Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supplementary information (SI) to the paper titled

Invar-like thermal expansion in $TiFe_2$ alloys driven by nanoscale magnetic inhomogeneity

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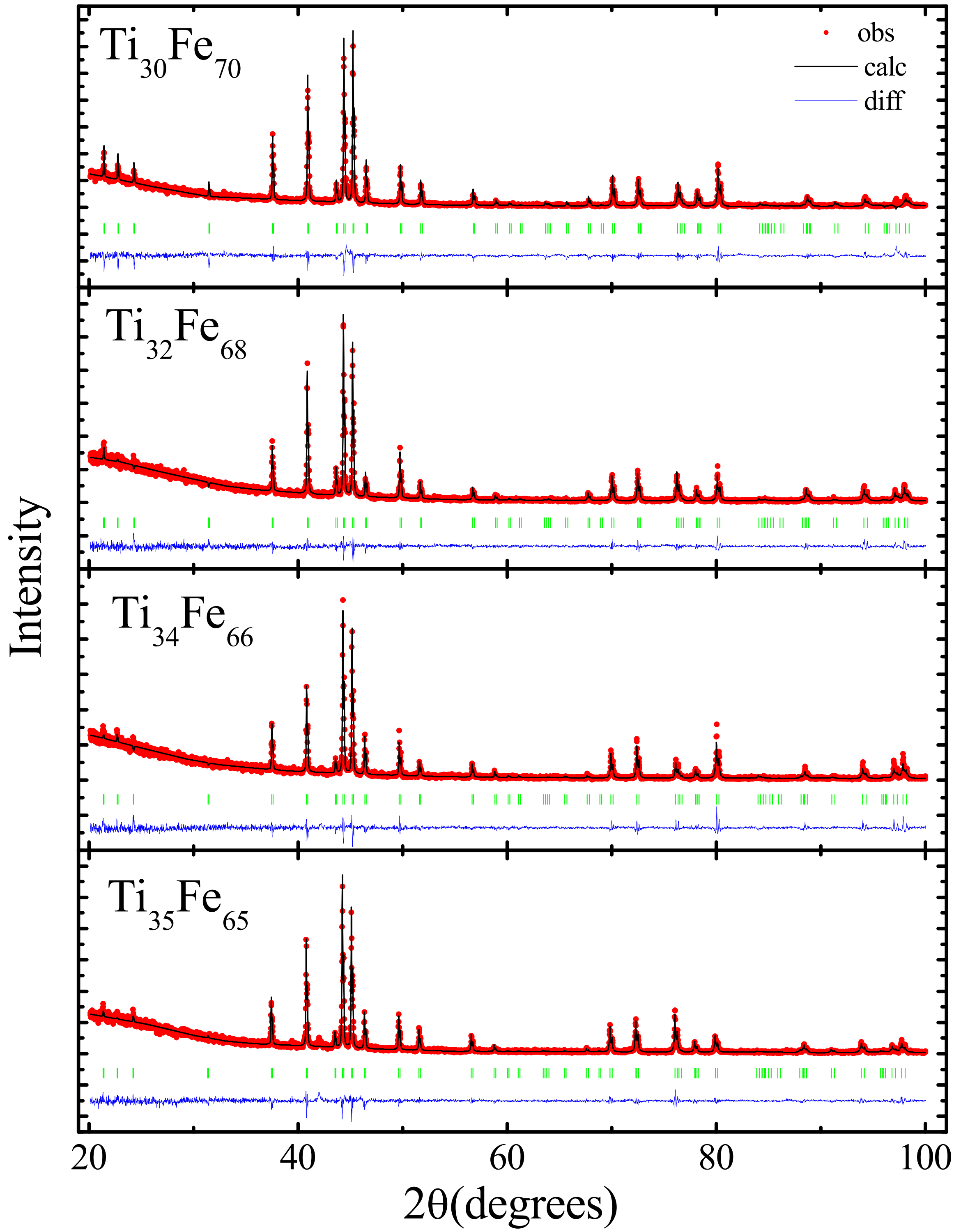

FIG. S1. Le bail refined XRD plots of (a) $Ti_{30}Fe_{70}$ (b) $Ti_{32}Fe_{68}$ (c) $Ti_{34}Fe_{66}$ (d) $Ti_{35}Fe_{65}$

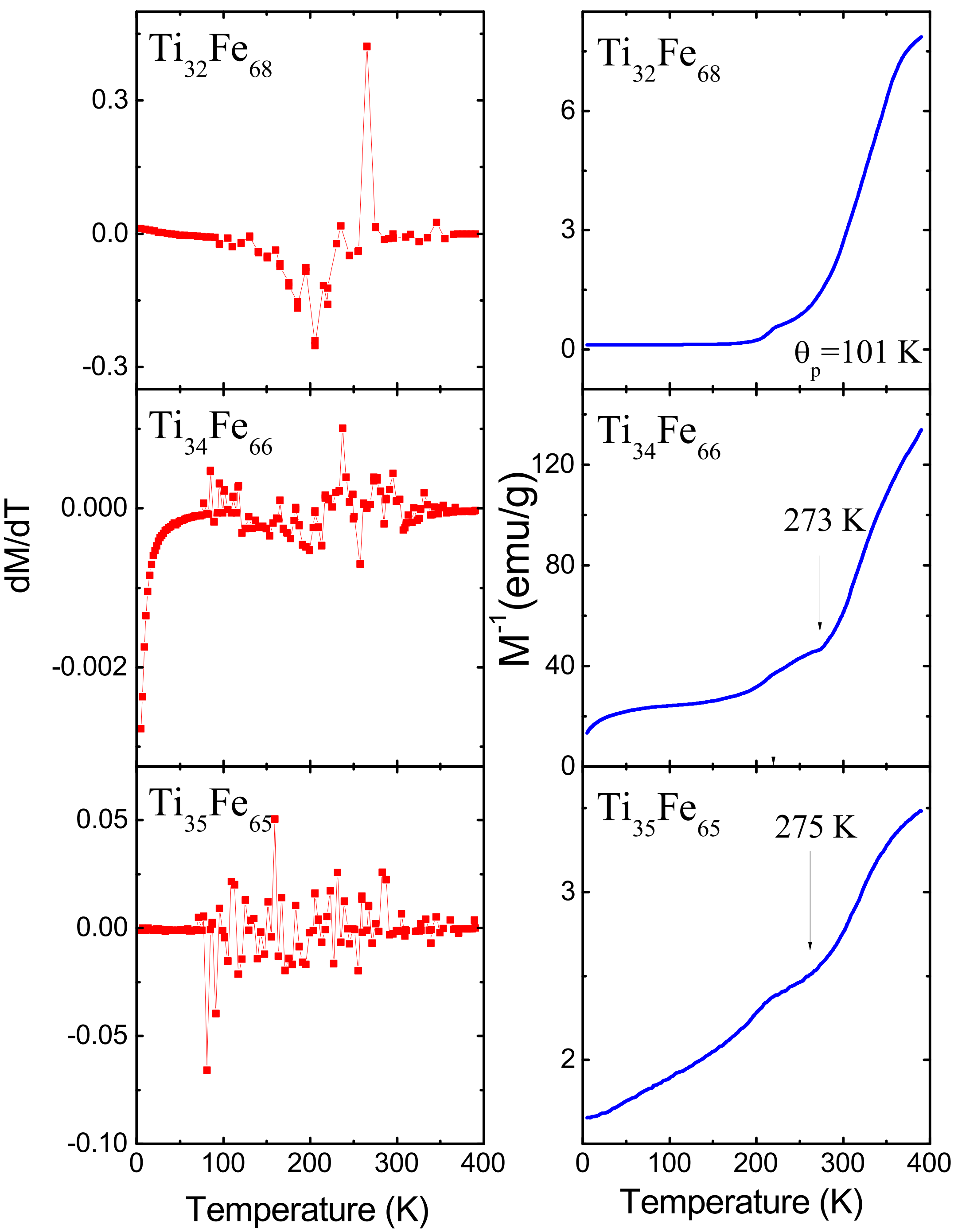

FIG. S2. The derivative of magnetization and inverse magnetization as a function of temperature for the $Ti_{33-x}Fe_{67+x}$ (x= -2, -1, 1). Since magnetization in the paramagnetic region was not recorded for $Ti_{30}Fe_{70}$, the inverse magnetization and derivative plot is not shown for this sample.

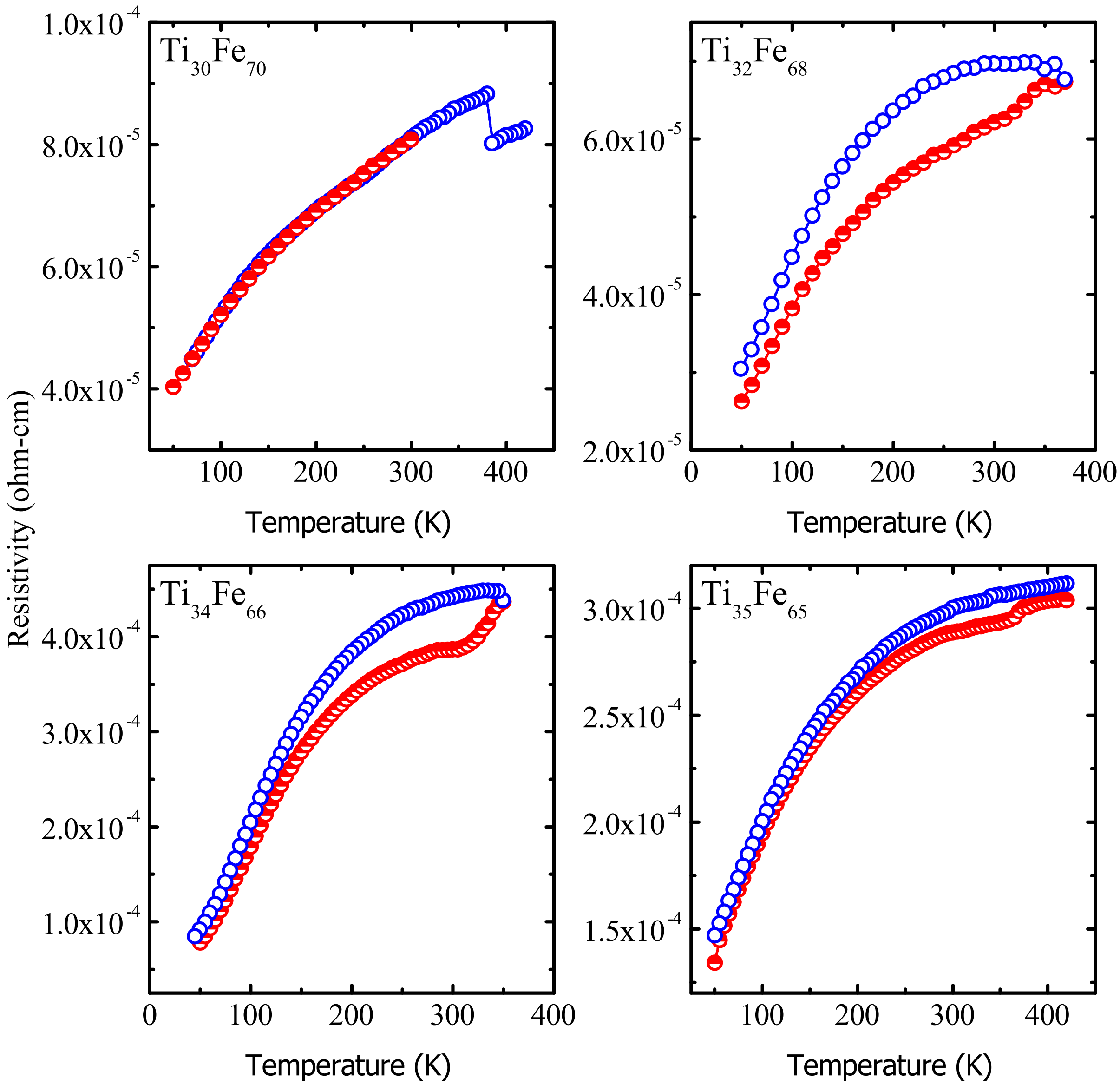

FIG. S3. Resistivity as a function of temperature recorded during warming and cooling cycles for the $Ti_{33-x}Fe_{67+x}$ (x= -2, -1, 1, 3)

TABLE SI. Atomic positions, isotropic temperature factor and occupancy obtained through Rietveld refinement performed on the neutron diffraction data recorded for $Ti_{32}Fe_{68}$ at 400 K.

Atom	Wyckoff site	Atomic positions			B_{iso}	Occupancy
		x	**y**	**z**		
Ti	4f	0.3333	0.6667	0.5663	0.3239	0.1596(49)
Fe	4f	0.3333	0.6667	0.5663	0.3239	0.0098(49)
Fe	2a	0.0000	0.0000	0.0000	0.4211	0.0844(52)
Fe	6h	0.1704	0.3407	0.2500	0.4848	0.2542(76)

TABLE SII. Atomic positions, isotropic temperature factor and occupancy obtained through Rietveld refinement performed on the neutron diffraction data recorded for $Ti_{35}Fe_{65}$ at 400 K.

Atom	Wyckoff site	Atomic positions			B_{iso}	Occupancy
		x	**y**	**z**		
Ti	4f	0.3333	0.6667	0.5618	0.4583	0.1645(193)
Fe	2a	0.0000	0.0000	0.0000	0.4254	0.0802(40)
Fe	2a	0.0000	0.0000	0.0000	0.4254	0.0031(40)
Fe	6h	0.1719	0.3437	0.2500	0.4883	0.2536(78)

TABLE SIII. Crystallographic data, magnetic moment and reliability factors for $Ti_{32}Fe_{68}$

Temperature (K)	Lattice constants		Magnetic moment	Rp
	a	**c**		
4	4.7762(18)	7.8150(32)	1.256(92)	G.O.F. = 0.11
				$R_p = 8.15$
				$wR_p = 11.27$
200	4.7835(18)	7.8132(33)	1.107(100)	
225	4.7851(17)	7.8131(33)	1.046(110)	
250	4.7867(17)	7.8134(17)	0.967(112)	
300	4.7888(17)	7.8152(33)	0.985(120)	
400	4.7943(17)	7.8221(33)	0	

TABLE SIV. Crystallographic data, magnetic moment and reliability factors for $Ti_{35}Fe_{65}$

Temperature (K)	Lattice constants		Magnetic moment	Rp
	a	**c**		
4	4.7889(20)	7.8373(36)	1.926(3)	G.O.F. = 0.11
				$R_p = 6.95$
				$wR_p = 9.5$
200	4.7967(20)	7.8344(36)	1.785(3)	
225	4.7984(20)	7.8340(36)	1.657(3)	
250	4.8000(20)	7.8336(36)	1.536(3)	
275	4.8018(20)	7.8327(36)	1.427(3)	
300	4.8029(20)	7.8331(35)	1.329(3)	
400	4.7984(18)	7.8313(35)	0(0)	

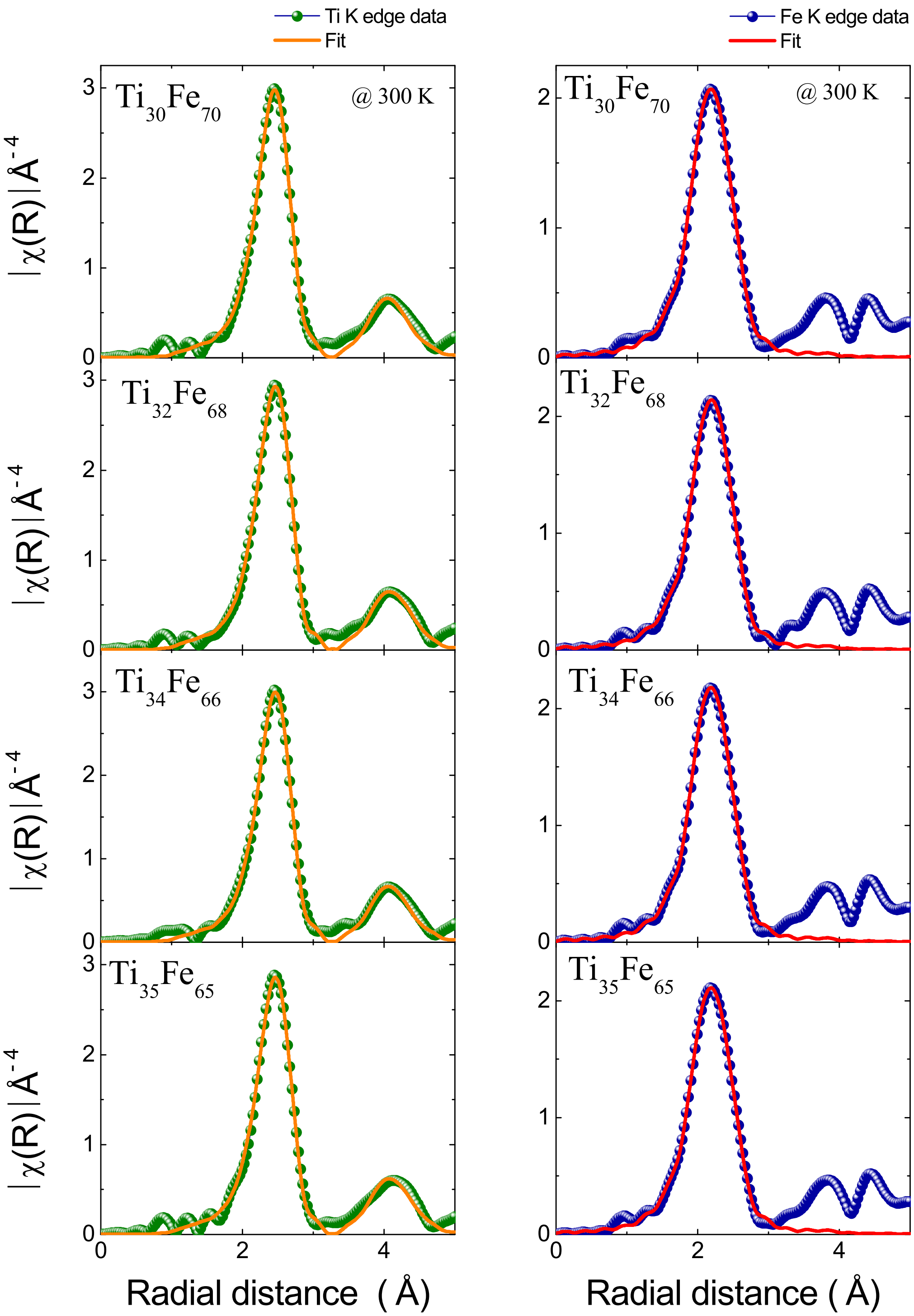

FIG. S4. Magnitude of Fourier transforms of k^3 weighted Ti (left panel) and Fe (right panel) K edge EXAFS data in $Ti_{33-x}Fe_{67+x}$ $(-2 \leq x \leq 3)$ alloys at $T = 300$ K

TABLE SV. Fitting parameters used in fitting Ti and Fe EXAFS data in $Ti_{33-x}Fe_{67+x}$ ($-2 \leq x \leq 3$) alloys. Each path has three unique parameters representing coordination number (CN), change in path length (ΔR) and mean square radial displacement (σ^2). Additionally there are two common parameters, Amplitude reduction factor, S_0^2 and ΔE_0. S_0^2 for Ti and Fe were estimated from fitting the respective metal foils and were kept fixed. CNs were also kept fixed to their bulk crystallographic values. A total of 14 parameters were varied in a single fit consisting both, Ti and Fe EXAFS data set.

Ti EXAFS			Fe EXAFS		
ΔE_0	en-Ti		ΔE_0	en-Fe	
Path	ΔR	σ^2	Path	ΔR	σ^2
Ti-Fe	delr1	ss1	Fe2a-Fe6h	delr5	ss5
Ti-Ti	delr2	ss2	Fe2a-Ti	delr1	ss1
Ti-Fe	delr3	ss3	Fe6h-Fe6h[a]	delr6	ss6
Ti-Fe	delr3	ss3	Fe6h-Fe2a	delr5	ss5
Ti-Ti	delr4	ss4	Fe6h-Fe6h[b]	− delr6	ss5
			Fe6h-Ti	delr1	ss1

[a] represents intra triangle Fe6h-Fe6h bond distance
[b] represents inter triangle Fe6h-Fe6h bond distance

TABLE SVI. Local structural parameters like coordination number (C.N.), bond distance (R), and σ^2 for $Ti_{30}Fe_{70}$ obtained through simultaneous analysis of Ti and Fe EXAFS data at different temperatures

Temperature (K)	Bond	C.N.	R (Å)	σ^2 (Å^2)
100 K	Fe2a-Fe6h	6	2.377(20)	0.004(3)
	Fe2a-Ti	6	2.790(5)	0.004(1)
$S0^2(Ti) = 0.61(3)$	Fe6h-Fe6h	2	2.360(160)	0.02(2)
$S0^2(Fe) = 0.73(6)$	Fe6h-Fe2a	2	2.377(20)	0.004(3)
$\Delta E0(Ti) = 5.5(7)$	Fe6h-Fe6h	2	2.436(160)	0.004(3)
$\Delta E0(Fe) = 5.1(8)$	Fe6h-Ti	6	2.782(5)	0.004(1)
	Ti-Fe	12	2.784(5)	0.004(1)
	Ti-Ti	4	2.896(22)	0.002(1)
200 K	Fe2a-Fe6h	6	2.379(20)	0.005(2)
	Fe2a-Ti	6	2.795(6)	0.006(1)
$S0^2(Ti) = 0.61(5)$	Fe6h-Fe6h	2	2.324(142)	0.023(19)
$S0^2(Fe) = 0.72(6)$	Fe6h-Fe2a	2	2.379(20)	0.005(2)
$\Delta E0(Ti) = 5.3(9)$	Fe6h-Fe6h	2	2.416(142)	0.005(2)
$\Delta E0(Fe) = 5.2(7)$	Fe6h-Ti	6	2.786(6)	0.006(1)
	Ti-Fe	12	2.788(6)	0.006(1)
	Ti-Ti	4	2.895(38)	0.005(2)
225 K	Fe2a-Fe6h	6	2.374(16)	0.005(4)
	Fe2a-Ti	6	2.788(7)	0.006(1)
$S0^2(Ti) = 0.60(4)$	Fe6h-Fe6h	2	2.352(193)	0.02(3)
$S0^2(Fe) = 0.71(8)$	Fe6h-Fe2a	2	2.374(16)	0.005(4)
$\Delta E0(Ti) = 5.2(7)$	Fe6h-Fe6h	2	2.444(193)	0.005(4)
$\Delta E0(Fe) = 4.5(1.1)$	Fe6h-Ti	6	2.779(7)	0.006(1)
	Ti-Fe	12	2.781(7)	0.006(1)
	Ti-Ti	4	2.905(24)	0.004(2)
250 K	Fe2a-Fe6h	6	2.376(14)	0.005(2)
	Fe2a-Ti	6	2.792(6)	0.007(1)
$S0^2(Ti) = 0.60(4)$	Fe6h-Fe6h	2	2.355(130)	0.023(22)
$S0^2(Fe) = 0.72(6)$	Fe6h-Fe2a	2	2.376(14)	0.005(2)
$\Delta E0(Ti) = 5.2(7)$	Fe6h-Fe6h	2	2.441(130)	0.005(2)
$\Delta E0(Fe) = 4.5(8)$	Fe6h-Ti	6	2.783(6)	0.007(1)
	Ti-Fe	12	2.785(6)	0.007(1)
	Ti-Ti	4	2.897(30)	0.005(2)
275 K	Fe2a-Fe6h	6	2.376(21)	0.006(4)
	Fe2a-Ti	6	2.790(7)	0.007(1)
$S0^2(Ti) = 0.60(4)$	Fe6h-Fe6h	2	2.356(184)	0.021(24)
$S0^2(Fe) = 0.73(7)$	Fe6h-Fe2a	2	2.376(21)	0.006(4)
$\Delta E0(Ti) = 5.2(7)$	Fe6h-Fe6h	2	2.438(184)	0.006(4)
$\Delta E0(Fe) = 4.5(9)$	Fe6h-Ti	6	2.781(7)	0.007(1)
	Ti-Fe	12	2.784(7)	0.007(1)
	Ti-Ti	4	2.898(28)	0.005(2)
300 K	Fe2a-Fe6h	6	2.376(18)	0.006(3)
	Fe2a-Ti	6	2.793(6)	0.008(1)
$S0^2(Ti) = 0.60(5)$	Fe6h-Fe6h	2	2.327(144)	0.024(22)
$S0^2(Fe) = 0.70(6)$	Fe6h-Fe2a	2	2.376(18)	0.006(3)
$\Delta E0(Ti) = 5.1(8)$	Fe6h-Fe6h	2	2.413(144)	0.006(3)
$\Delta E0(Fe) = 4.6(8)$	Fe6h-Ti	6	2.784(6)	0.008(1)
	Ti-Fe	12	2.786(6)	0.00(1)
	Ti-Ti	4	2.898(3)	0.006(3)

TABLE SVII. Local structural parameters like coordination number (C.N.), bond distance (R), and σ^2 for $Ti_{32}Fe_{68}$ obtained through simultaneous analysis of Ti and Fe EXAFS data at different temperatures

Temperature (K)	Bond	C.N.	R (Å)	σ^2 (Å^2)
100 K	Fe2a-Fe6h	6	2.377(17)	0.004(3)
	Fe2a-Ti	6	2.791(5)	0.004(1)
$S0^2(Ti) = 0.59(3)$	Fe6h-Fe6h	2	2.360(147)	0.019(19)
$S0^2(Fe) = 0.70(6)$	Fe6h-Fe2a	2	2.377(17)	0.004(3)
$\Delta E0(Ti) = 5.5(7)$	Fe6h-Fe6h	2	2.436(147)	0.004(3)
$\Delta E0(Fe) = 5.2(7)$	Fe6h-Ti	6	2.782(5)	0.004(1)
	Ti-Fe	12	2.784(5)	0.004(1)
	Ti-Ti	4	2.896(18)	0.002(1)
200 K	Fe2a-Fe6h	6	2.375(17)	0.005(3)
	Fe2a-Ti	6	2.789(5)	0.005(1)
$S0^2(Ti) = 0.57(3)$	Fe6h-Fe6h	2	2.326(157)	0.019(19)
$S0^2(Fe) = 0.70(6)$	Fe6h-Fe2a	2	2.375(17)	0.005(3)
$\Delta E0(Ti) = 5.2(6)$	Fe6h-Fe6h	2	2.412(157)	0.005(3)
$\Delta E0(Fe) = 4.7(7)$	Fe6h-Ti	6	2.780(5)	0.005(1)
	Ti-Fe	12	2.783(5)	0.005(1)
	Ti-Ti	4	2.900(18)	0.002(1)
225 K	Fe2a-Fe6h	6	2.377(19)	0.005(3)
	Fe2a-Ti	6	2.792(6)	0.006(1)
$S0^2(Ti) = 0.57(3)$	Fe6h-Fe6h	2	2.326(157)	0.021(21)
$S0^2(Fe) = 0.70(6)$	Fe6h-Fe2a	2	2.377(19)	0.005(3)
$\Delta E0(Ti) = 5.1(7)$	Fe6h-Fe6h	2	2.414(157)	0.005(3)
$\Delta E0(Fe) = 4.8(8)$	Fe6h-Ti	6	2.783(6)	0.006(1)
	Ti-Fe	12	2.785(6)	0.006(1)
	Ti-Ti	4	2.890(23)	0.003(2)
250 K	Fe2a-Fe6h	6	2.373(18)	0.005(4)
	Fe2a-Ti	6	2.785(6)	0.006(1)
$S0^2(Ti) = 0.57(3)$	Fe6h-Fe6h	2	2.329(201)	0.020(27)
$S0^2(Fe) = 0.70(7)$	Fe6h-Fe2a	2	2.373(18)	0.005(4)
$\Delta E0(Ti) = 5.0(6)$	Fe6h-Fe6h	2	2.409(201)	0.005(4)
$\Delta E0(Fe) = 3.8(9)$	Fe6h-Ti	6	2.776(6)	0.006(1)
	Ti-Fe	12	2.778(6)	0.006(1)
	Ti-Ti	4	2.903(13)	0.002(1)
275 K	Fe2a-Fe6h	6	2.373(13)	0.005(3)
	Fe2a-Ti	6	2.787(6)	0.006(1)
$S0^2(Ti) = 0.58(3)$	Fe6h-Fe6h	2	2.331(157)	0.019(23)
$S0^2(Fe) = 0.69(7)$	Fe6h-Fe2a	2	2.373(13)	0.005(3)
$\Delta E0(Ti) = 5.2(6)$	Fe6h-Fe6h	2	2.409(157)	0.005(3)
$\Delta E0(Fe) = 4.1(9)$	Fe6h-Ti	6	2.778(6)	0.006(1)
	Ti-Fe	12	2.780(6)	0.006(1)
	Ti-Ti	4	2.912(1)	0.003(2)
300 K	Fe2a-Fe6h	6	2.373(17)	0.006(4)
	Fe2a-Ti	6	2.786(6)	0.007(1)
$S0^2(Ti) = 0.57(3)$	Fe6h-Fe6h	2	2.331(213)	0.019(28)
$S0^2(Fe) = 0.71(8)$	Fe6h-Fe2a	2	2.373(17)	0.006(4)
$\Delta E0(Ti) = 5.0(6)$	Fe6h-Fe6h	2	2.409(213)	0.006(4)
$\Delta E0(Fe) = 3.9(9)$	Fe6h-Ti	6	2.777(6)	0.007(1)
	Ti-Fe	12	2.779(6)	0.007(1)
	Ti-Ti	4	2.905(15)	0.003(1)

TABLE SVIII. Local structural parameters like coordination number (C.N.), bond distance (R), and σ^2 for $Ti_{34}Fe_{66}$ obtained through simultaneous analysis of Ti and Fe EXAFS data at different temperatures

Temperature (K)	Bond	C.N.	R (Å)	σ^2 (Å^2)
100 K	Fe2a-Fe6h	6	2.378(17)	0.003(3)
	Fe2a-Ti	6	2.790(5)	0.003(1)
$S0^2(Ti) = 0.58(3)$	Fe6h-Fe6h	2	2.358(164)	0.016(20)
$S0^2(Fe) = 0.69(6)$	Fe6h-Fe2a	2	2.378(17)	0.003(3)
$\Delta E0(Ti) = 5.3(6)$	Fe6h-Fe6h	2	2.438(164)	0.003(3)
$\Delta E0(Fe) = 5.2(7)$	Fe6h-Ti	6	2.781(5)	0.003(1)
	Ti-Fe	12	2.783(5)	0.003(1)
	Ti-Ti	4	2.900(16)	0.001(1)
200 K	Fe2a-Fe6h	6	2.377(16)	0.005(3)
	Fe2a-Ti	6	2.790(6)	0.006(1)
$S0^2(Ti) = 0.57(3)$	Fe6h-Fe6h	2	2.354(157)	0.018(24)
$S0^2(Fe) = 0.70(6)$	Fe6h-Fe2a	2	2.377(16)	0.005(3)
$\Delta E0(Ti) = 5.1(6)$	Fe6h-Fe6h	2	2.442(164)	0.005(3)
$\Delta E0(Fe) = 4.7(7)$	Fe6h-Ti	6	2.782(6)	0.006(1)
	Ti-Fe	12	2.784(6)	0.006(1)
	Ti-Ti	4	2.907(18)	0.003(2)
225 K	Fe2a-Fe6h	6	2.377(18)	0.005(4)
	Fe2a-Ti	6	2.788(6)	0.006(1)
$S0^2(Ti) = 0.57(3)$	Fe6h-Fe6h	2	2.331(190)	0.019(27)
$S0^2(Fe) = 0.70(6)$	Fe6h-Fe2a	2	2.377(18)	0.005(4)
$\Delta E0(Ti) = 5.0(6)$	Fe6h-Fe6h	2	2.413(190)	0.005(4)
$\Delta E0(Fe) = 4.5(7)$	Fe6h-Ti	6	2.779(6)	0.006(1)
	Ti-Fe	12	2.781(6)	0.006(1)
	Ti-Ti	4	2.910(21)	0.003(2)
250 K	Fe2a-Fe6h	6	2.377(15)	0.005(4)
	Fe2a-Ti	6	2.789(6)	0.006(1)
$S0^2(Ti) = 0.58(3)$	Fe6h-Fe6h	2	2.333(199)	0.017(27)
$S0^2(Fe) = 0.70(6)$	Fe6h-Fe2a	2	2.377(15)	0.005(4)
$\Delta E0(Ti) = 5.0(6)$	Fe6h-Fe6h	2	2.413(199)	0.005(4)
$\Delta E0(Fe) = 4.6(7)$	Fe6h-Ti	6	2.780(6)	0.006(1)
	Ti-Fe	12	2.782(6)	0.006(1)
	Ti-Ti	4	2.913(16)	0.002(1)
275 K	Fe2a-Fe6h	6	2.377(10)	0.005(3)
	Fe2a-Ti	6	2.792(5)	0.006(1)
$S0^2(Ti) = 0.56(3)$	Fe6h-Fe6h	2	2.337(157)	0.016(23)
$S0^2(Fe) = 0.68(7)$	Fe6h-Fe2a	2	2.377(10)	0.005(3)
$\Delta E0(Ti) = 4.9(5)$	Fe6h-Fe6h	2	2.414(157)	0.005(3)
$\Delta E0(Fe) = 4.1(8)$	Fe6h-Ti	6	2.783(5)	0.006(1)
	Ti-Fe	12	2.785(5)	0.006(1)
	Ti-Ti	4	2.919(17)	0.003(1)
300 K	Fe2a-Fe6h	6	2.378(11)	0.005(3)
	Fe2a-Ti	6	2.792(5)	0.007(1)
$S0^2(Ti) = 0.56(3)$	Fe6h-Fe6h	2	2.334(135)	0.018(20)
$S0^2(Fe) = 0.70(6)$	Fe6h-Fe2a	2	2.378(11)	0.005(3)
$\Delta E0(Ti) = 4.9(6)$	Fe6h-Fe6h	2	2.414(135)	0.005(3)
$\Delta E0(Fe) = 4.4(8)$	Fe6h-Ti	6	2.783(5)	0.007(1)
	Ti-Fe	12	2.786(5)	0.007(1)
	Ti-Ti	4	2.907(20)	0.004(2)

TABLE SIX. Local structural parameters like coordination number (C.N.), bond distance (R), and σ^2 for $Ti_{35}Fe_{65}$ obtained through simultaneous analysis of Ti and Fe EXAFS data at different temperatures

Temperature (K)	Bond	C.N.	R (Å)	σ^2 (Å^2)
100 K	Fe2a-Fe6h	6	2.380(14)	0.003(3)
	Fe2a-Ti	6	2.791(5)	0.004(1)
$S0^2(Ti) = 0.57(3)$	Fe6h-Fe6h	2	2.355(180)	0.014(23)
$S0^2(Fe) = 0.69(6)$	Fe6h-Fe2a	2	2.380(14)	0.003(3)
$\Delta E0(Ti) = 5.1(6)$	Fe6h-Fe6h	2	2.441(180)	0.003(3)
$\Delta E0(Fe) = 4.8(7)$	Fe6h-Ti	6	2.782(5)	0.004(1)
	Ti-Fe	12	2.784(5)	0.004(1)
	Ti-Ti	4	2.903(12)	0.001(1)
200 K	Fe2a-Fe6h	6	2.379(10)	0.004(5)
	Fe2a-Ti	6	2.790(5)	0.005(1)
$S0^2(Ti) = 0.56(3)$	Fe6h-Fe6h	2	2.347(241)	0.014(33)
$S0^2(Fe) = 0.69(7)$	Fe6h-Fe2a	2	2.379(10)	0.004(5)
$\Delta E0(Ti) = 5.0(6)$	Fe6h-Fe6h	2	2.449(241)	0.004(5)
$\Delta E0(Fe) = 4.4(9)$	Fe6h-Ti	6	2.782(5)	0.005(1)
	Ti-Fe	12	2.784(5)	0.005(1)
	Ti-Ti	4	2.911(14)	0.002(1)
225 K	Fe2a-Fe6h	6	2.379(9)	0.005(3)
	Fe2a-Ti	6	2.792(5)	0.006(1)
$S0^2(Ti) = 0.60(4)$	Fe6h-Fe6h	2	2.337(160)	0.015(22)
$S0^2(Fe) = 0.71(7)$	Fe6h-Fe2a	2	2.379(9)	0.005(3)
$\Delta E0(Ti) = 5.3(7)$	Fe6h-Fe6h	2	2.415(160)	0.005(3)
$\Delta E0(Fe) = 4.3(9)$	Fe6h-Ti	6	2.783(5)	0.006(1)
	Ti-Fe	12	2.785(5)	0.006(1)
	Ti-Ti	4	2.912(15)	0.003(1)
250 K	Fe2a-Fe6h	6	2.381(14)	0.005(3)
	Fe2a-Ti	6	2.793(5)	0.006(1)
$S0^2(Ti) = 0.57(3)$	Fe6h-Fe6h	2	2.332(147)	0.017(18)
$S0^2(Fe) = 0.68(7)$	Fe6h-Fe2a	2	2.381(14)	0.005(3)
$\Delta E0(Ti) = 5.2(6)$	Fe6h-Fe6h	2	2.417(147)	0.005(3)
$\Delta E0(Fe) = 4.3(8)$	Fe6h-Ti	6	2.784(5)	0.006(1)
	Ti-Fe	12	2.787(5)	0.006(1)
	Ti-Ti	4	2.915(18)	0.003(1)
275 K	Fe2a-Fe6h	6	2.378(11)	0.005(5)
	Fe2a-Ti	6	2.790(5)	0.006(1)
$S0^2(Ti) = 0.58(4)$	Fe6h-Fe6h	2	2.349(264)	0.014(32)
$S0^2(Fe) = 0.68(8)$	Fe6h-Fe2a	2	2.378(11)	0.005(5)
$\Delta E0(Ti) = 5.5(6)$	Fe6h-Fe6h	2	2.447(264)	0.005(5)
$\Delta E0(Fe) = 4.6(8)$	Fe6h-Ti	6	2.781(5)	0.006(1)
	Ti-Fe	12	2.783(5)	0.006(1)
	Ti-Ti	4	2.916(13)	0.003(1)
300 K	Fe2a-Fe6h	6	2.379(11)	0.006(4)
	Fe2a-Ti	6	2.792(6)	0.007(1)
$S0^2(Ti) = 0.57(3)$	Fe6h-Fe6h	2	2.337(180)	0.016(25)
$S0^2(Fe) = 0.69(6)$	Fe6h-Fe2a	2	2.379(11)	0.006(4)
$\Delta E0(Ti) = 5.2(6)$	Fe6h-Fe6h	2	2.415(180)	0.006(4)
$\Delta E0(Fe) = 4.6(7)$	Fe6h-Ti	6	2.783(6)	0.007(1)
	Ti-Fe	12	2.785(6)	0.007(1)
	Ti-Ti	4	2.910(19)	0.004(2)