DOE/PC/93066--T8

QUARTERLY TECHNICAL PROGRESS REPORT
(July-September, 1996)

CONTRACT TITLE:	MÖSSBAUER SPECTROSCOPY STUDIES OF IRON-CATALYSTS USED IN FISCHER-TROPSCH (FT) PROCESSES
Contract Number:	DE-AC22-94PC93066
	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:	July 1, 1996 - September 30, 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.

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. Burt Davis of the Center for Applied Energy Research, University of Kentucky, Dr.D.B. Bukur of Texas A&M University and Mr. Robert Gormley of PETC, US DOE have 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 30 iron-based catalysts during the period under review. The catalysts withdrawn from both the slurry and fixed-bed reactors were received from Dr.D.B. Bukur, Texas A&M University.

The catalysts consist of $100Fe/3Cu/4K/16SiO_2$ or $100Fe/5Cu/6K/24SiO_2$ or $100Fe/5Cu/5K/2Ca/24SiO_2$. The catalysts with 24 parts of SiO_2 were reduced in H_2 at 250°C for 4 hrs and those containing 16 parts of SiO_2 wee reduced in H_2 at 240°C for 2 hrs. All the tests were carried out at 260°C, 200-300 psig, and various gas feed space velocities with H_2/CO feed ratio of 0.67. The details of the Mössbauer results are enclosed.

RESULTS:

The phase distributions as determined from Mössbauer measurements are given in the figures enclosed. The phase distributions of the FT run catalysts consisted of epsilon carbide ($Fe_{2.2}C$), chi-carbide (Fe_5C_2), magnetite (Fe_3O_4) and a superparamagnetic (spm) phase. The reduced catalysts contained Fe-metal as can be expected under H_2 activation. The formation of Fe-metal under H_2 activation and epsilon-carbide in the catalysts subjected to FT synthesis is consistent with earlier observations. Efforts are being made to gather the conversion figures for the catalysts to investigate the possible correlations between the phases and the conversions.

Summary of Technical Progress:

During the period under review only the scheduled Task 2 was carried out.
Mössbauer spectroscopy measurements on 30 iron catalysts received from Dr. D.B. Bukur, Texas A&M University . 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.

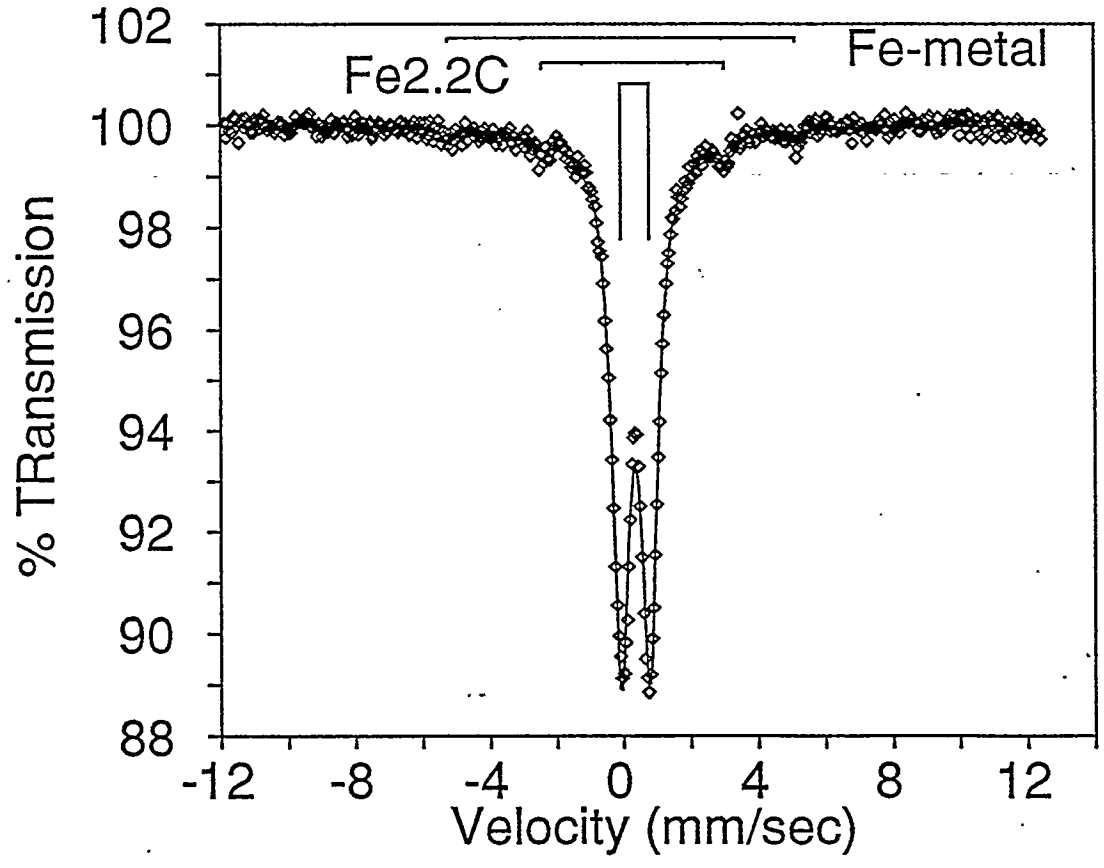
Mössbauer Analysis UK96-024

D.B.Bukur, Texas A&M University

SB-2585, TOS=0h, 100Fe/5Cu/6K/24SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.34	0.85	0.60	95
e'-Fe2.2C	169	0.32	-0.04	0.44	3
Fe-metal	321	-0.04	0.00	0.44	2

Mössbauer run MK2285 on sample 96-014 at 293K



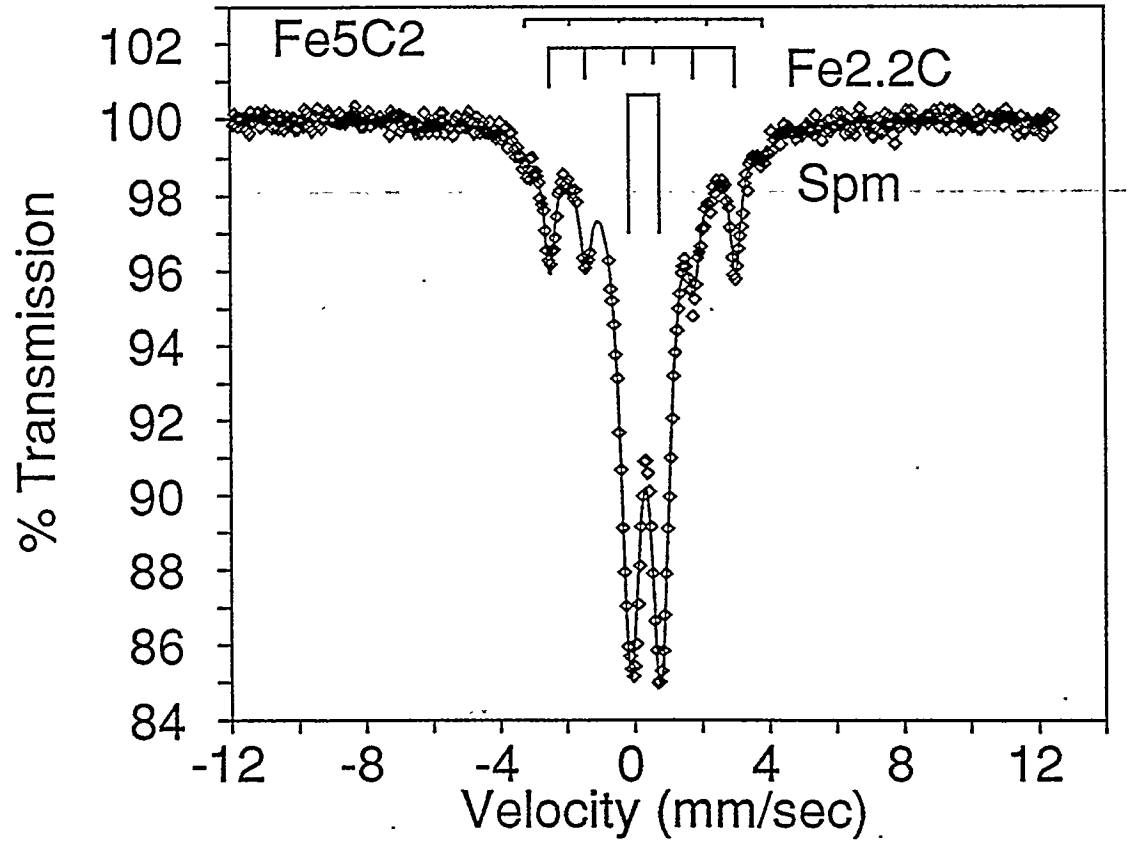
Mössbauer Analysis UK96-025

D.B.Bukur, Texas A&M University

SB-2585, TOS=120h, 100Fe/5Cu/6K/24SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.36	0.88	0.67	75
e'-Fe2.2C	171	0.23	0.04	0.40	20
Fe5C2	218	0.24	0.07	0.49	5

Mössbauer run MK2283 on sample 96-015 at 293K



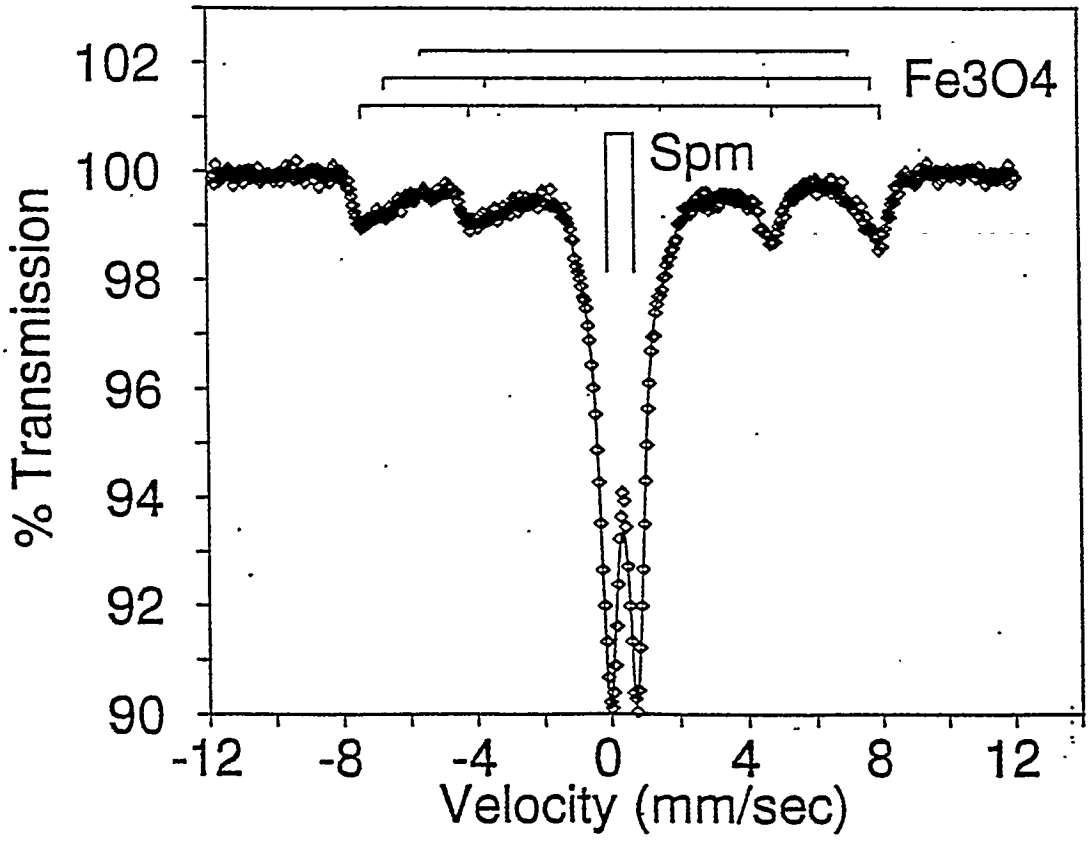
Mössbauer Analysis UK96-030

D.B.Bukur, Texas A&M University

SB-2145, TOS=0h, 100Fe/3Cu/4K/16SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.35	0.79	0.61	69
Fe3O4	478	0.33	0.00	0.45	8
Fe3O4	447	0.53	0.00	0.89	14
Fe3O4	392	0.74	0.00	1.36	9

Mössbauer run MK2296 on sample 96-020 at 293K



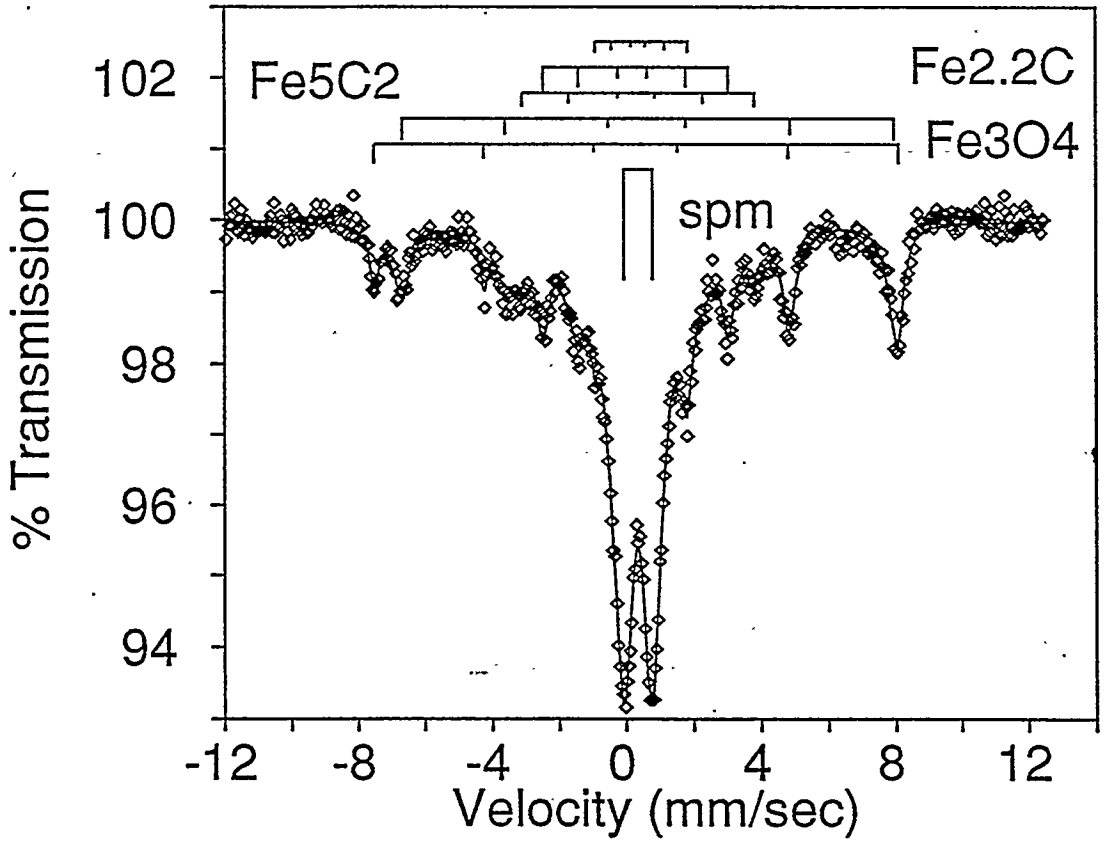
Mössbauer Analysis UK96-027

D.B.Bukur, Texas A&M University

SB-2145, TOS=67h, 100Fe/3Cu/4K/16SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.35	0.84	0.66	48
e'-Fe2.2C	171	0.23	0.05	0.44	14
Fe5C2	215	0.33	0.03	0.62	10
Fe5C2	85	0.40	0.06	0.32	4
Fe3O4	484	0.29	0.00	0.30	7
Fe3C4	454	0.62	0.00	0.62	17

Mössbauer run MK2190 on sample 96-017 at 293K



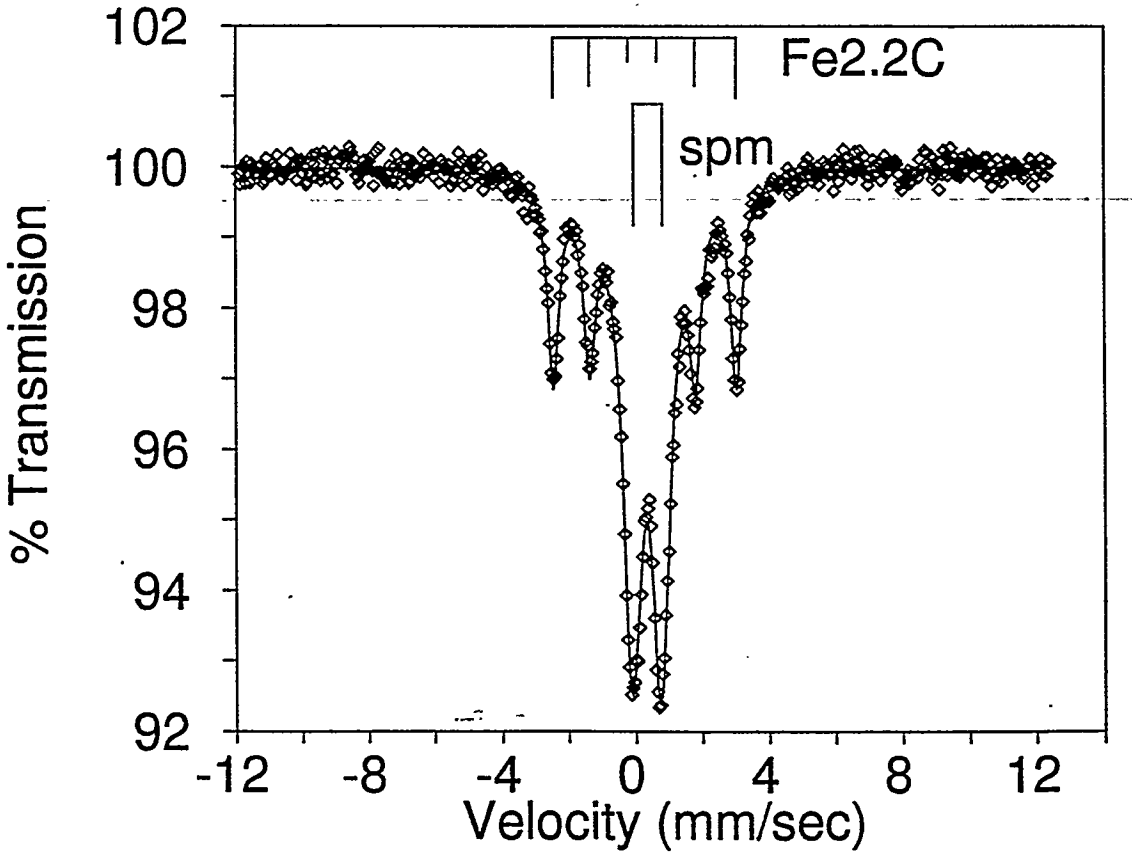
Mössbauer Analysis UK96-028

D.B.Bukur, Texas A&M University

SB-2145, TOS=145h, 100Fe/3Cu/4K/16SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.34	0.84	0.69	63
e'-Fe2.2C	170	0.24	0.04	0.41	37

Mössbauer run MK2288 on sample 96-018 at 293K



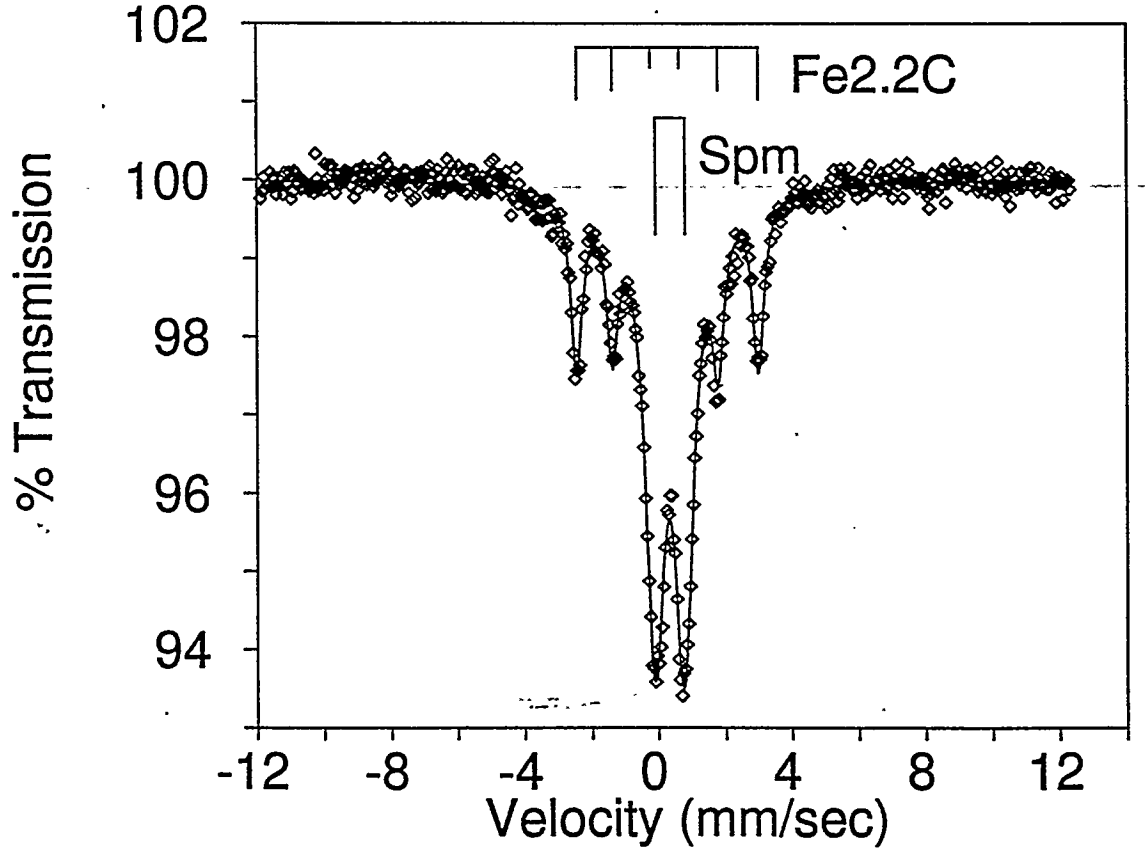
Mössbauer Analysis UK96-029

D.B.Bukur, Texas A&M University

SB-2145, TOS=213h, 100Fe/3Cu/4K/16SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.34	0.86	0.68	65
e'-Fe2.2C	169	0.24	0.04	0.42	35

Mössbauer run MK2295 on sample 96-019 at 293K



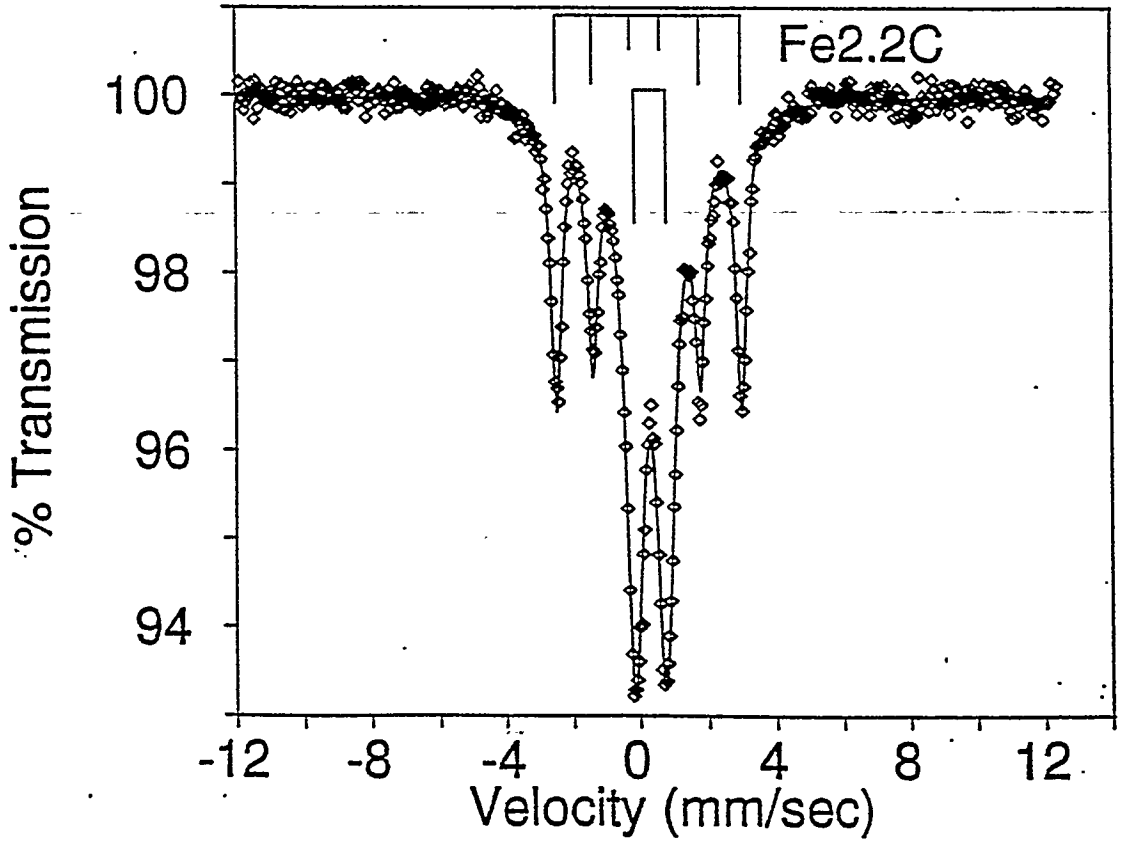
Mössbauer Analysis UK96-026

D.B.Bukur, Texas A&M University

SB-2145, TOS=401h, 100Fe/3Cu/4K/16SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.34	0.91	0.64	55
e'-Fe2.2C	170	0.24	0.04	0.39	45

Mössbauer run MK2286 on sample 96-016 at 293K



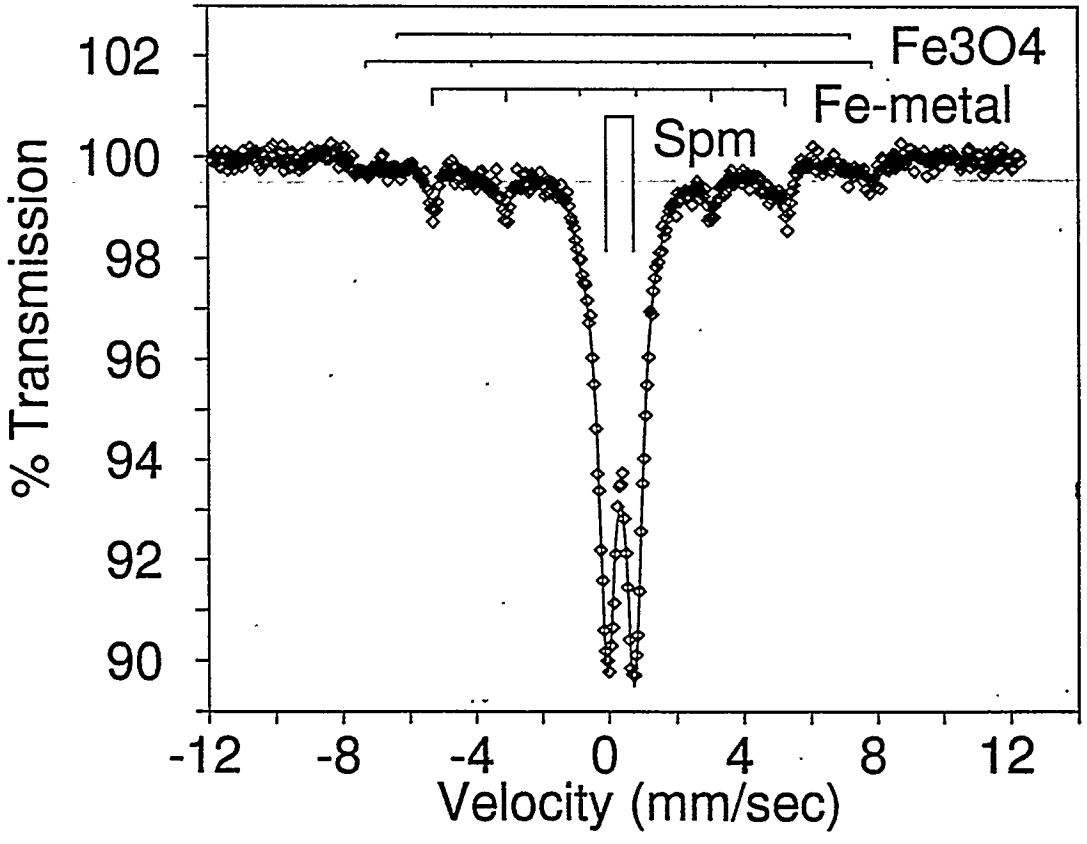
Mössbauer Analysis UK96-031

D.B.Bukur, Texas A&M University

SA-2715, TOS=0h, 100Fe/3Cu/4K/16SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.33	0.80	0.62	81
Fe-metal	327	-0.01	-0.01	0.46	12
Fe3O4	468	0.28	0.00	0.46	4
Fe3O4	419	0.42	0.00	0.46	3

Mössbauer run MK2299 on sample 96-021 at 293K



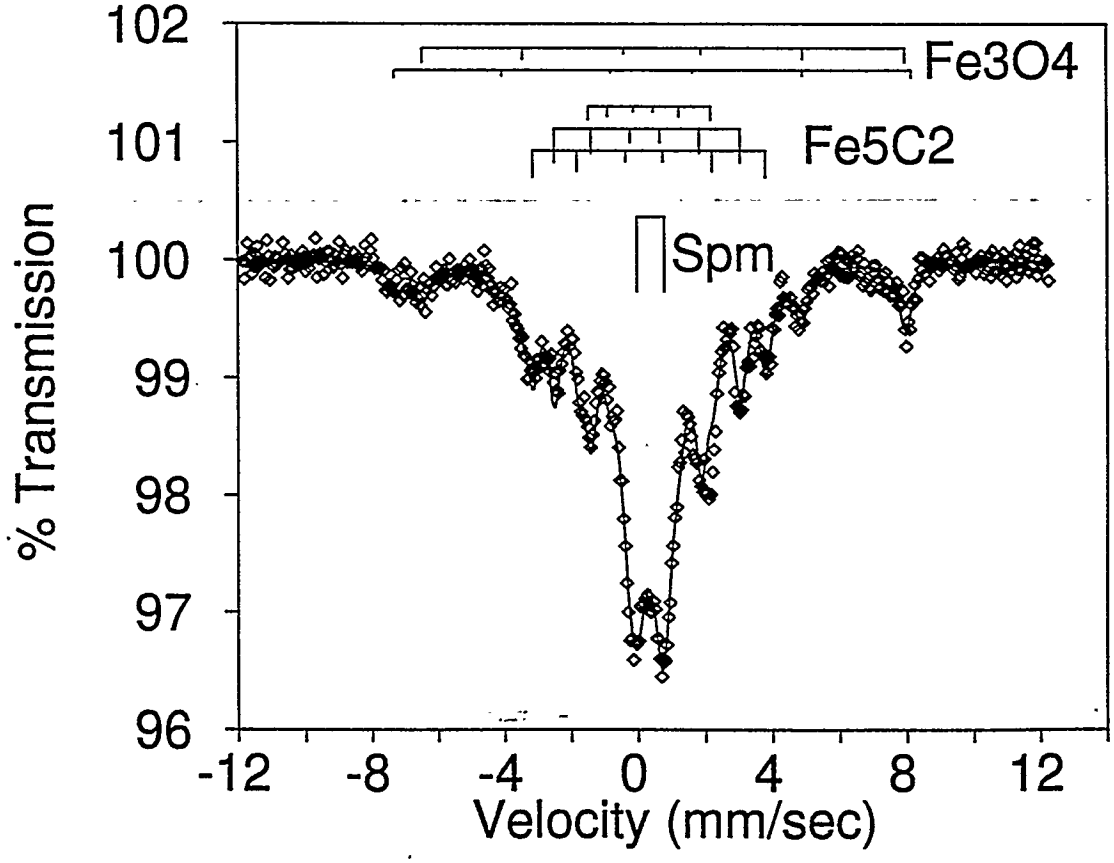
Mössbauer Analysis UK96-032

D.B.Bukur, Texas A&M University

SA-2715,TOS=138h,100Fe/3Cu/4K/16SiO,batch-3

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.37	0.80	0.85	43
Fe5C2	215	0.25	0.07	0.44	16
Fe5C2	172	0.24	0.03	0.44	20
Fe5C2	113	0.24	0.09	0.44	8
Fe3O4	479	0.37	0.00	0.44	4
Fe304	447	0.69	0.00	0.44	9

Mössbauer run MK2301 on sample 96-022 at 293K



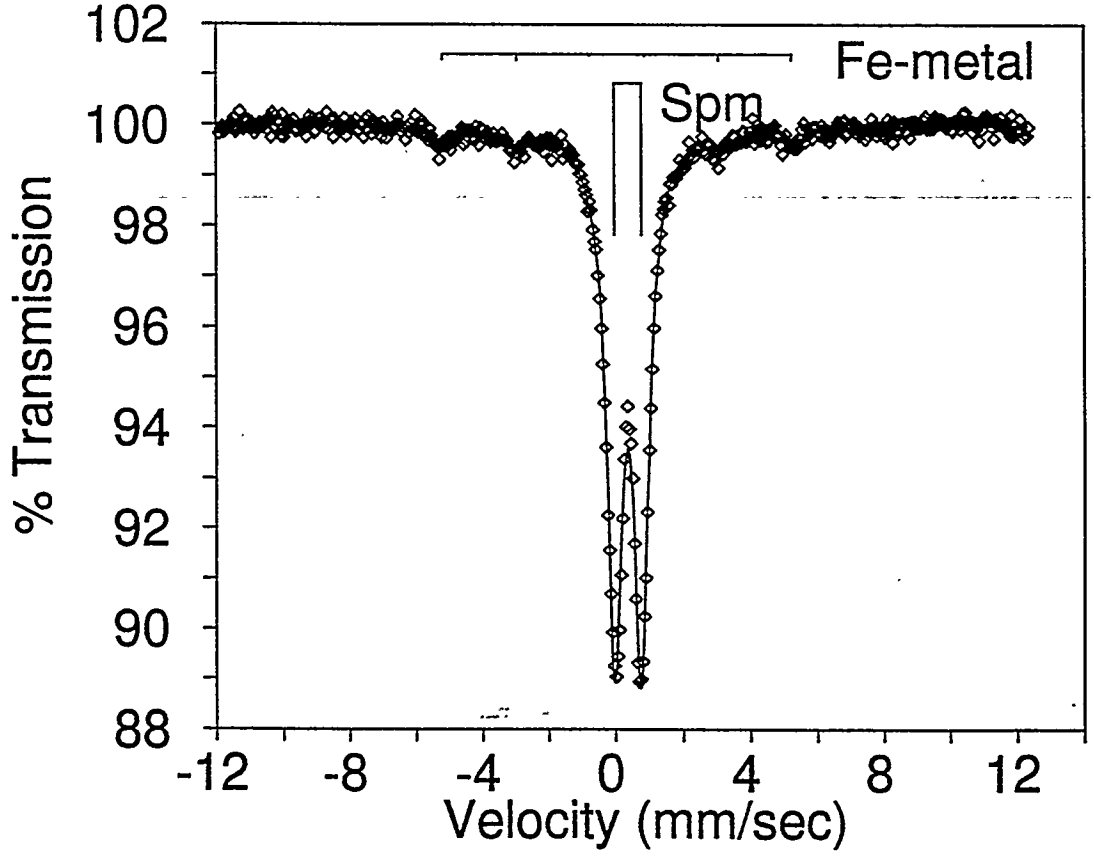
Mössbauer Analysis UK96-033

D.B.Bukur, Texas A&M University

SA-2615, TOS=0h, 100Fe/5Cu/6K/24SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.36	0.79	0.54	92
Fe-metal	323	0.02	-0.02	0.66	8

Mössbauer run MK2305 on sample 96-023 at 293K



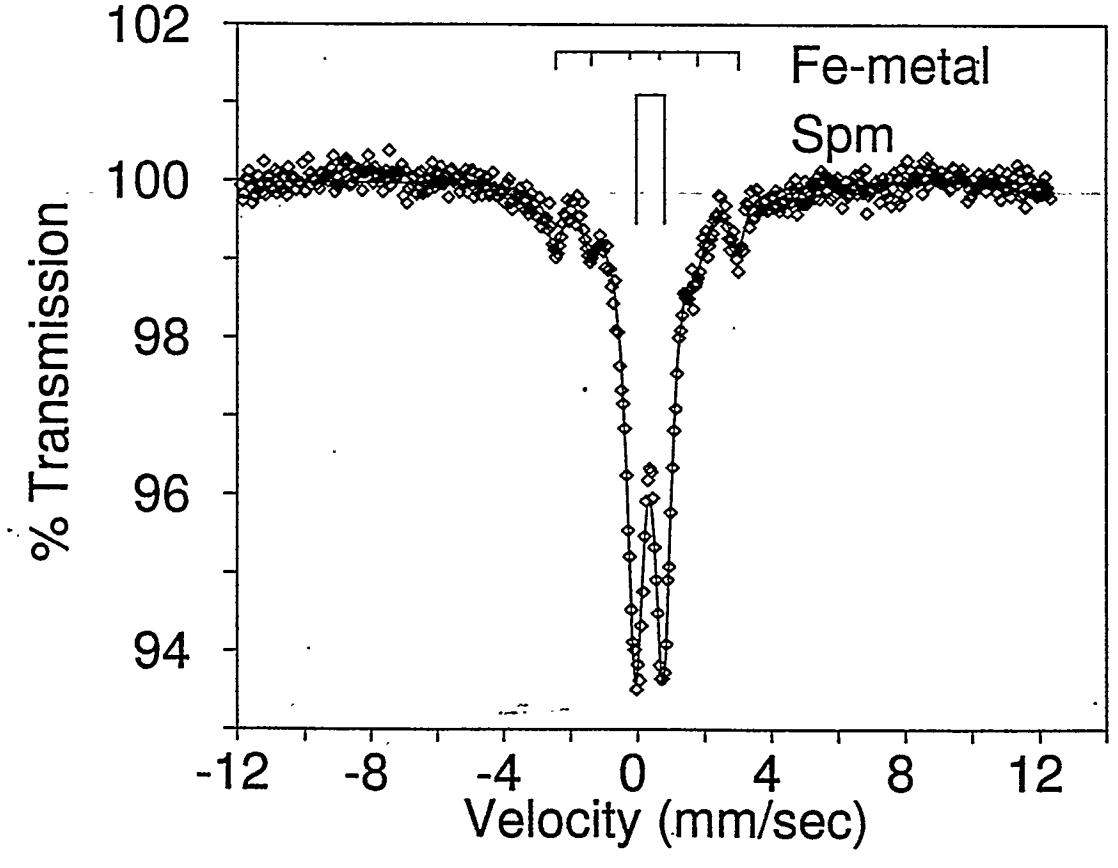
Mössbauer Analysis UK96-034

D.B.Bukur, Texas A&M University

SA-2615, TOS=119h, 100Fe/5Cu/6K/24SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.35	0.83	0.61	83
Fe2.2C	169	0.22	0.04	0.49	17

Mössbauer run MK2306 on sample 96-024 at 293K



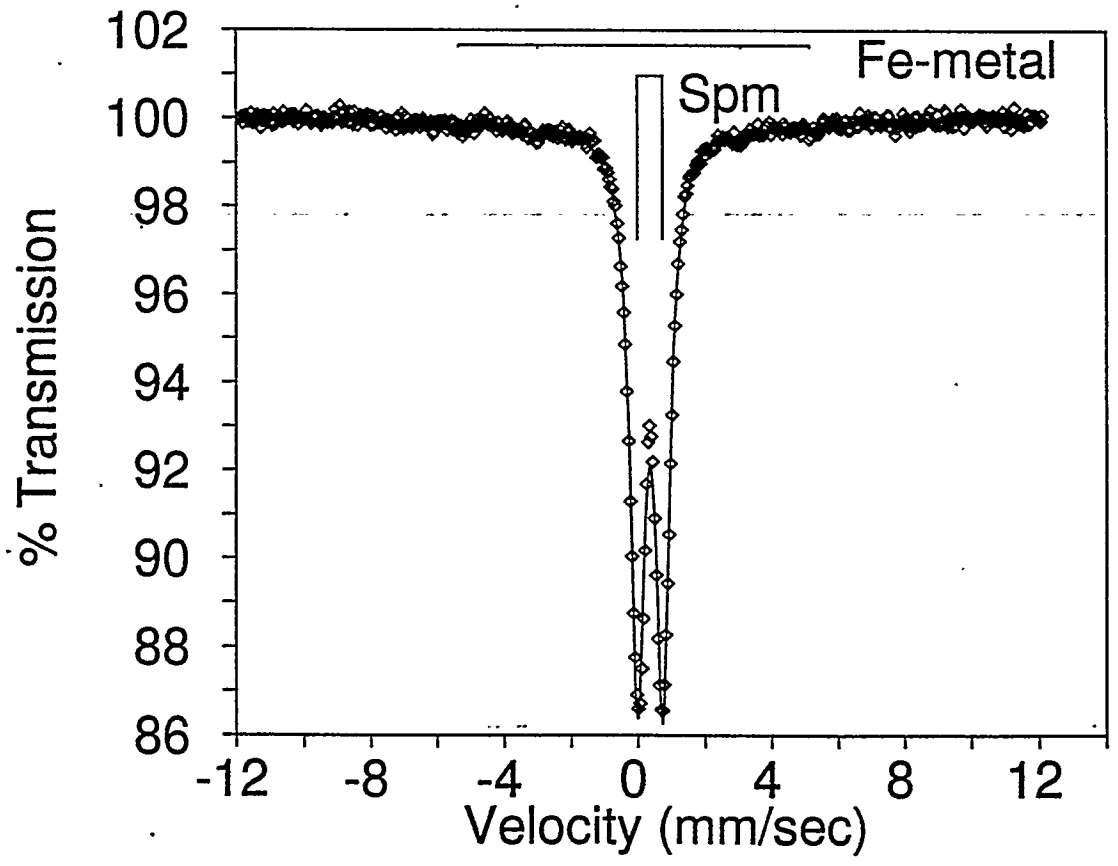
Mössbauer Analysis UK96-035

D.B.Bukur, Texas A&M University

SB-2695, TOS=0h, 100Fe/3Cu/6K/16SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.35	0.75	0.51	95
Fe-metal	325	-0.03	-0.08	0.86	5

Mössbauer run MK2310 on sample 96-025 at 293K



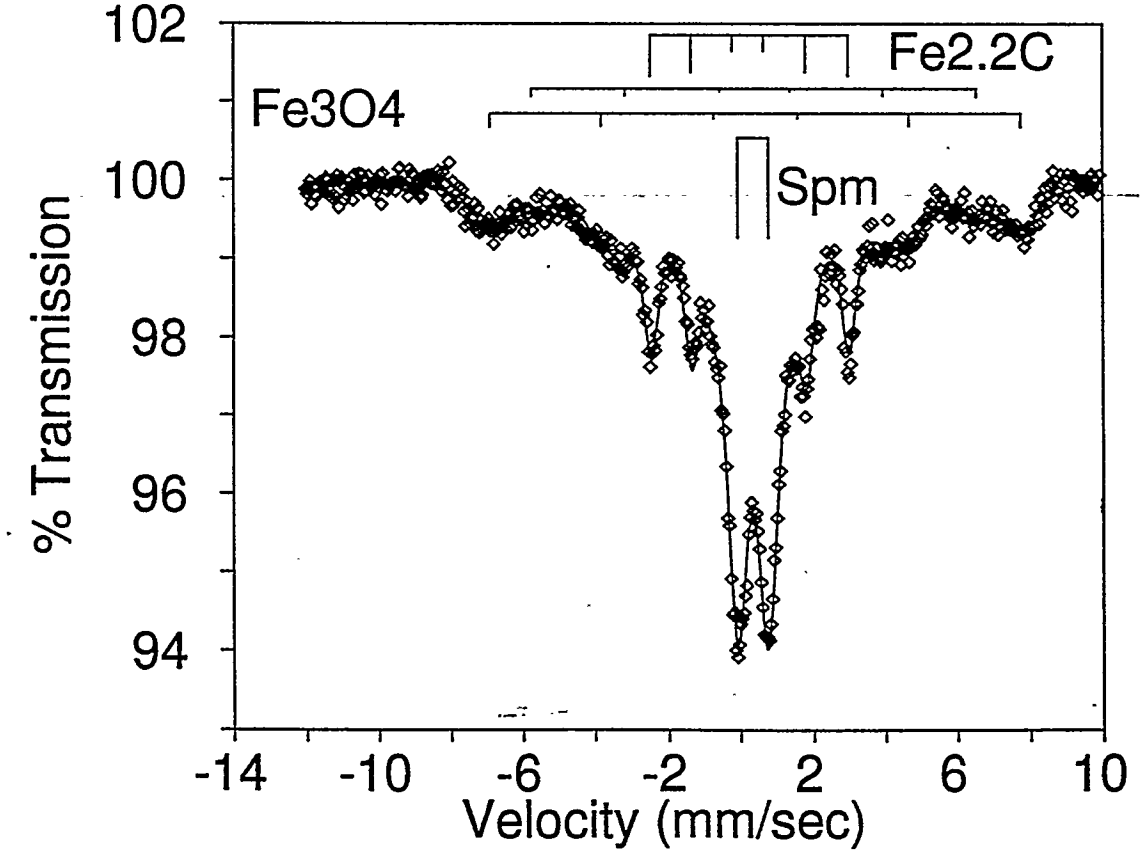
Mössbauer Analysis UK96-036

D.B.Bukur, Texas A&M University

SB-2695,TOS=142h,100Fe/3Cu/4K/16SiO 2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.35	0.84	0.72	47
Fe2.2C	169	0.25	0.02	0.51	29
Fe3O4	454	0.44	0.00	0.86	16
Fe3O4	387	0.40	0.00	0.78	8

Mössbauer run MK2311 on sample 96-026 at 293K



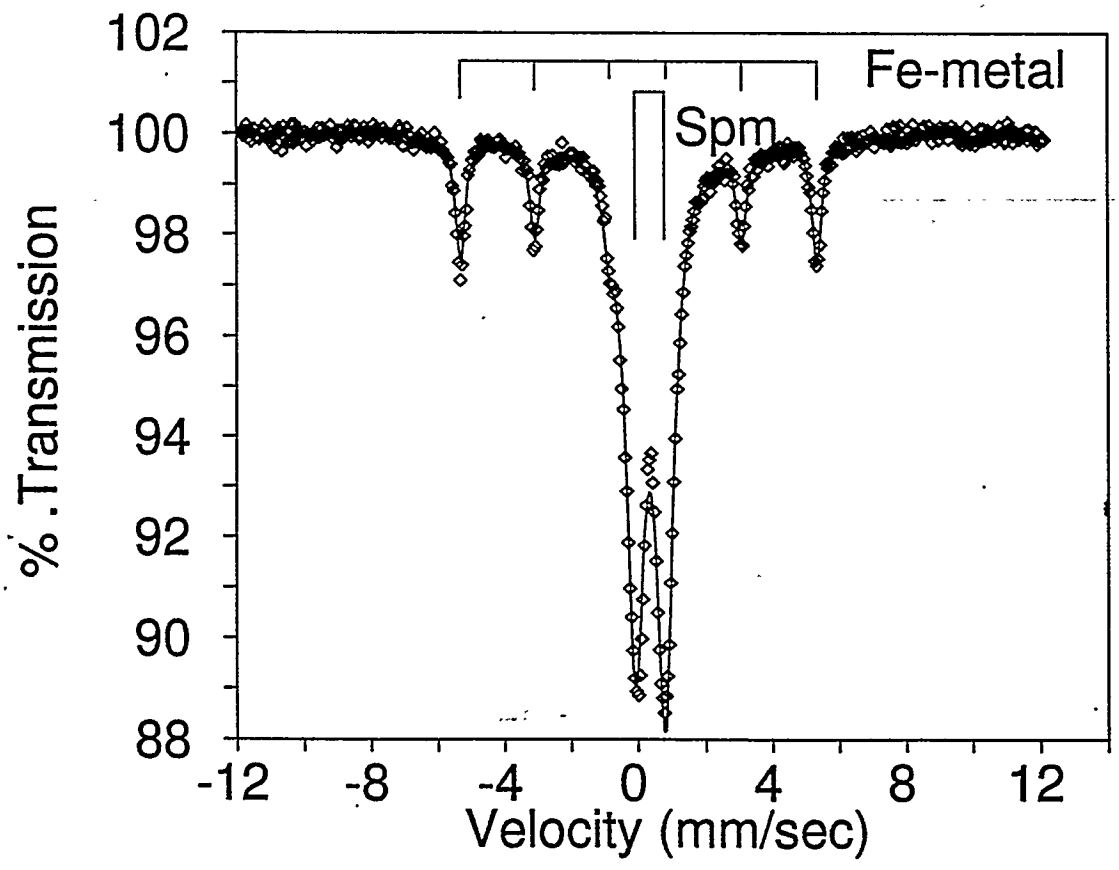
Mössbauer Analysis UK96-037

D.B.Bukur, Texas A&M University

SA-2215, TOS=0h, 100Fe/5Cu/5K/2Ca/24SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.35	0.86	0.64	81
Fe-metal	330	0.00	0.00	0.35	19

Mössbauer run MK2312 on sample 96-027 at 293K



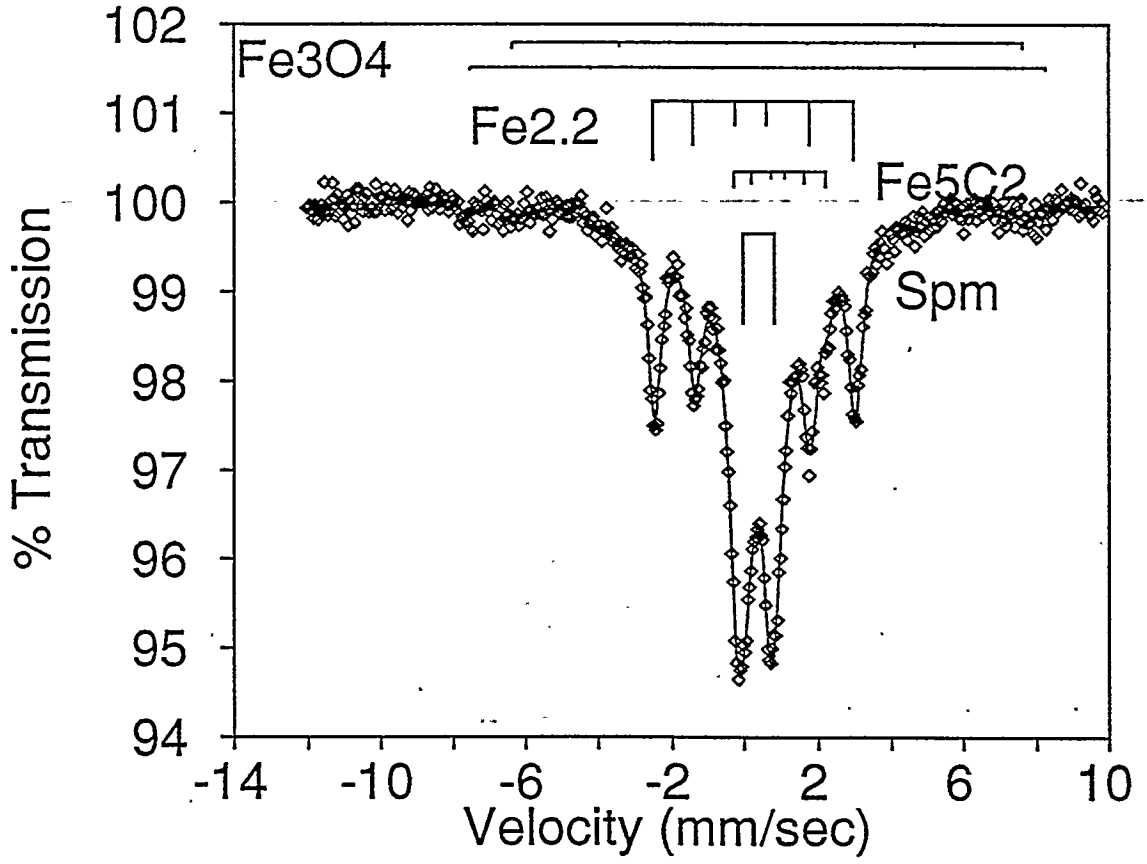
Mössbauer Analysis UK96-038

D.B.Bukur, Texas A&M University

SA-2215, TOS=550h, 100Fe/5Cu/5K/2Ca/24SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.35	0.86	0.68	44
Fe2.2C	170	0.25	0.03	0.47	40
Fe3O4	488	0.40	0.00	0.47	2
Fe3O4	433	0.66	0.00	0.47	4
Fe5C2	77	0.94	0.03	0.47	10

Mössbauer run MK2313 on sample 96-028 at 293K



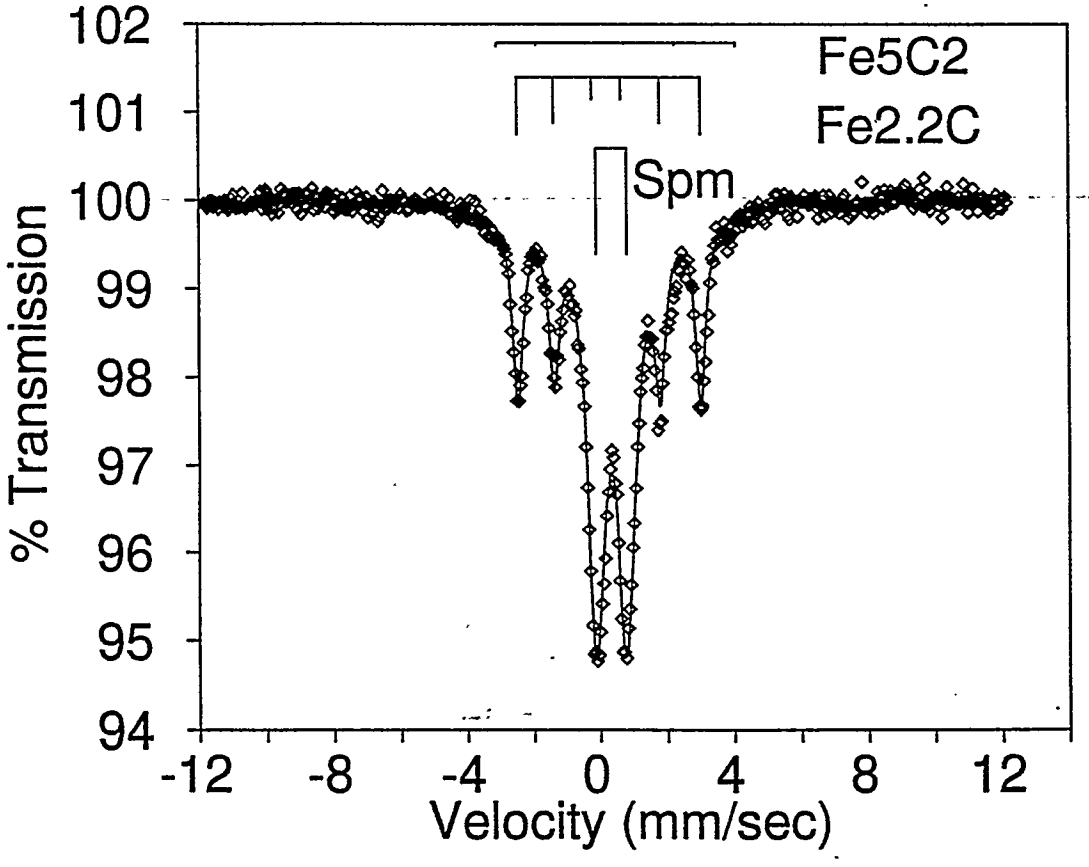
Mössbauer Analysis UK96-039

D.B.Bukur, Texas A&M University

SA-2215,TOS=693h,100Fe/5Cu/5K/2Ca/24SiO2,batch-3

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.36	0.91	0.64	58
Fe2.2C	170	0.24	0.03	0.39	39
Fe5C2	222	0.37	0.16	0.47	3

Mössbauer run MK2314 on sample 96-029 at 293K



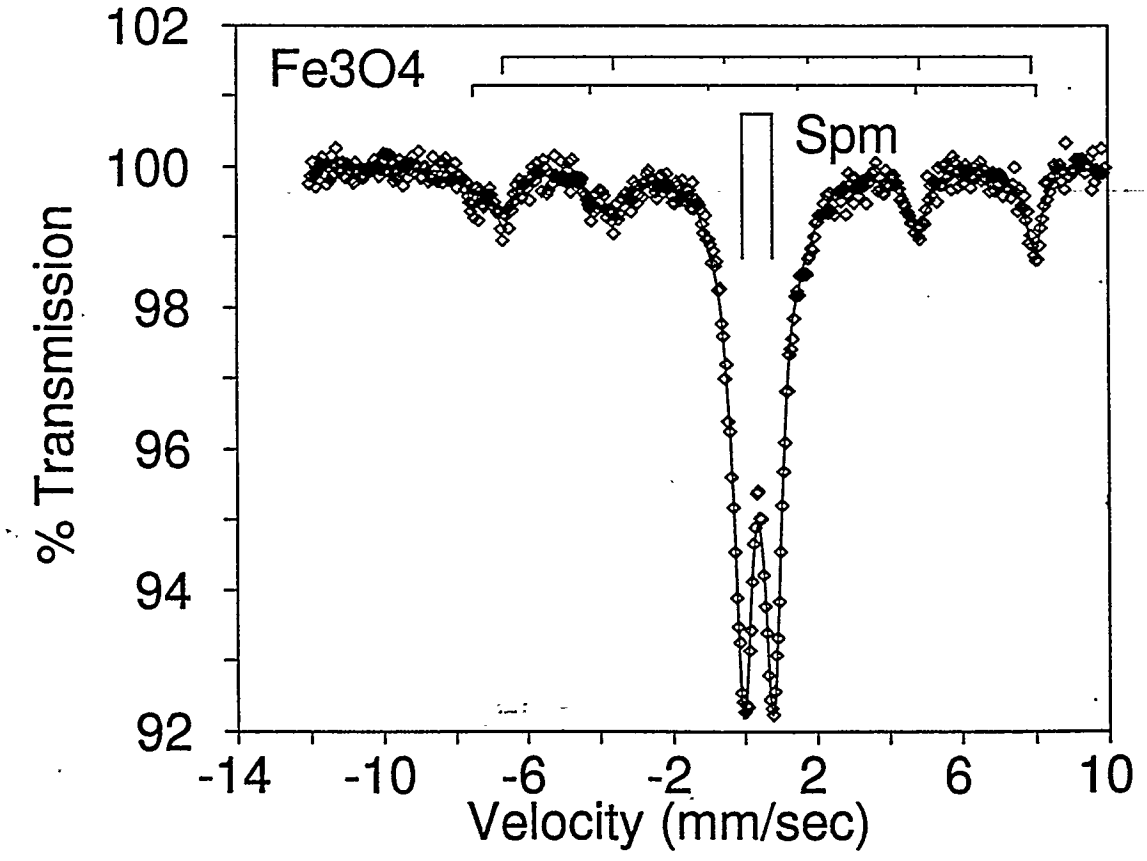
Mössbauer Analysis UK96-040

D.B.Bukur, Texas A&M University

SA-3155, TOS=0h, 100Fe/5Cu/6K/24SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.36	0.83	0.63	79
Fe3O4	481	0.27	0.00	0.29	5
Fe3O4	451	0.63	0.00	0.61	16

Mössbauer run MK2317 on sample 96-030 at 293K



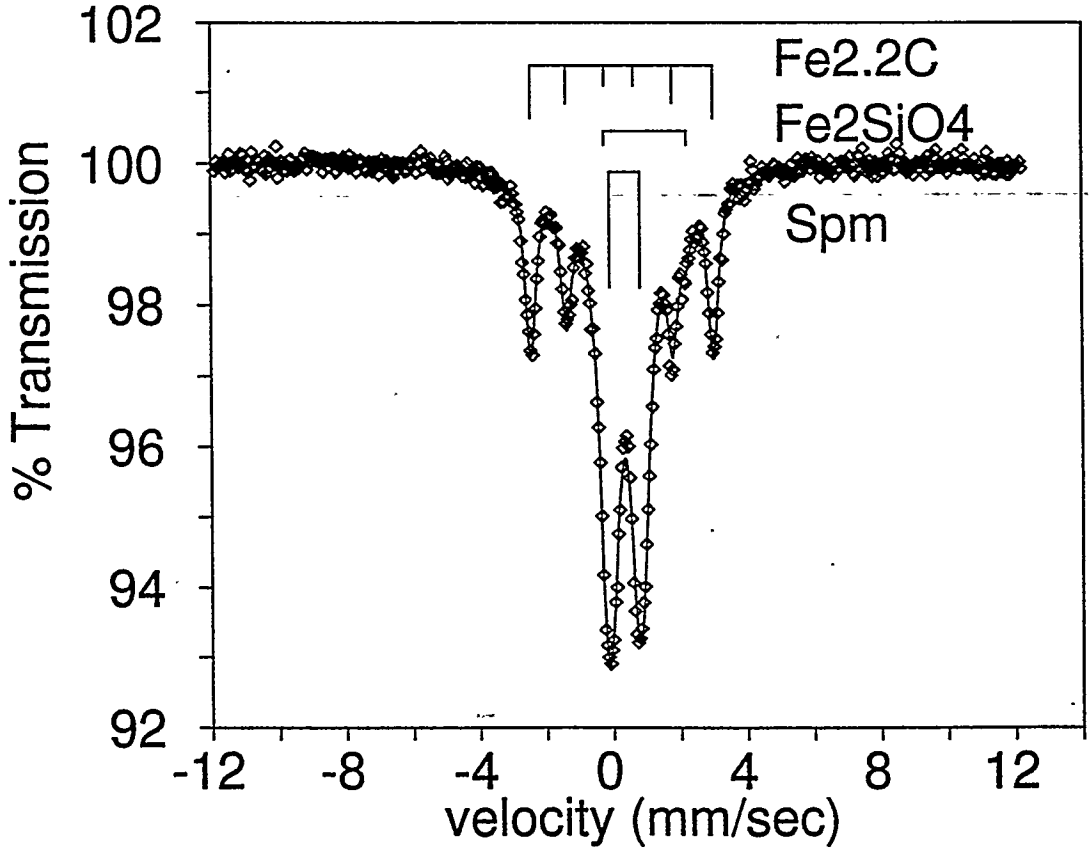
Mössbauer Analysis UK96-041

D.B.Bukur, Texas A&M University

SA-3155, TOS=400h, 100Fe/5Cu/6K/24SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.37	0.90	0.62	62
Fe2.2C	169	0.23	0.04	0.39	34
Fe2SiO4?		0.94	2.48	0.40	4

Mössbauer run MK231.87 on sample 96-031 at 293K



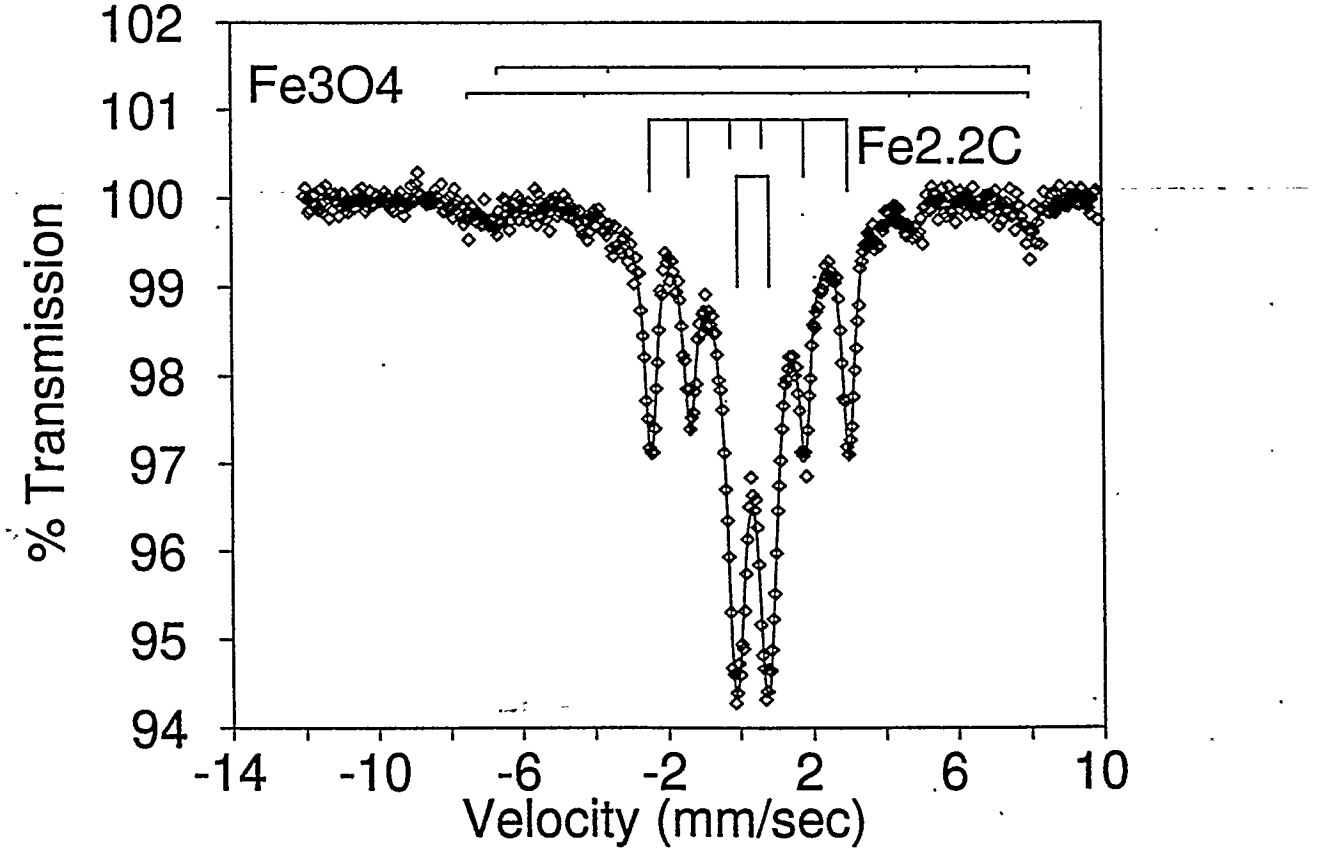
Mössbauer Analysis UK96-042

D.B.Bukur, Texas A&M University

SB-3115, TOS=354h, 100Fe/3Cu/6K/16SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.36	0.87	0.64	49
Fe2.2C	169	0.24	0.04	0.41	42
Fe3O4	479	0.25	0.00	0.31	2
Fe3O4	454	0.68	0.00	0.62	6

Mössbauer run MK2320 on sample 96-032 at 293K



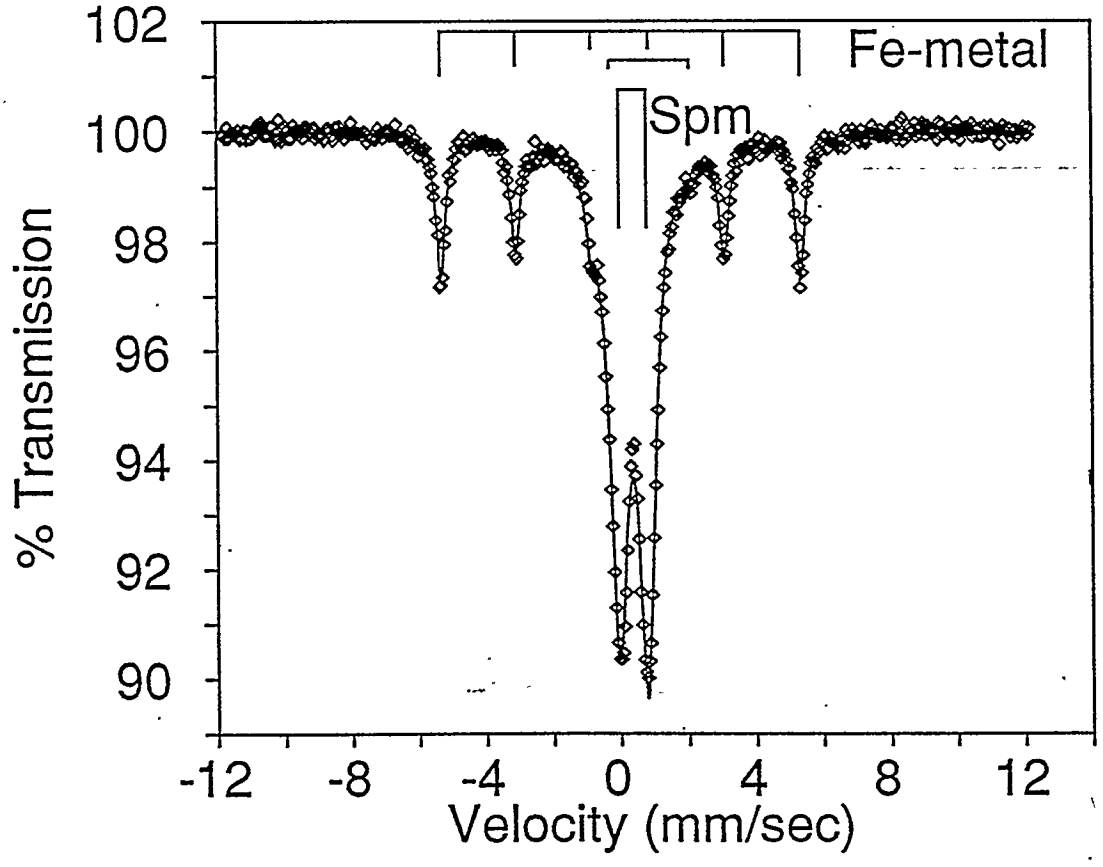
Mössbauer Analysis UK96-043

D.B.Bukur, Texas A&M University

SB-3425, TOS=0 .h, 100Fe/3Cu/4K/16SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.36	0.82	0.62	76
Fe-metal	330	0.00	0.01	0.33	22
Fe2SiO4?		0.87	2.32	0.62	2

Mössbauer run MK2322 on sample 96-033 at 293K



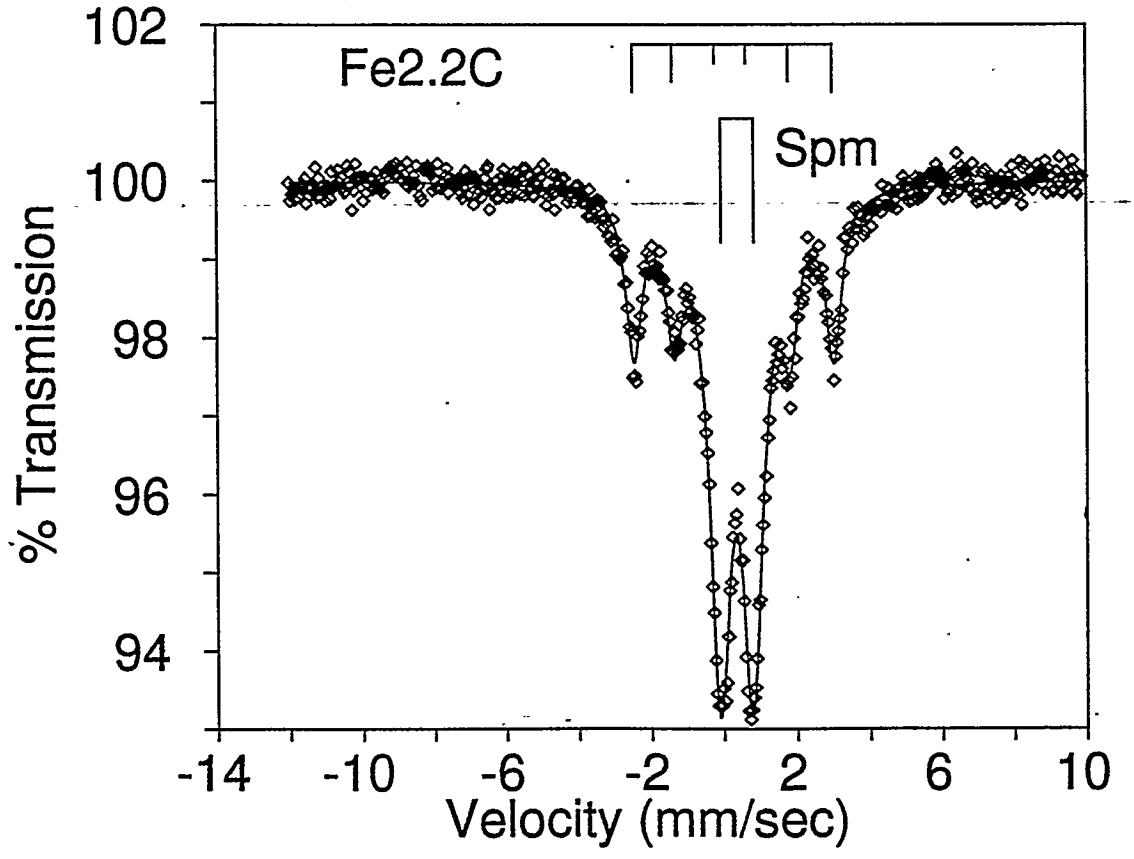
Mössbauer Analysis UK96-044

D.B.Bukur, Texas A&M University

SB-3425, TOS=1114h; 100Fe/3Cu/4K/16SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.35	0.90	0.69	63
Fe2.2C	169	0.24	0.03	0.53	37

Mössbauer run MK2321 on sample 96-034 at 293K



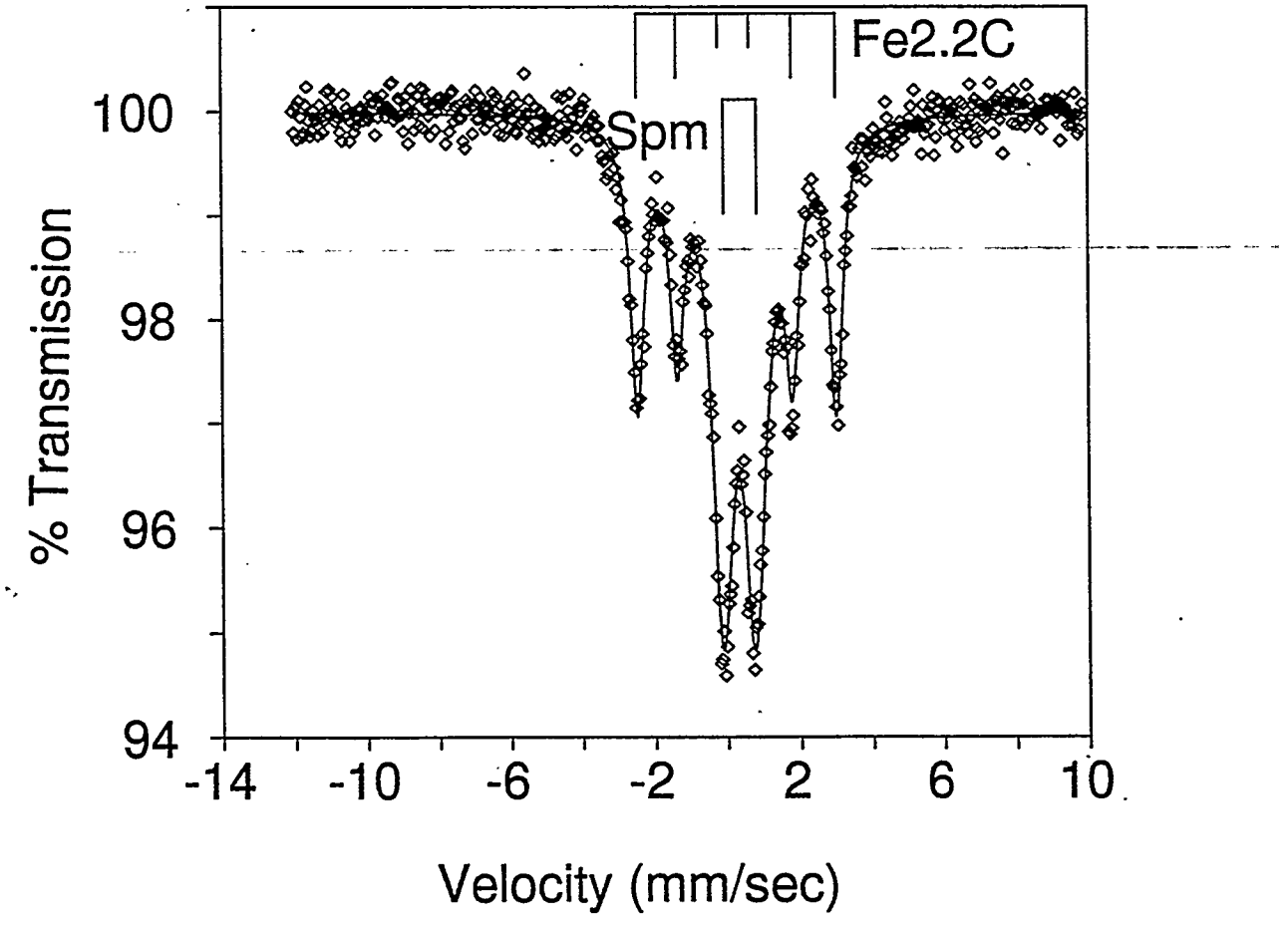
Mössbauer Analysis UK96-045

D.B.Bukur, Texas A&M University

SB-3425, TOS=233h, 100Fe/3Cu/4K/16SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.37	0.90	0.72	52
Fe2.2C	169	0.24	0.03	0.45	48

Mössbauer run MK2323 on sample 96-035 at 293K



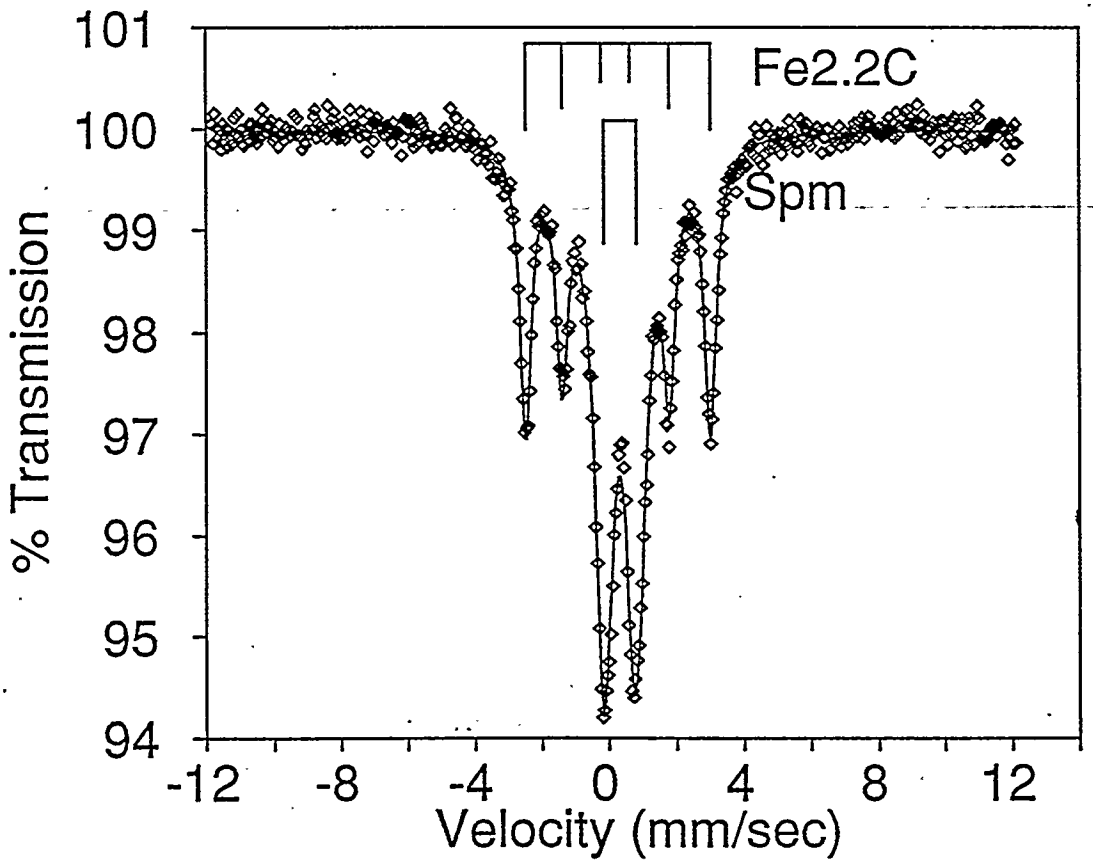
Mössbauer Analysis UK96-046

D.B.Bukur, Texas A&M University

SB-3425, TOS=330h, 100Fe/3Cu/4K/16SiO2

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.36	0.95	0.68	53
Fe2.2C	170	0.24	0.03	0.43	47

Mössbauer run MK2324 on sample 96-036 at 293K



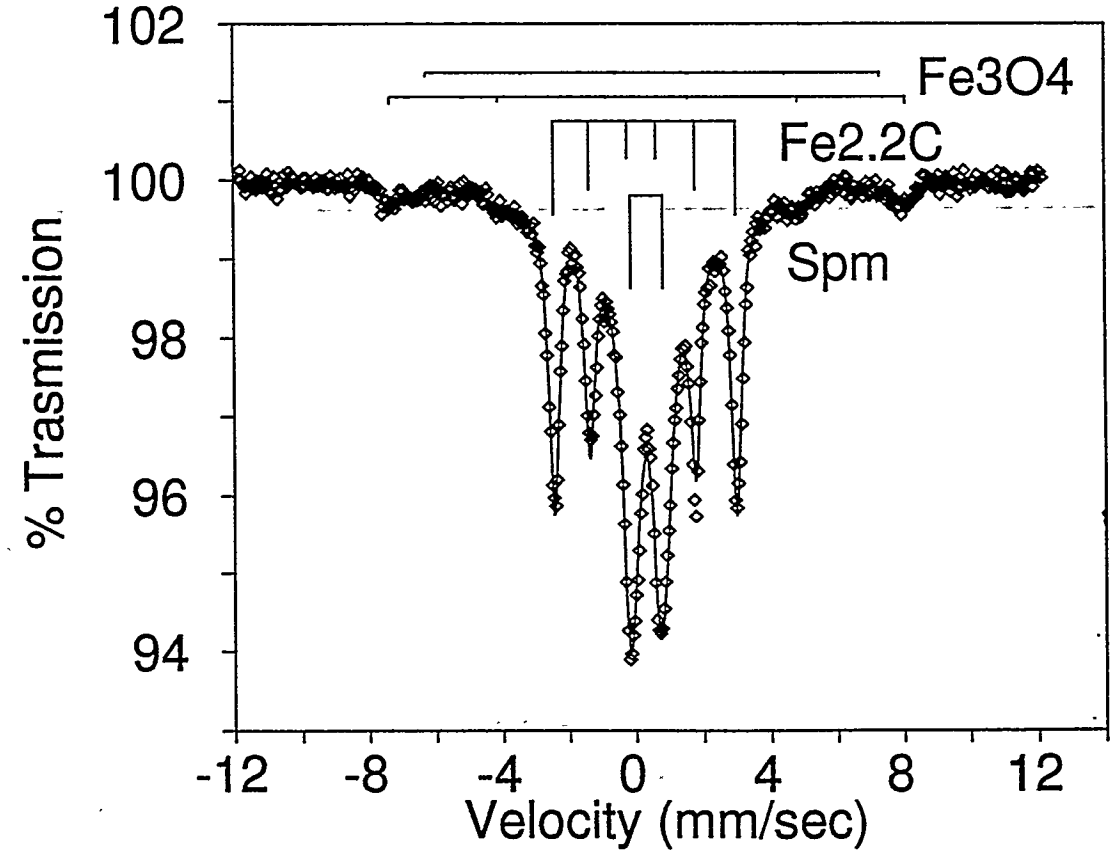
Mössbauer Analysis UK96-047

D.B.Bukur, Texas A&M University

SB-3425,TOS=384h,100Fe/3Cu/4K/16SiO2,batch-4

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.36	0.94	0.67	41
Fe2.2C	169	0.24	0.04	0.39	48
Fe3O4	478	0.36	0.00	0.56	5
Fe3O4	421	0.51	0.00	1.12	6

Mössbauer run MK2325 on sample 96-037 at 293K



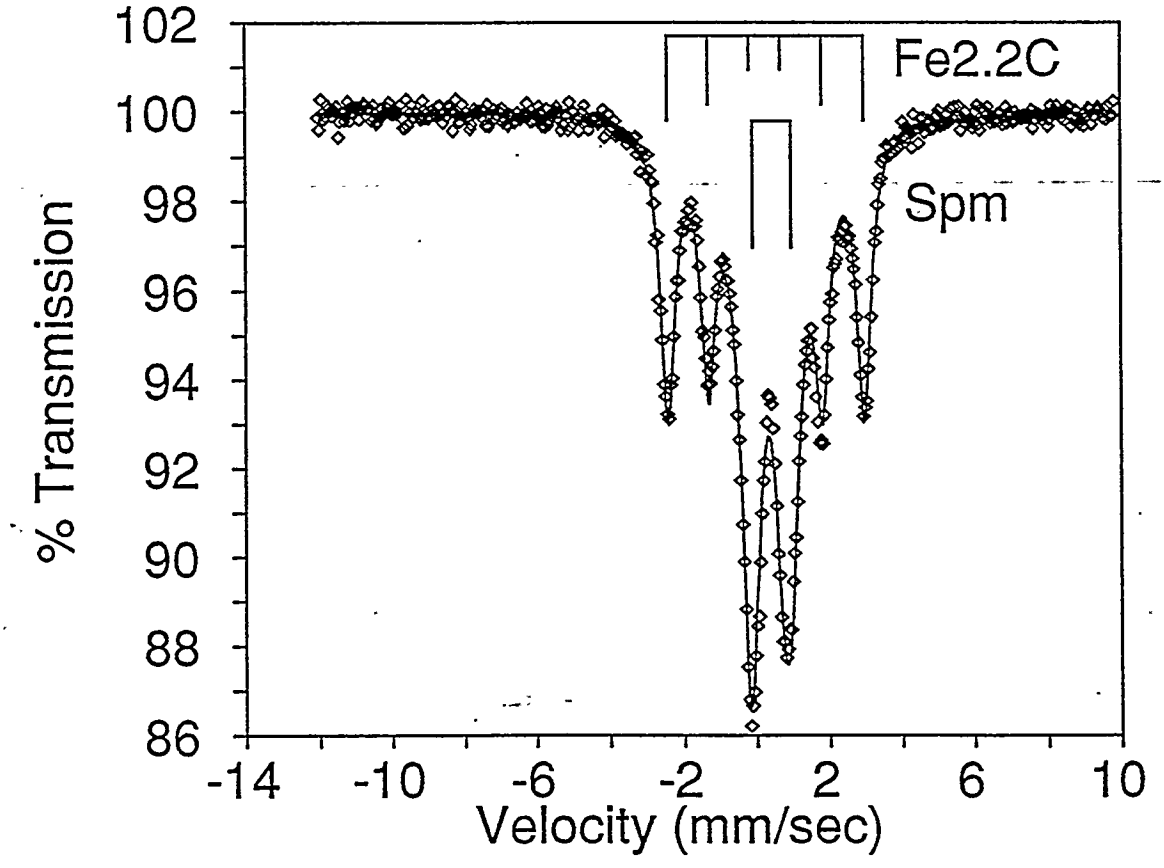
Mössbauer Analysis UK96-048

D.B.Bukur, Texas A&M University

FB-2975,Top,100Fe/5Cu/6K/24SiO2,cal@400C,eor=120

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.36	1.05	0.68	54
Fe2.2C	167	0.25	0.02	0.47	46

Mössbauer run MK2326 on sample 96-038 at 293K



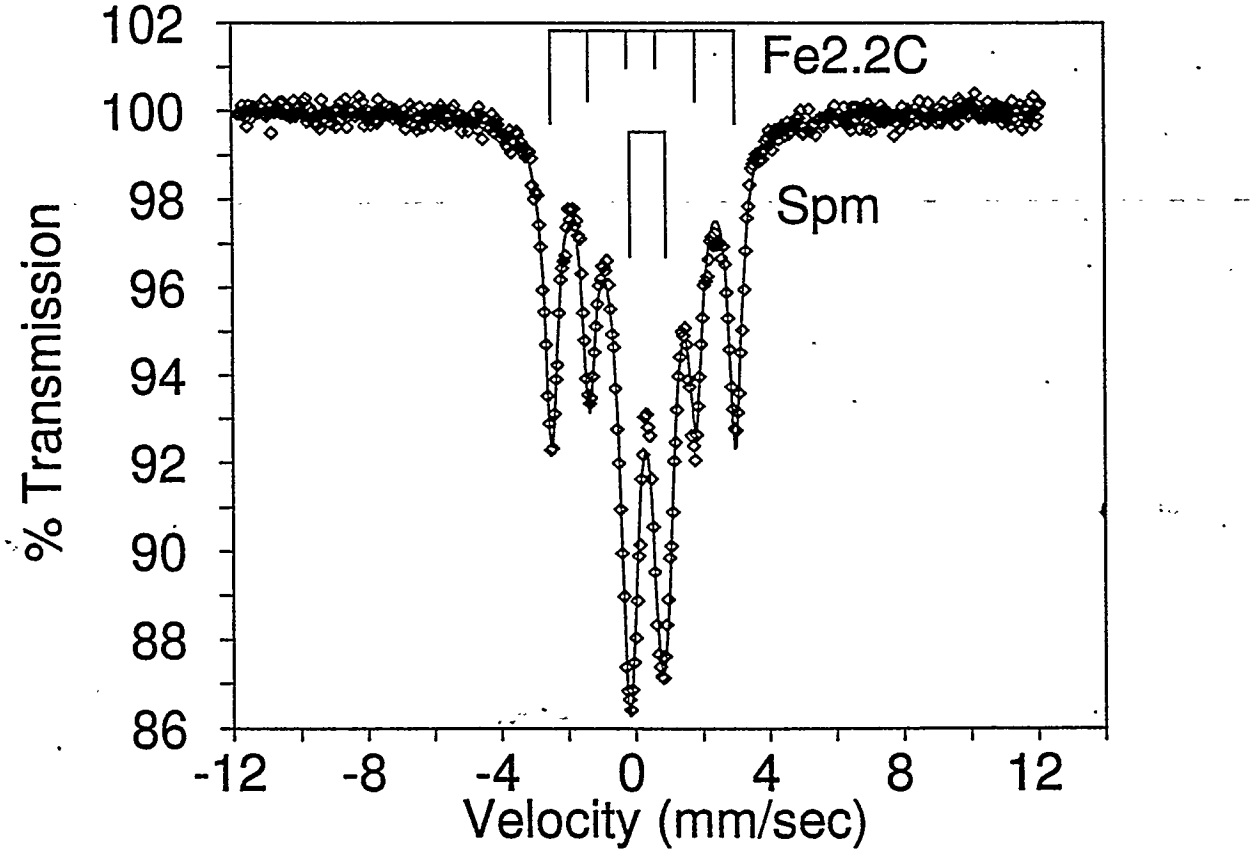
Mössbauer Analysis UK96-049

D.B.Bukur, Texas A&M University

FB-2975,BOTTOM,100Fe/5Cu/6K/24SiO2,Cal@400C,EOR

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.36	1.04	0.71	53
Fe2.2C	170	0.24	0.02	0.47	47

Mössbauer run MK2332 on sample 96-039 at 293K



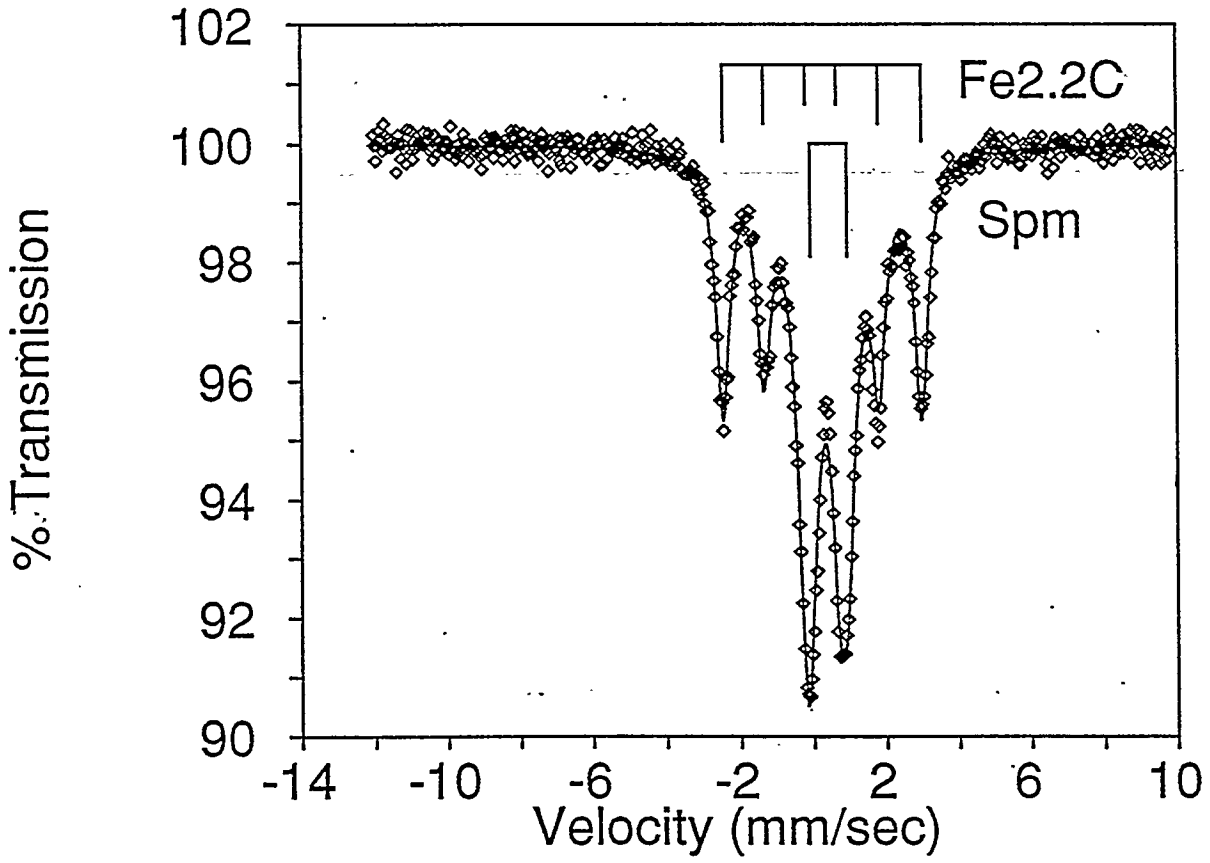
Mössbauer Analysis UK96-050

D.B.Bukur, Texas A&M University

FA-3305,TOP,100Fe/3Cu/4K/16SiO2,Cal@400C,EOR=120

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.36	1.01	0.65	55
Fe2.2C	168	0.24	0.02	0.45	45

Mössbauer run MK2329 on sample 96-040 at 293K



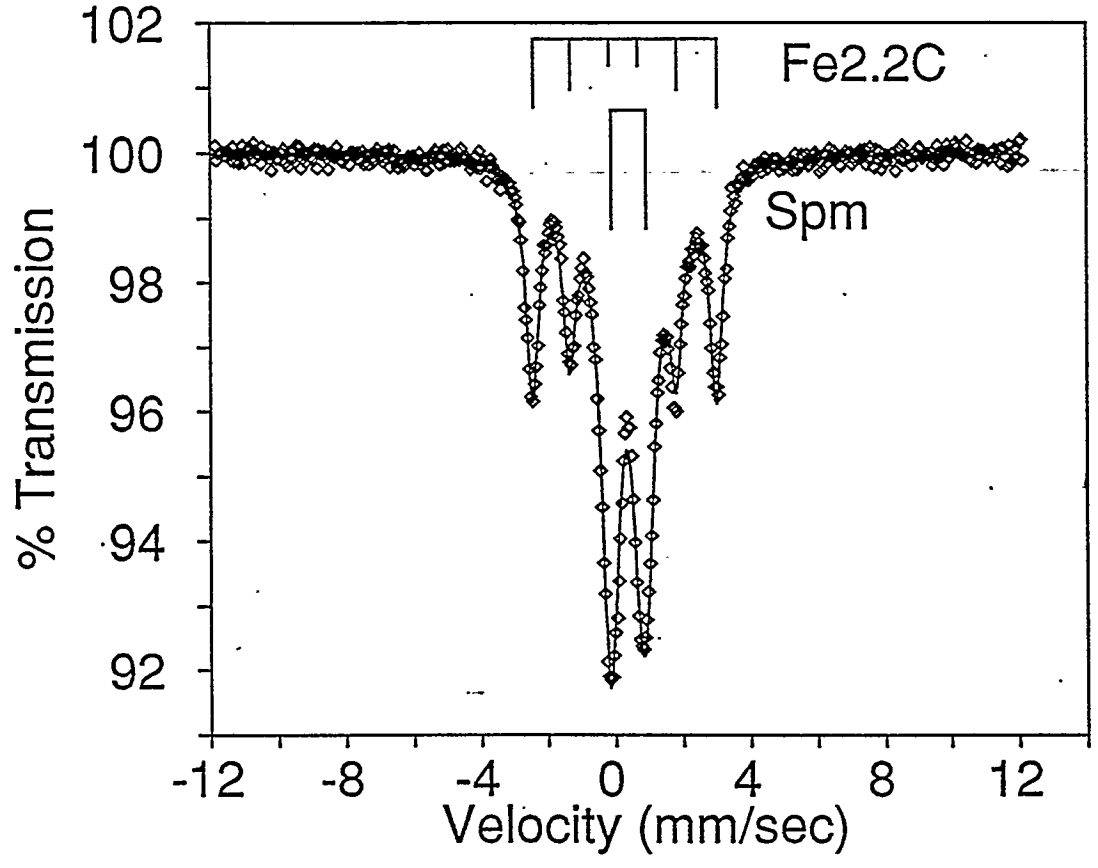
Mössbauer Analysis UK96-051

D.B.Bukur, Texas A&M University

FA-3305,Bottom,100Fe/3Cu/4K/16SiO2,Cal@400C

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.39	1.02	0.67	52
Fe2.2C	169	0.25	0.02	0.46	48

Mössbauer run MK2330 on sample 96-041 at 293K



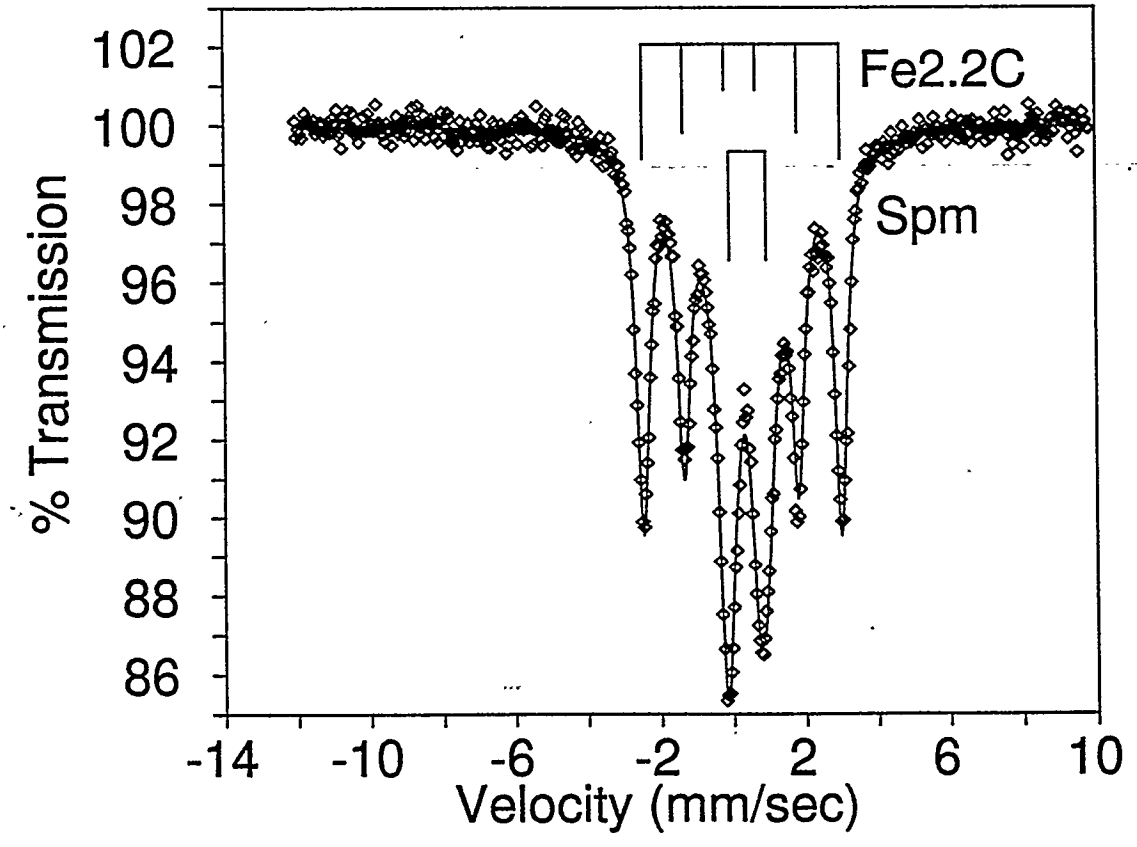
Mössbauer Analysis UK96-052

D.B.Bukur, Texas A&M University

FA-3495,TOP,100Fe/3Cu/4K/16SiO2,Cal@700C

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.37	1.04	0.69	45
Fe2.2C	169	0.24	0.02	0.43	55

Mössbauer run MK2327 on sample 96-042 at 293K



Mössbauer Analysis UK96-53

D.B.Bukur, Texas A&M University

FA-3495, Bottom, 100Fe/3Cu/4K/16SiO2,Cal@700C

Phase	H0 kGauss	I.S. mm/s	Q.S. mm/s	Wdth mm/s	%Fe
Spm oxide		0.39	0.97	0.71	42
e'-Fe2.2C	169	0.24	0.03	0.43	40
Fe3O4	484	0.30	0.00	0.29	5
Fe3O4	453	0.63	0.00	0.48	13

Mössbauer run MK2328 on sample 96-043 at 293K