirable to investigate the influence of the composition on the reduction behavior of the catalysts.

The Mössbauer spectra of the catalysts are enclosed.

(2) XAFS MEASUREMENTS:

Cu-edge XAFS measurements on 23 sample were carried at the Stanford Synchrotron Radiation Facility by our group. The data has not yet been analyzed. Analysis of the data would enable us to understand the valance state and form of Cu in these catalysts.

Table I

CATALYSTS RECEIVED FROM R.J. GORMLEY, PETC, DOE
COMPARISON OF IRON-PHASES PRESENT

Run No	Catalyst	Spm-phase	α-Fe_2O_3	Fe_3O_4	χ-Fe_5C_2	$\acute{\varepsilon}$-$Fe_{2.2}C$
MK1747	UCI 1185-85 Fresh		100.0			
MK1749	S3-03 END UCI 1185-85 Used	11		27	62	
MK1745	MB6C-FeCuK-Cal As prepared	63	37			
MK1750	S1-110 END Cat:MB6ABC	12		53	2	33
MK1743 T=300K	FH09-FeCoCuK-Cal As prepared T=300k	85	15			
MK1753 T=14.1K	FH09-FeCoCuK-Cal As prepared		100			
MK1748	S1-108 END Cat:FH09 FeCoCuK-Cal	25			22	53

Table II

IRON-CATALYSTS FROM: D.B. BUKUR, Texas A. & M University
COMPARISON OF IRON-PHASES IN REDUCED CATALYSTS

Sr.No.	Run No.	CFFLS#	Catalyst	Spm-phase	Fe_3O_4	χ-Fe_5C_2	ε-$Fe_{2.2}C$	Fe-metal
1	MK1757	1090	FB-1903,TOP Ruhrchemie	47		53		
2	MK1760	1091	FB1903,BOTTOM Ruhrchemie	48		52		
3	MK1770	1092	FA-2073,TOP Ruhrchemie	92				8
4	MK1761	1093	FA-2073,BOTTOM Ruhrchemie	92				8
5	MK1769	1094	FA-2153,TOP 100Fe/0.3Cu/0.8K	30	9	61		
6	MK1767	1095	FA-2153,BOTTOM 100Fe/0.3Cu/0.8K	33	2	65		
7	MK1763	1096	FA-2223,TOP 100Fe/0.3Cu/0.8K	8	31		20	41
8	MK1768	1097	FA-2223 BOTTOM 100Fe/0.3Cu/0.8K		79			21

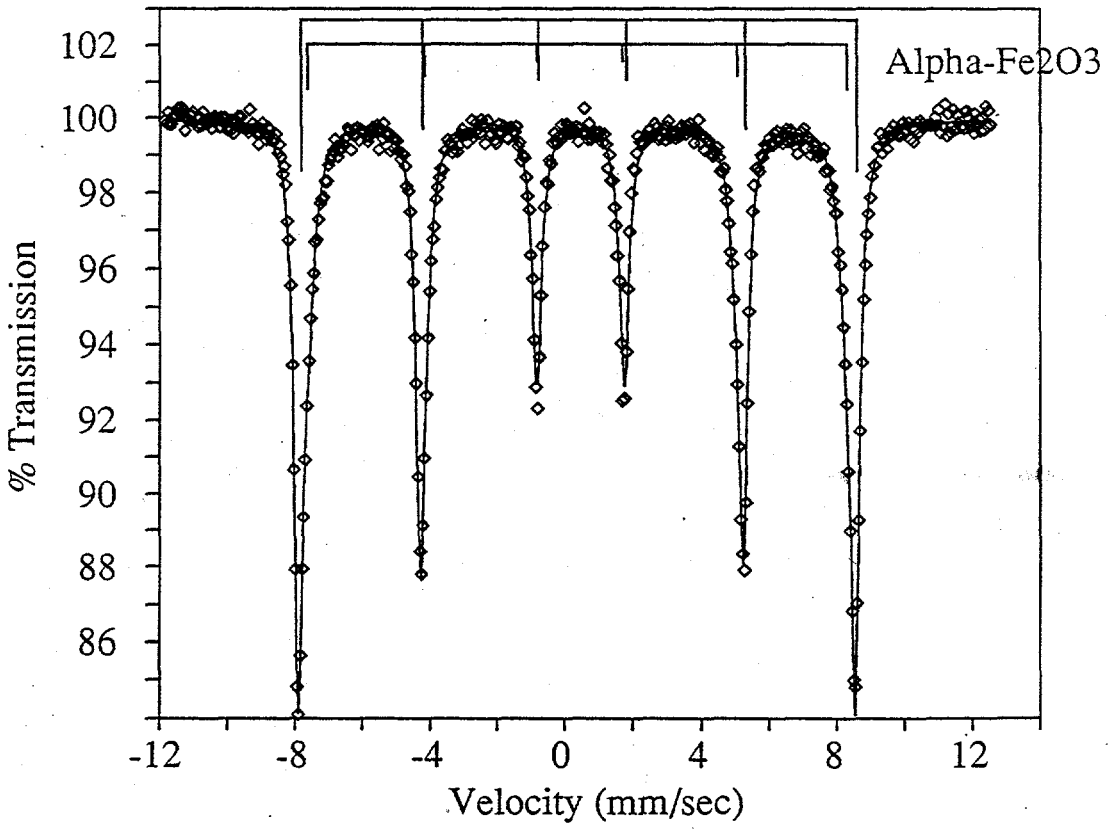
Mössbauer Analysis UK0193

R. J. Gormley, PETC/DOE

UCI 1185-78, Fresh

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Alpha-Fe2O3	510	0.39	-0.08	0.29	67
Alpha-Fe2O3	494	0.38	-0.06	0.52	33

Mössbauer run MK1747 on sample 1148 at 293K



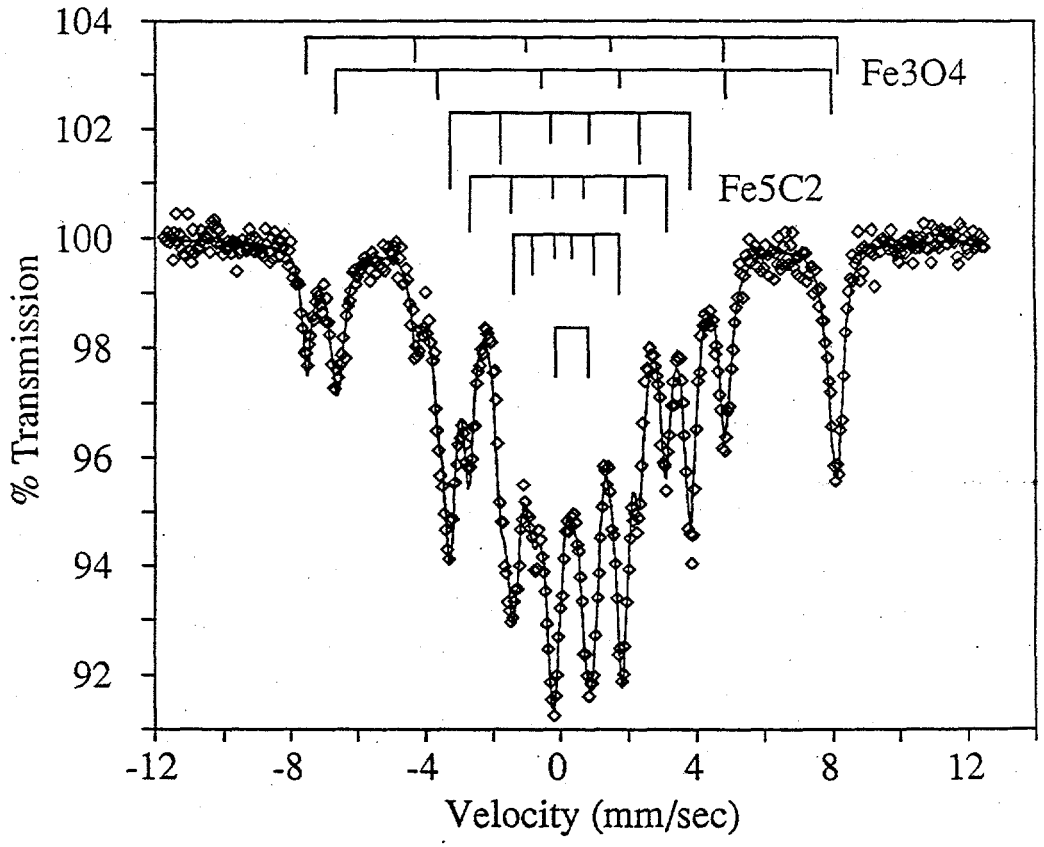
Mössbauer Analysis UK0194

R. J. Gormley, PETC/DOE

S3-03 END, UCI 1185-78 USED

	Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
	Fe3O4	487	0.29	0.03	0.32	9
	Fe3O4	453	0.66	0.03	0.51	18
	Fe5C2	220	0.27	0.00	0.42	25
-	Fe5C2	180	0.19	0.00	0.37	16
	Fe5C2	97	0.17	0.05	0.45	21
	Spm phase		0.36	0.95	0.62	11

Mössbauer run MK1749 on sample 1151 at 293K



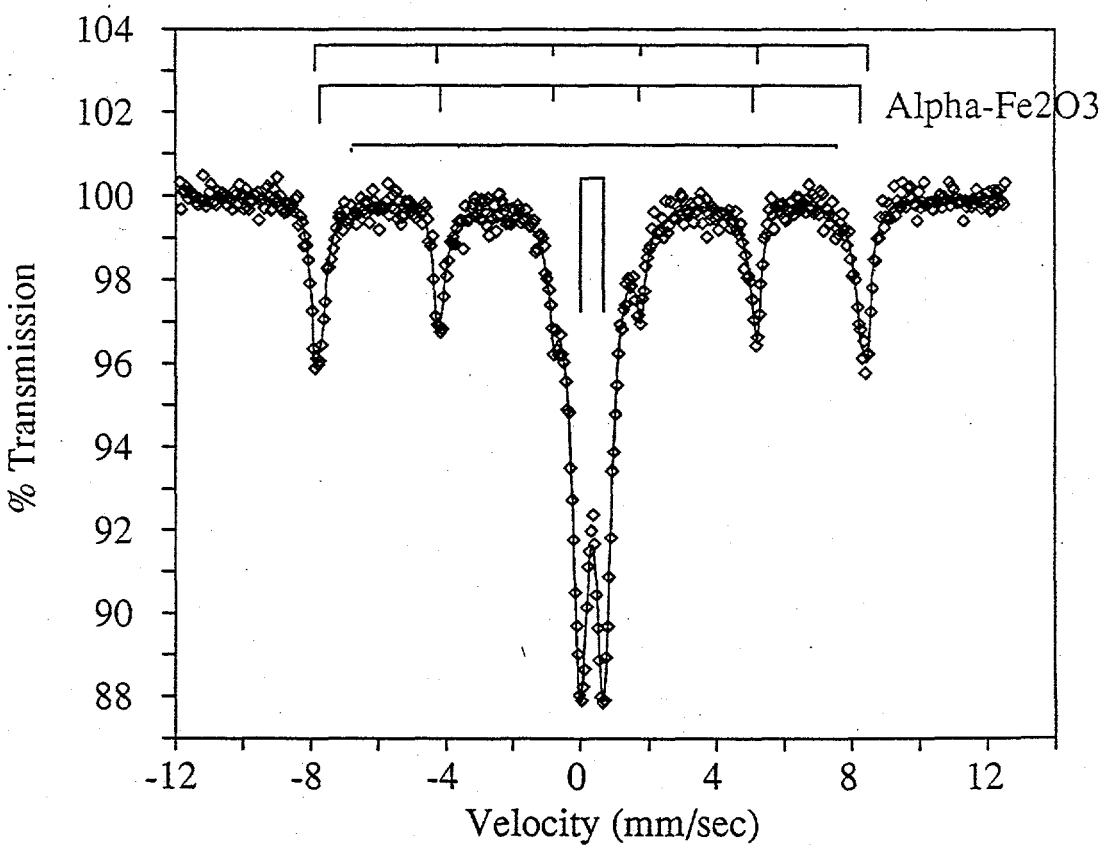
Mössbauer Analysis UK0195

R. J. Gormley, PETC/DOE

MB6C-FeCuK-Cal, As prepared

	Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
	Alpha-Fe2O3	507	0.39	-0.09	0.22	8
	Alpha-Fe2O3	496	0.39	-0.10	0.46	26
	Alpha-Fe2O3	444	0.50	-0.07	0.60	3
-	Spm phase		0.33	0.69	0.55	63

Mössbauer run MK1745 on sample 1149 at 293K



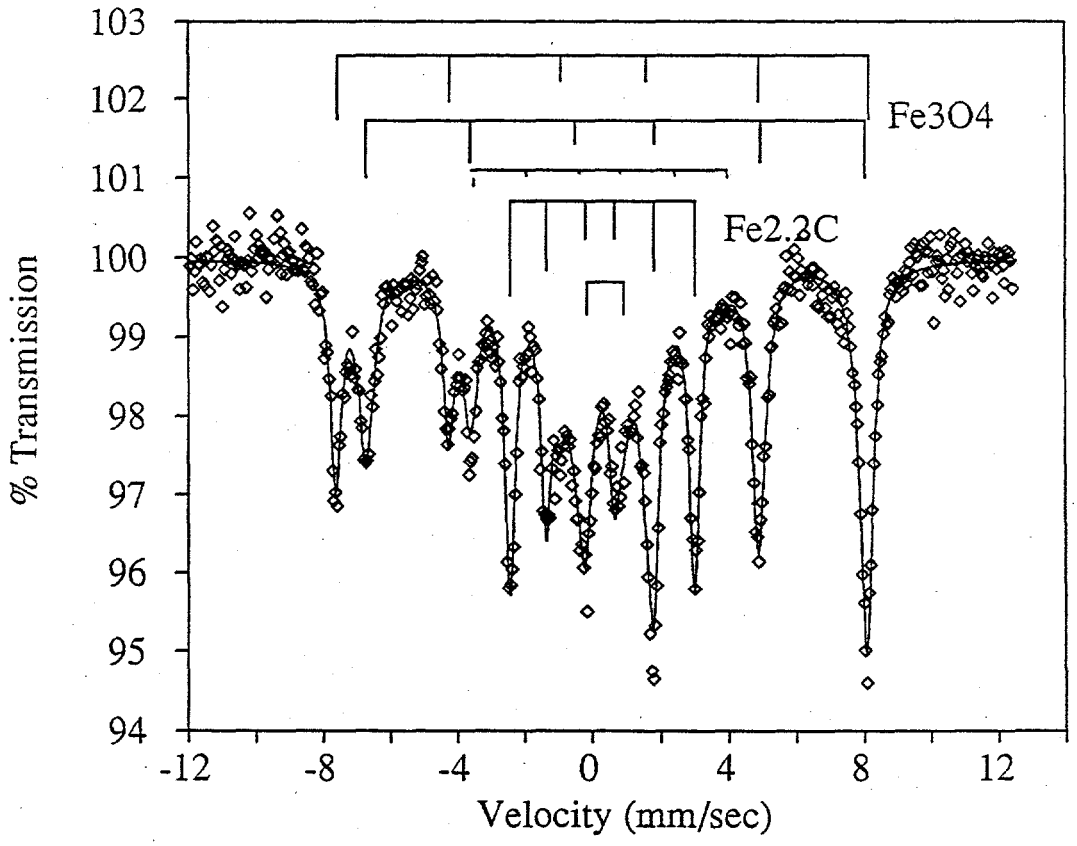
Mössbauer Analysis UK0196

R. J. Gormley, PETC/DOE

S1-110 END, Cat:MB6ABC

	Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
	Fe3O4	488	0.27	-0.03	0.38	23
	Fe3O4	457	0.65	-0.01	0.56	30
	Fe5C2	233	0.21	-0.02	0.18	2
-	Fe2.2C	168	0.25	0.04	0.38	33
	Spm Phase		0.37	1.07	0.84	12

Mössbauer run MK1750 on sample 1152 at 293K



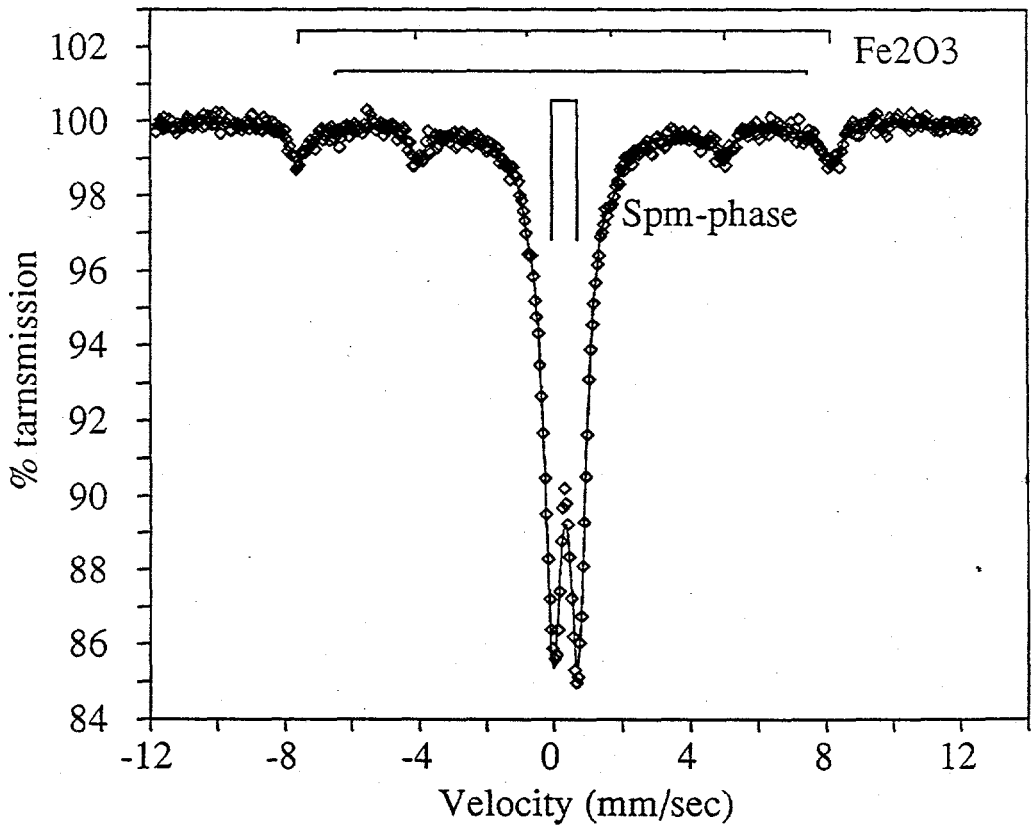
Mössbauer Analysis UK0197

R. J. Gormley, PETC/DOE

FH09, FeCoCuK-Cal, As prepared

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm-Fe2O3	489	0.38	-0.10	0.55	10
Spm-Fe2O3	431	0.39	0.03	1.04	4
Spm phase		0.34	0.74	0.63	86

Mössbauer run MK1743 on sample 1150 at 293K



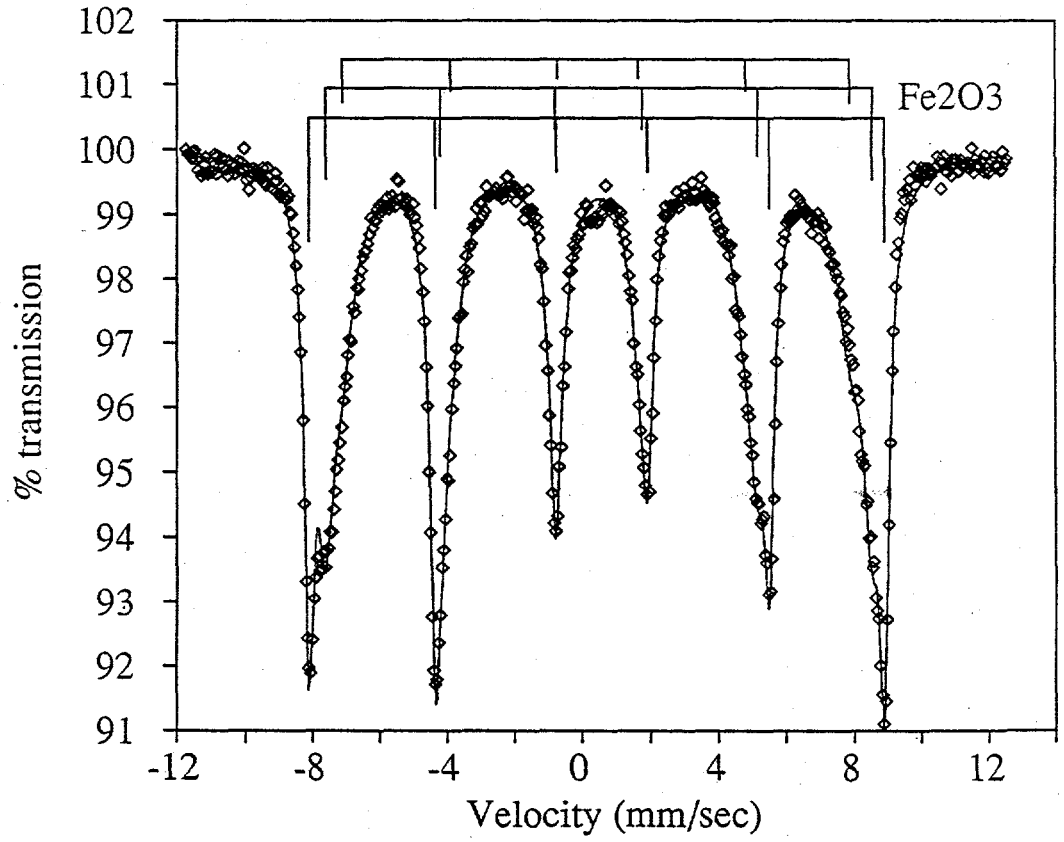
Mössbauer Analysis UK0198

R. J. Gormley, PETC/DOE

FH09, FeCoCuK-Cal, As prepared

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Fe2O3	527	0.48	-0.09	0.33	28
Fe2O3	501	0.46	-0.01	0.68	44
Fe2O3	465	0.41	-0.04	0.96	28

Mössbauer run MK1753 on sample 1150 at 14.1K



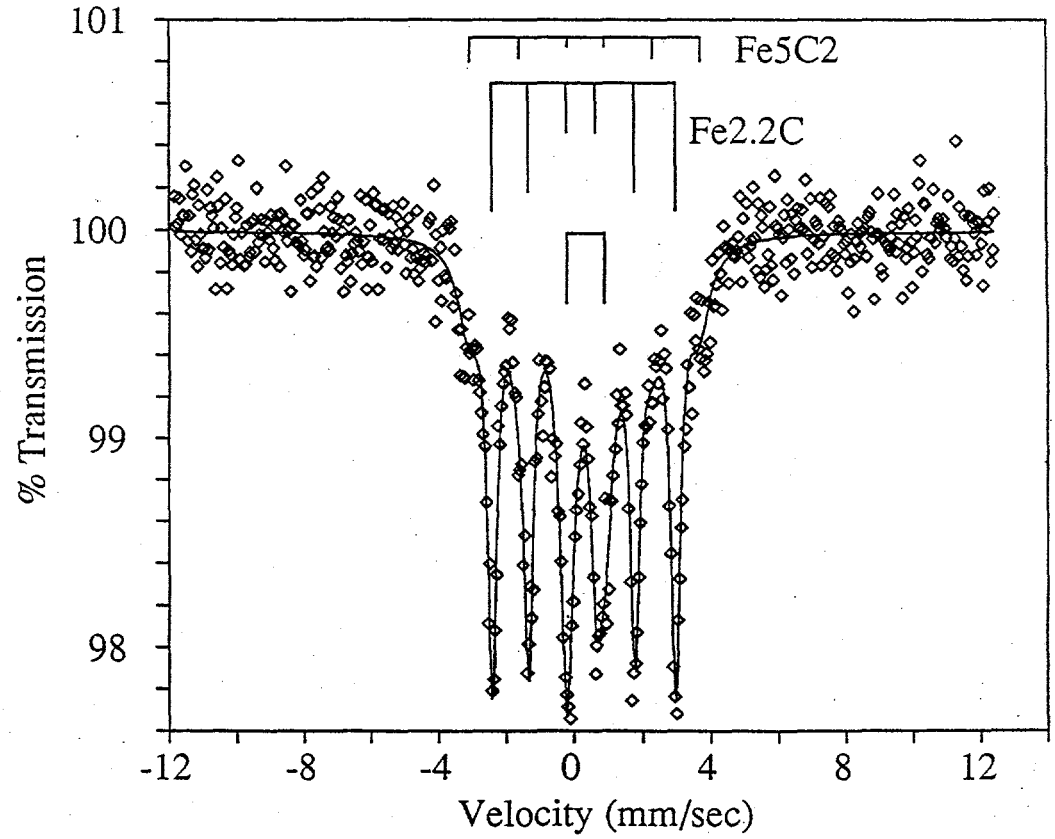
Mössbauer Analysis UK0199

R. J. Gormley, PETC/DOE

S1-108 END,Cat:FH09, FeCoCuK-Cal.

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Fe2.2C	167	0.25	0.03	0.34	53
Fe5C2	210	0.31	-0.02	0.75	22
Spm-phase		0.34	1.09	0.66	25

Mössbauer run MK1748 on sample 1153 at 300K



Mössbauer Analysis UK0200

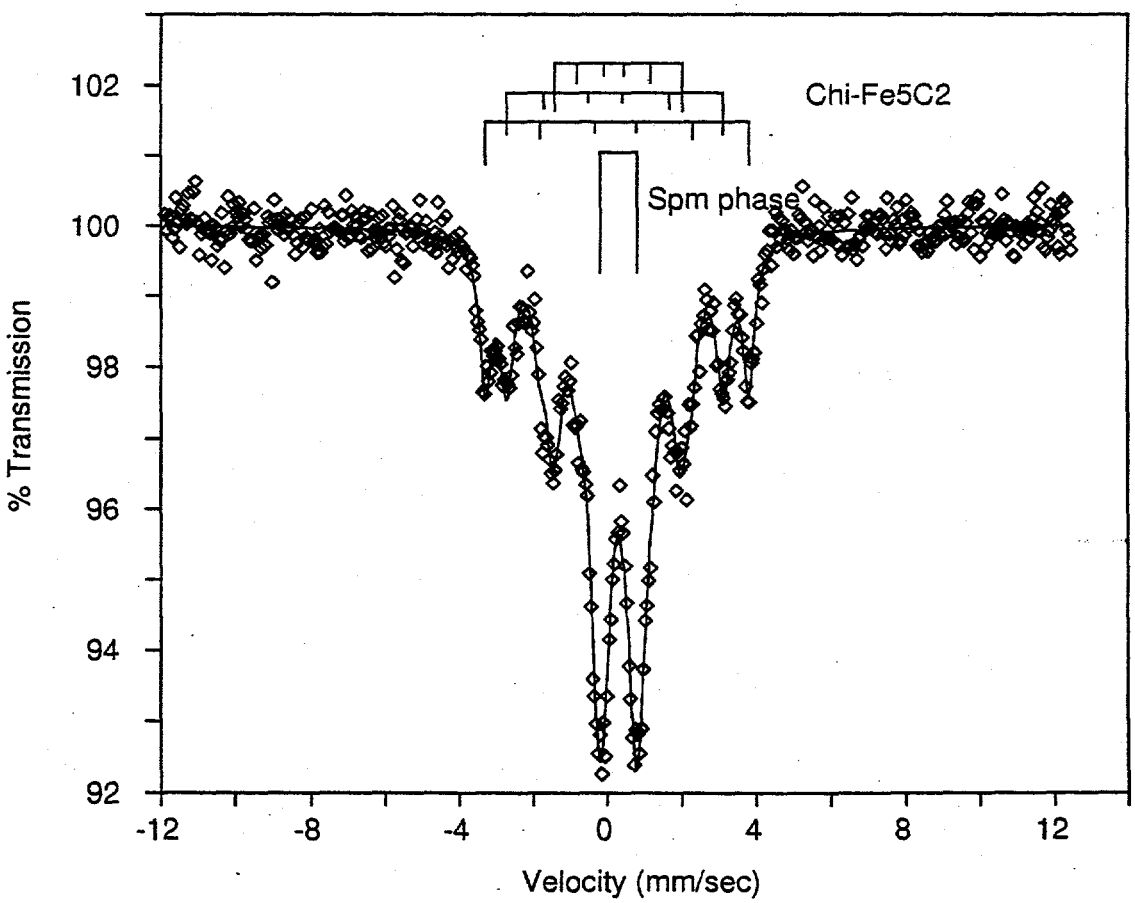
FB-1903,Top, W/O separation, Ruhrchemie

Prof. D.B. Bukur, TAMU, College Station, TX

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm phase		0.33	0.99	0.61	47
Chi-Fe5C2	220	0.25	0.01	0.37	15
Chi-Fe5C2	181	0.09	0.11	0.47	18
Chi-Fe5C2	106	0.26	0.06	0.45	20

Mössbauer run MK1757 on sample 1090 AT RT

CFFLS, University of Kentucky, Lexington, KY



Mössbauer Analysis UK0201

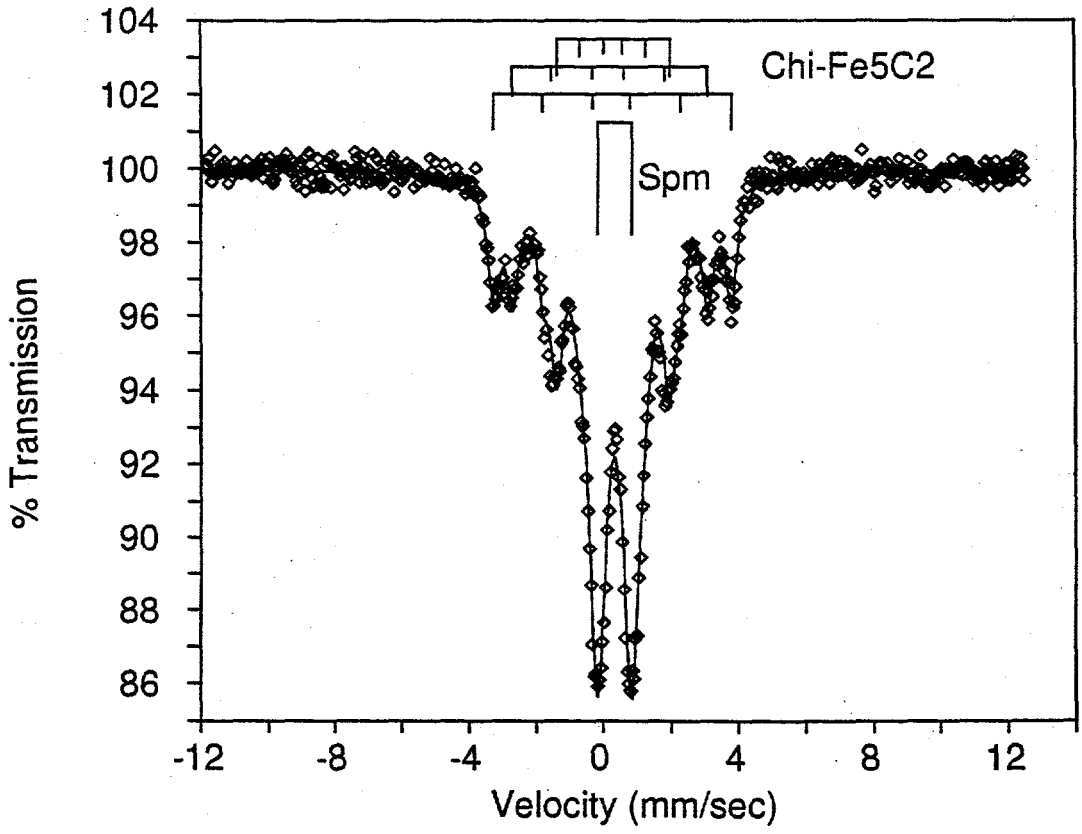
FB-1903,Bot, W/O separation, Ruhrchemie

Prof. D.B. Bukur, TAMU, College Station, TX

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm phase		0.35	1.02	0.59	48
Chi-Fe5C2	218	0.26	0.02	0.36	13
Chi-Fe5C2	180	0.17	0.02	0.58	19
Chi-Fe5C2	103	0.29	0.01	0.49	20

Mössbauer run MK1760 on sample 1091 AT RT

CFFLS, University of Kentucky, Lexington, KY



Mössbauer Analysis UK0202

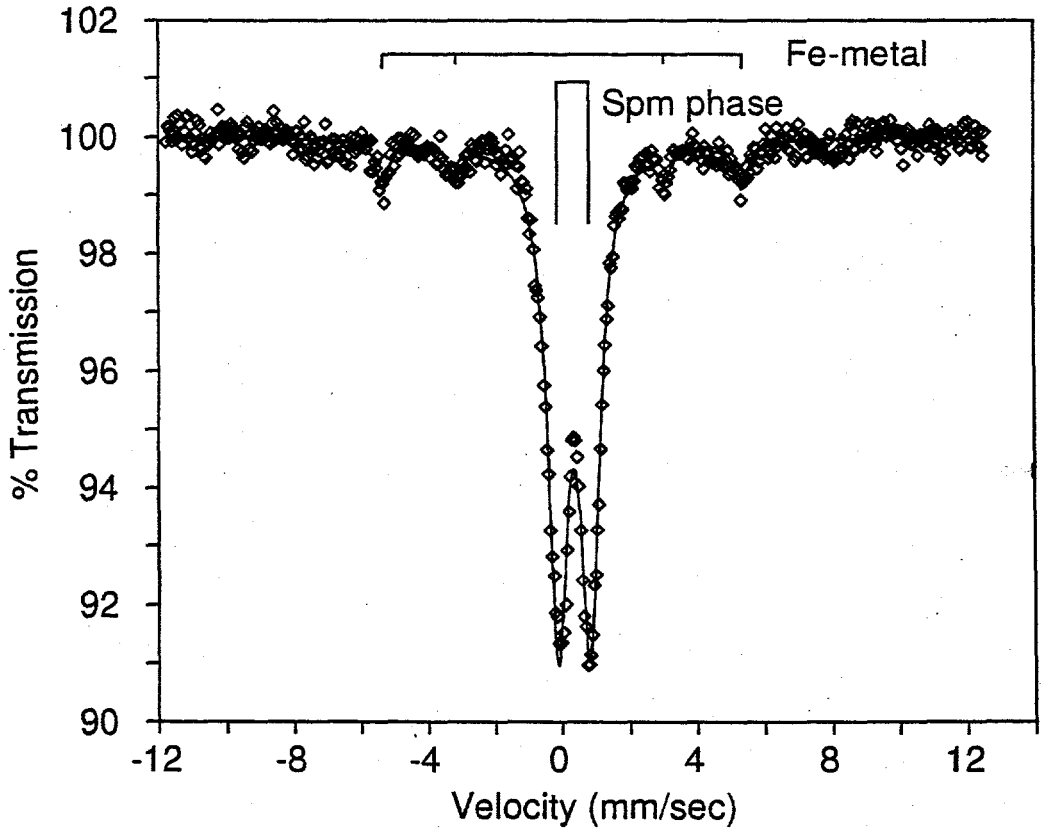
FA-2073,Top, W/O separation, Ruhrchemie

Prof. D.B. Bukur, TAMU, College Station, TX

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm phase		0.34	0.95	0.70	92
Fe-metal	331	-0.04	0.03	0.46	8

Mössbauer run MK1770 on sample 1092 AT RT

CFFLS, University of Kentucky, Lexington, KY



Mössbauer Analysis UK0203

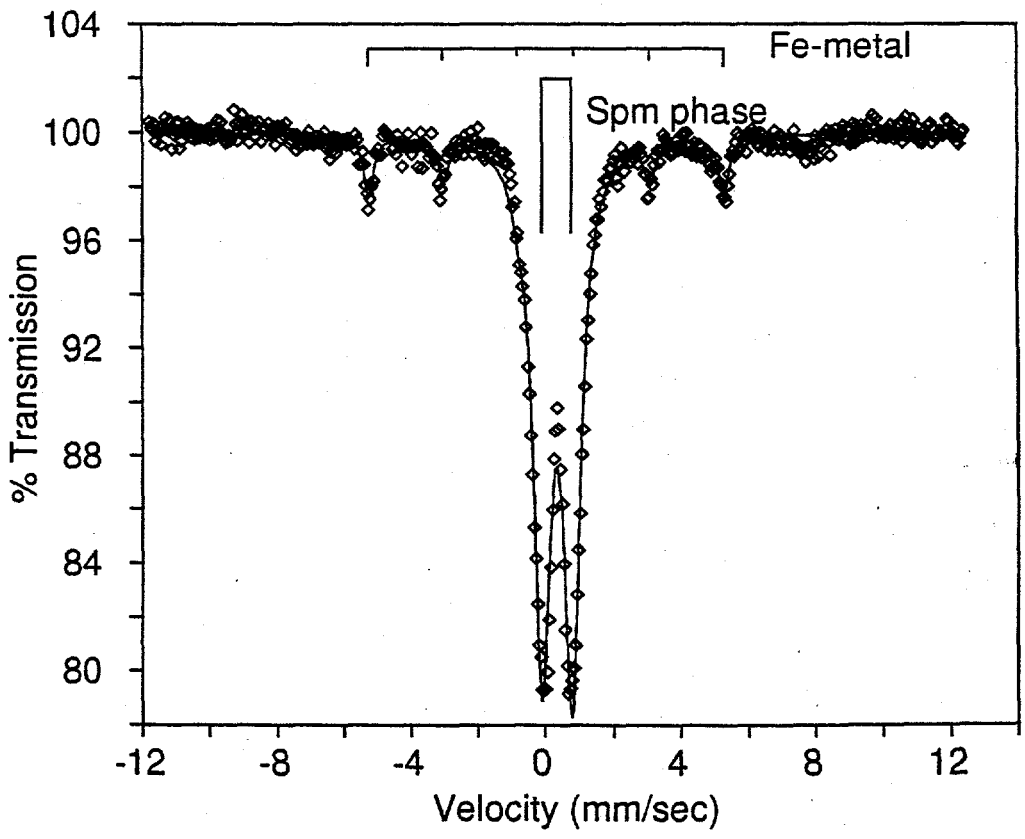
FA-2073, Bot, W/O Sep. Ruhrchemie

Prof. D.B. Bukur, TAMU, College Station, TX

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm phase		0.35	0.87	0.61	92
Fe-metal	328	0.01	-0.01	0.36	8

Mössbauer run MK1761 on sample 1093 AT RT

CFFLS, University of Kentucky, Lexington, KY



Mössbauer Analysis UK0204

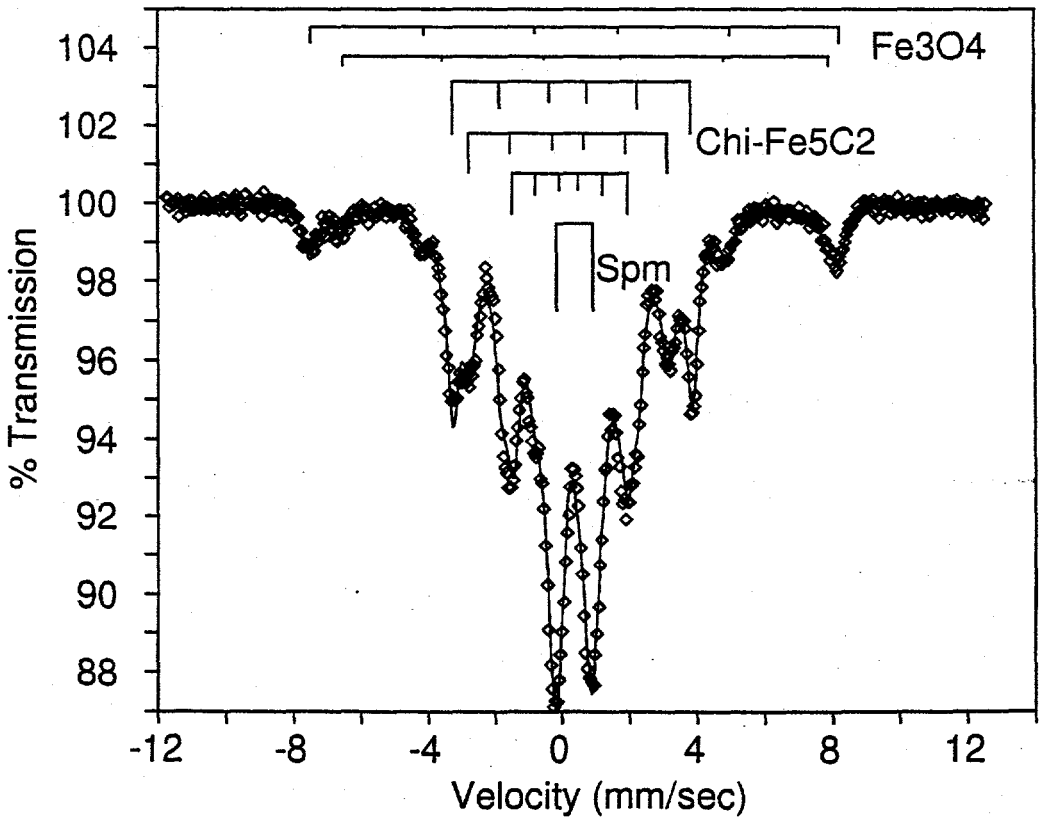
FA-2153, Top, W/O Sep. 100Fe/0.3Cu/0.8K

Prof. D.B. Bukur, TAMU, College Station, TX

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm phase		0.37	1.07	0.62	30
Fe3O4	487	0.38	-0.03	0.42	6
Fe3O4	448	0.59	0.03	0.41	4
Chi-Fe5C2	220	0.26	0.04	0.43	21
Chi-Fe5C2	183	0.22	-0.01	0.42	15
Chi-Fe5C2	107	0.23	0.02	0.63	24

Mössbauer run MK1769 on sample 1094 AT RT

CFFLS, University of Kentucky, Lexington, KY



Mössbauer Analysis UK0205

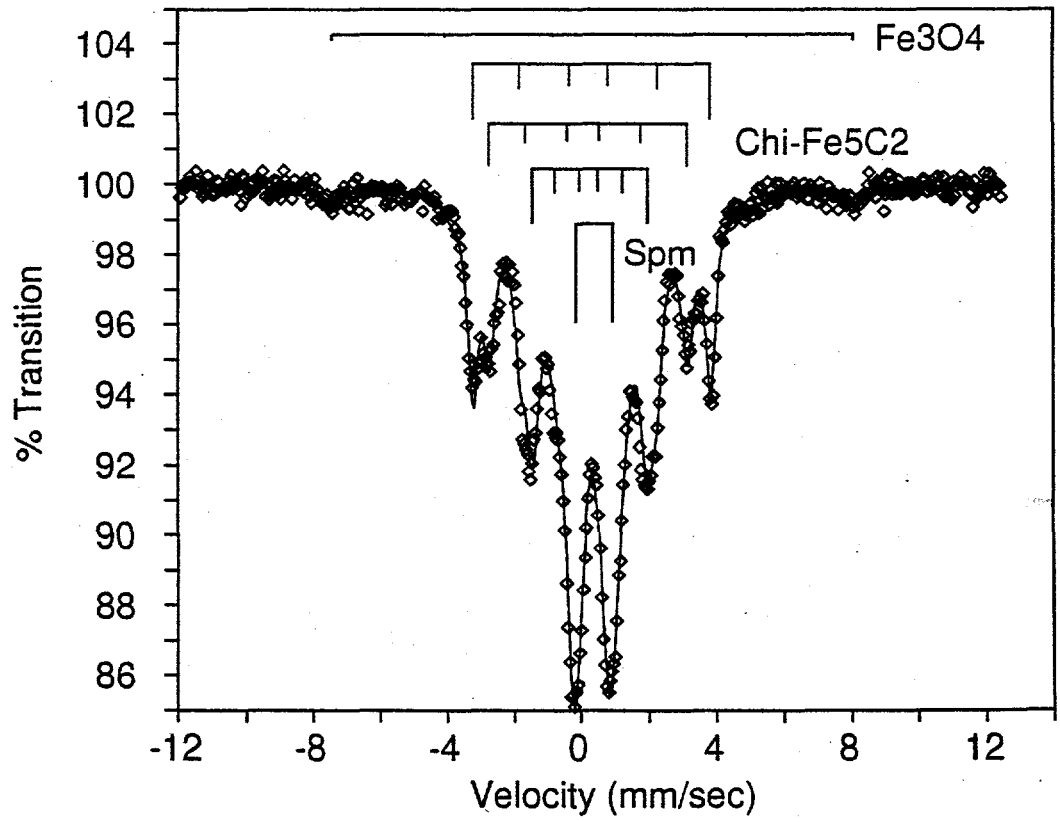
FA-2153, Bot, W/O Sep. 100Fe/0.3Cu/0.8K

Prof. D.B. Bukur, TAMU, College Station, TX

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm phase		0.36	1.07	0.56	33
Chi-Fe5C2	219	0.26	0.04	0.36	18
Chi-Fe5C2	183	0.13	0.07	0.50	19
Chi-Fe5C2	106	0.28	0.02	0.52	27
Fe3O4	480	0.35	-0.06	0.49	3

Mössbauer run MK1767 on sample 1095 AT RT

CFFLS, University of Kentucky, Lexington, KY



Mössbauer Analysis UK0206

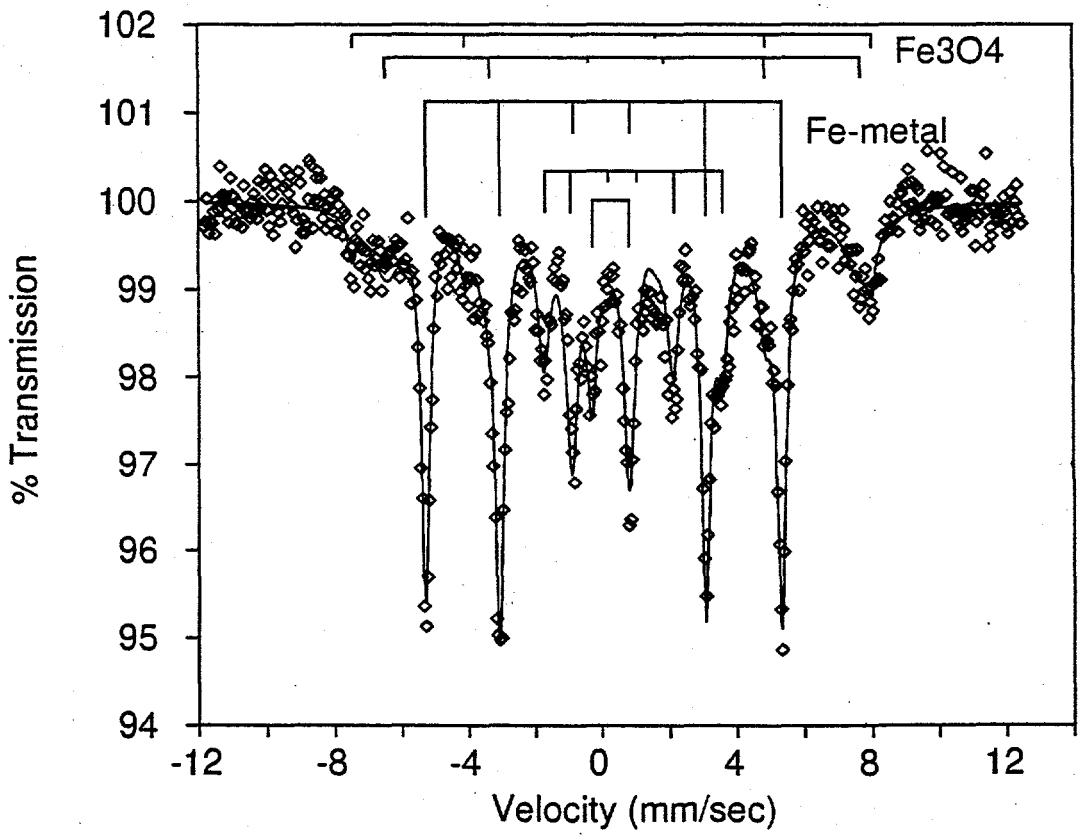
FA-2223, Top, W/O Sep. 100Fe/0.3Cu/0.8K

Prof. D.B. Bukur, TAMU, College Station, TX

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm phase		0.22	1.06	0.34	8
Fe-metal	329	0.00	0.00	0.30	41
Fe3O4	479	0.31	-0.05	0.29	4
Fe3O4	438	0.67	-0.08	1.12	27
Epsilon-Fe2.2C	164	0.74	0.17	0.42	20

Mössbauer run MK1763 on sample 1096 AT RT

CFFLS, University of Kentucky, Lexington, KY



Mössbauer Analysis UK0207

FA-2223, Bot, W/O Sep. 100Fe/0.3Cu/0.8K

Prof. D.B. Bukur, TAMU, College Station, TX

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Fe3O4	489	0.31	-0.01	0.47	43
Fe3O4	455	0.64	0.00	0.50	36
Fe-metal	329	0.00	-0.01	0.27	21

Mössbauer run MK1768 on sample 1097 AT RT

CFFLS, University of Kentucky, Lexington, KY