Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Slow magnetization relaxation of a high-spin iron(III) in mayenite $Ca_{12}Al_{14}O_{33}$.

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Supporting information

X-ray powder diffraction data

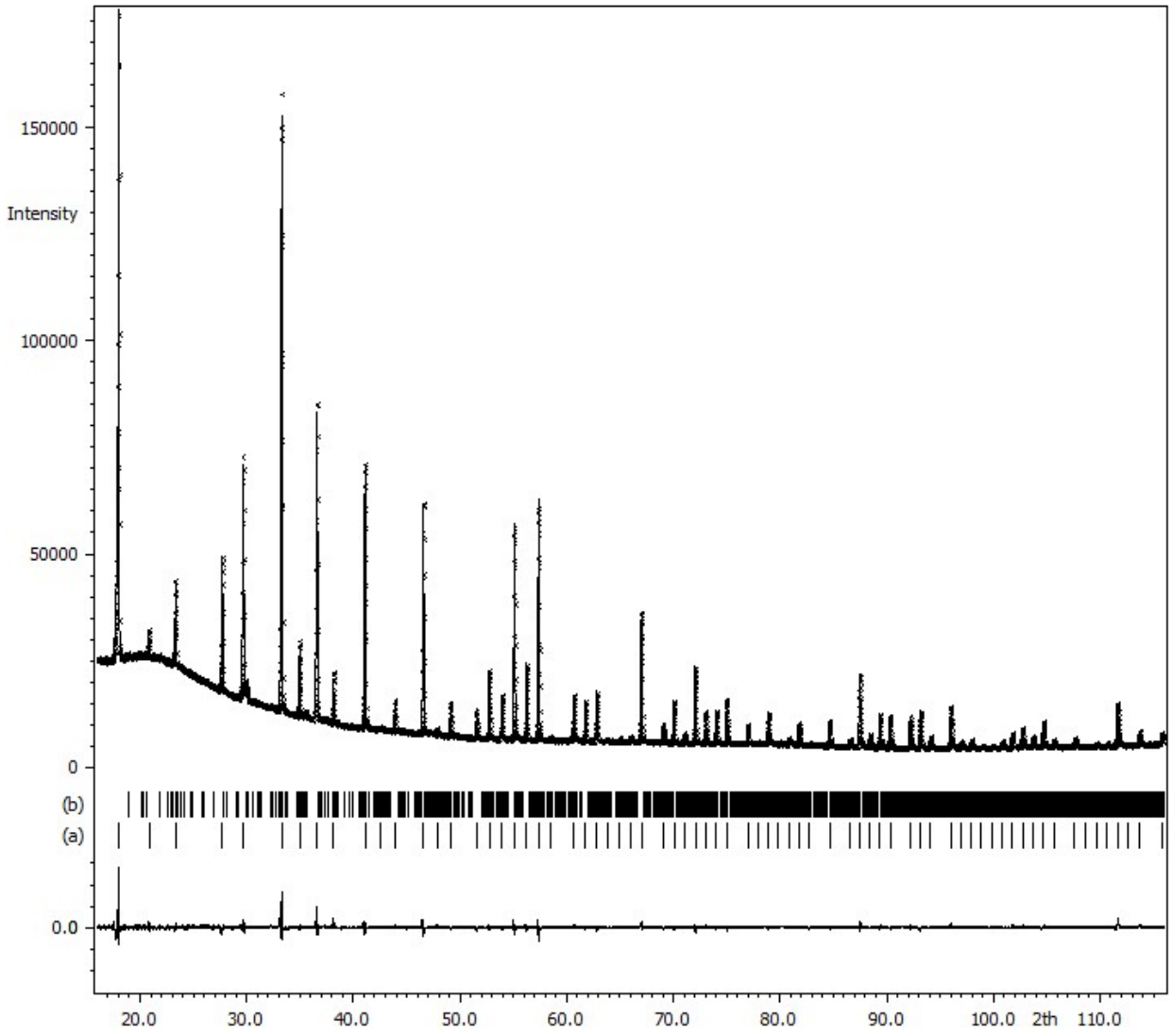


Figure S1. Powder X-ray diffraction pattern of $Ca_{12}Al_{14}O_{33}$ (Sample CAF0). Observed (crosses), calculated (solid line) and difference (solid line below) plots. Positions of Bragg reflections are indicated by vertical bars underneath. (a) the main phase; (b) admixture of $CaAl_2O_4$, 3.9 wt. %.

Table S1. Crystal structure refinement data for CAF0.

Temperature (K)	293 K
Wavelength (Å)	1.5406
Space group	*I*-43*d* (no. 220)
a (Å)	11.9902(1)
V (Å^3)	1723.75(1)
Z	2
2θ range (deg.)	16 – 116
R_{wp}	0.023
R_{all}	0.019
ΔF_{max}, ΔF_{min} (e Å^{-3})	0.19, -0.23

Table S2. Atomic parameters and thermal displacement parameters (Å^2) for CAF0.

Atom	**Wyck.**	**Occ.**	***x***	***y***	***z***	U_{iso}
Ca1	24*d*	0.89(1)	0.8901(3)	0	3/4	0.0063(7)
Al1	16*c*		0.01824(13)	0.01824(13)	0.01824(13)	0.0112(9)
Al2	12*b*		1.0	-1/4	5/8	0.0058(9)
O1	16*c*		0.9362(3)	-0.0638(3)	0.9362(3)	0.009(2)
O2	48*e*		0.9012(3)	-0.1925(2)	0.7133(3)	0.0079(10)
O3	48*e*	0.020(3)	0.77(3)	0.12(2)	-0.052(14)	0.03
Ca2	24*d*	0.11(1)	0.946(3)	0	3/4	0.022(8)

Table S3. Selected interatomic distances (Å) in the crystal structure of CAF0.

Ca1-O1	2.424(4)	2x
Ca1-O2	2.354(3)	2x
Ca1-O2	2.524(5)	2x
Ca2-O1	2.363(4)	2x
Ca2-O2	2.410(8)	2x
Ca2-O3	2.2(3)	
Al1-O1	1.703(4)	
Al1-O2	1.788(4)	3x
Al2-O2	1.732(3)	4x
Al1-O(av.)	1.767	

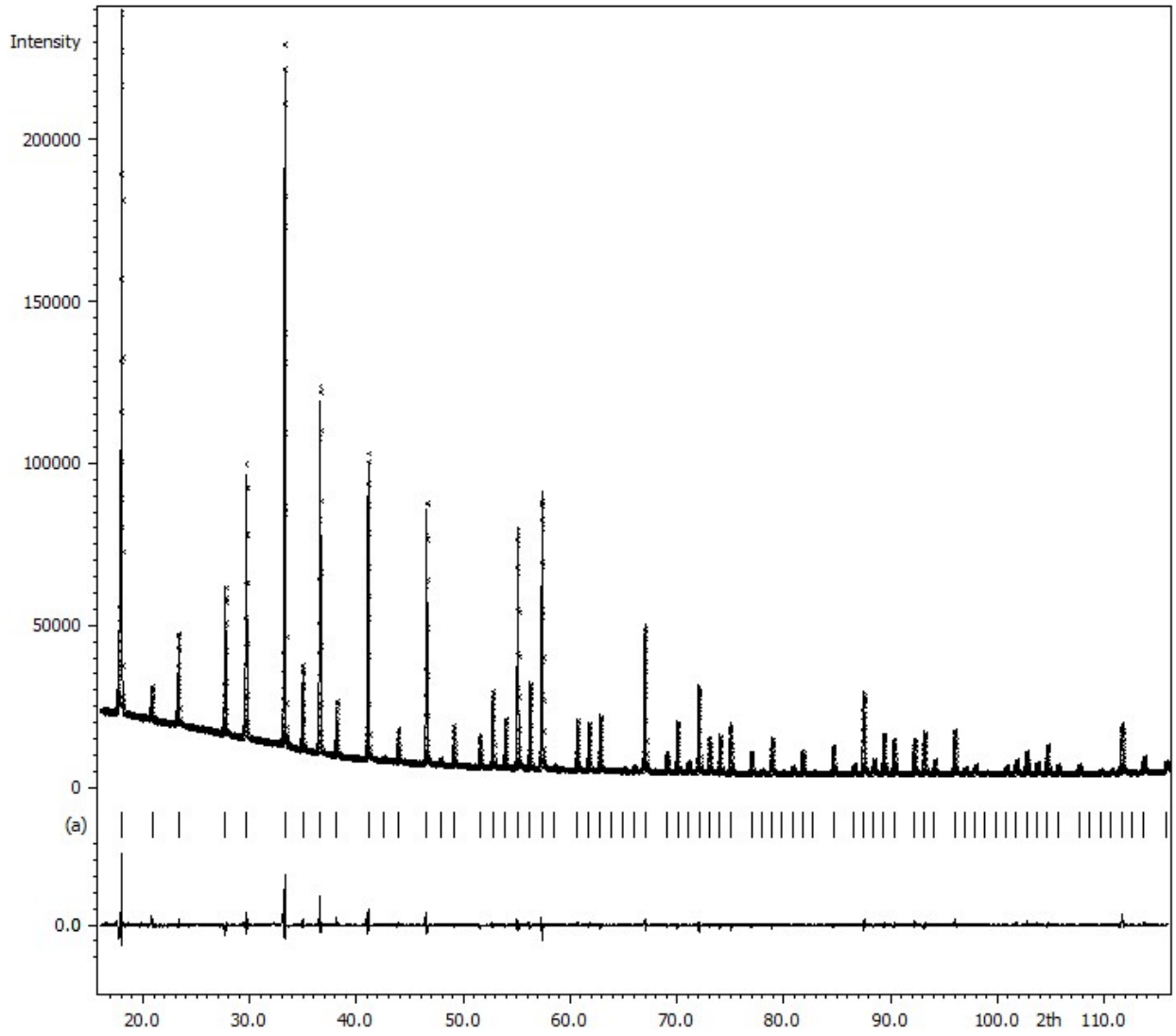


Figure S2. Powder X-ray diffraction pattern of $Ca_{12}Al_{13.95}Fe_{0.05}O_{33}$ (Sample CAF5). Observed (crosses), calculated (solid line) and difference (solid line below) plots. Positions of Bragg reflections are indicated by vertical bars underneath.

Table S4. Crystal structure refinement data for CAF5.

Temperature (K)	293 K
Wavelength (Å)	1.5406
Space group	*I*-43*d* (no. 220)
a (Å)	11.9895(1)
V (Å^3)	1723.45(1)
Z	2
2θ range (deg.)	16 – 116
R_{wp}	0.030
R_{all}	0.018
ΔF_{max}, ΔF_{min} (e Å^{-3})	0.17, -0.19

Table S5. Atomic parameters and thermal displacement parameters (Å^2) for CAF5.

Atom	**Wyck.**	**Occ.**	***x***	***y***	***z***	U_{iso}
Ca1	24*d*	0.87(1)	0.8892(4)	0	3/4	0.0056(8)
Al1	16*c*	0.994	0.01809(12)	0.01809(12)	0.01809(12)	0.0093(9)
Al2	12*b*		1.00000	-1/4	5/8	0.0059(9)
O1	16*c*		0.9359(3)	-0.0641(3)	0.9359(3)	0.008(2)
O2	48*e*		0.9006(3)	-0.1929(3)	0.7131(3)	0.0077(10)
O3	48*e*	0.033(4)	0.771(15)	0.119(13)	-0.062(9)	0.0300
Ca2	24*d*	0.13(1)	0.942(3)	0	3/4	0.025(7)
Fe1	16*c*	0.006	0.01809(12)	0.01809(12)	0.01809(12)	0.0093(9)

Table S6. Selected interatomic distances (Å) in the crystal structure of CAF5.

Ca1-O1	2.423(4)	2x
Ca1-O2	2.358(3)	2x
Ca1-O2	2.519(5)	2x
Ca2-O1	2.359(4)	2x
Ca2-O2	2.407(8)	2x
Ca2-O3	2.3(2)	
(Al,Fe)1-O1	1.707(4)	
(Al,Fe)1-O2	1.782(4)	3x
Al2-O2	1.732(3)	4x
(Al,Fe)1-O(av.)	1.763	

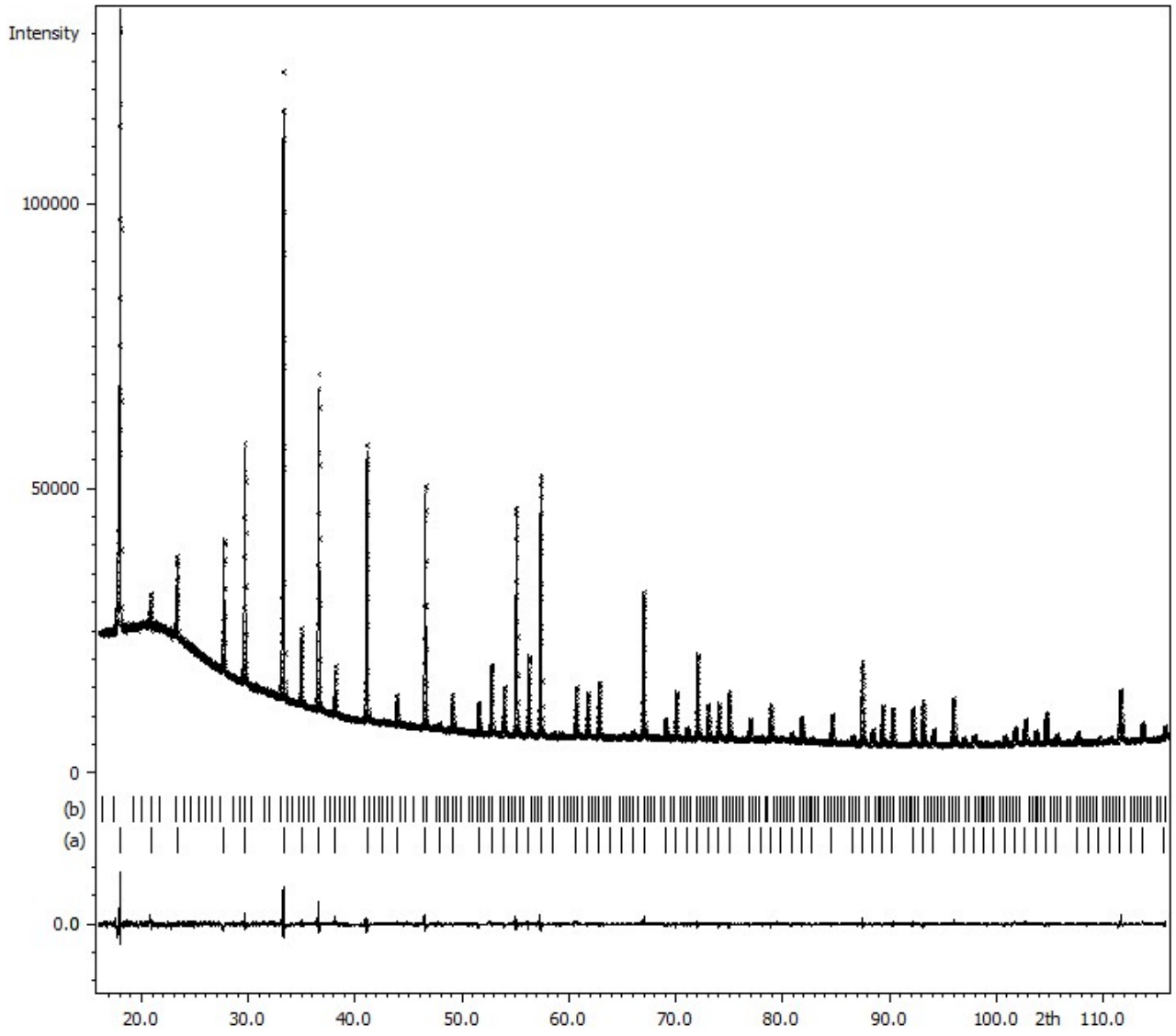


Figure S3. Powder X-ray diffraction pattern of $Ca_{12}Al_{13.75}Fe_{0.25}O_{33}$ (Sample CAF25). Observed (crosses), calculated (solid line) and difference (solid line below) plots. Positions of Bragg reflections are indicated by vertical bars underneath. (a) the main phase; (b) admixture of $Ca_3Al_2O_6$, 1.0 wt. %.

Table S7. Crystal structure refinement data for CAF25.

Temperature (K)	293 K
Wavelength (Å)	1.5406
Space group	*I*-43*d* (no. 220)
a (Å)	11.9926(1)
V (Å^3)	1724.80(1)
Z	2
2θ range (deg.)	16 – 116
R_{wp}	0.020
R_{all}	0.020
ΔF_{max}, ΔF_{min} (e Å^{-3})	0.22, -0.23

Table S8. Atomic parameters and thermal displacement parameters (Å^2) for CAF25.

Atom	**Wyck.**	**Occ.**	***x***	***y***	***z***	U_{iso}
Ca1	24*d*	0.89(1)	0.8899(3)	0	3/4	0.0010(7)
Al1	16*c*	0.971(9)	0.01821(13)	0.01821(13)	0.01821(13)	0.0074(12)
Al2	12*b*		1.00000	-1/4	5/8	0.0007(9)
O1	16*c*		0.9357(3)	-0.0643(3)	0.9357(3)	0.006(2)
O2	48*e*		0.9015(3)	-0.1921(2)	0.7131(3)	0.001(1)
O3	48*e*	0.030(4)	0.772(18)	0.114(16)	-0.057(10)	0.0300
Ca2	24*d*	0.11(1)	0.946(3)	0	3/4	0.017(8)
Fe1	16*c*	0.029(9)	0.01821(13)	0.01821(13)	0.01821(13)	0.0074(12)

Table S9. Selected interatomic distances (Å) in the crystal structure of CAF25.

Ca1-O1	2.420(4)	2x
Ca1-O2	2.350(3)	2x
Ca1-O2	2.525(4)	2x
Ca2-O1	2.360(4)	2x
Ca2-O2	2.406(8)	2x
Ca2-O3	2.1(2)	
(Al,Fe)1-O1	1.714(4)	
(Al,Fe)1-O2	1.794(4)	3x
Al2-O2	1.730(3)	4x
(Al,Fe)1-O(av.)	1.774	

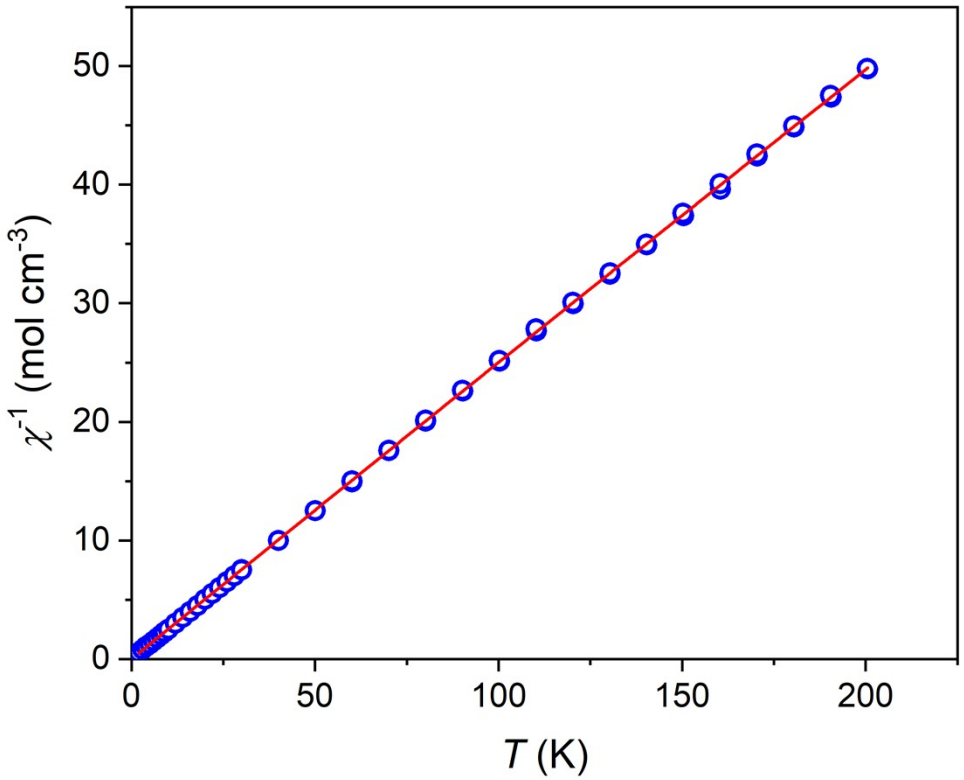


Figure S4. Temperature dependence of reciprocal susceptibility per mol of Fe in CAF5. Symbols – experimental data. Line – fit with the Curie-Weiss law.

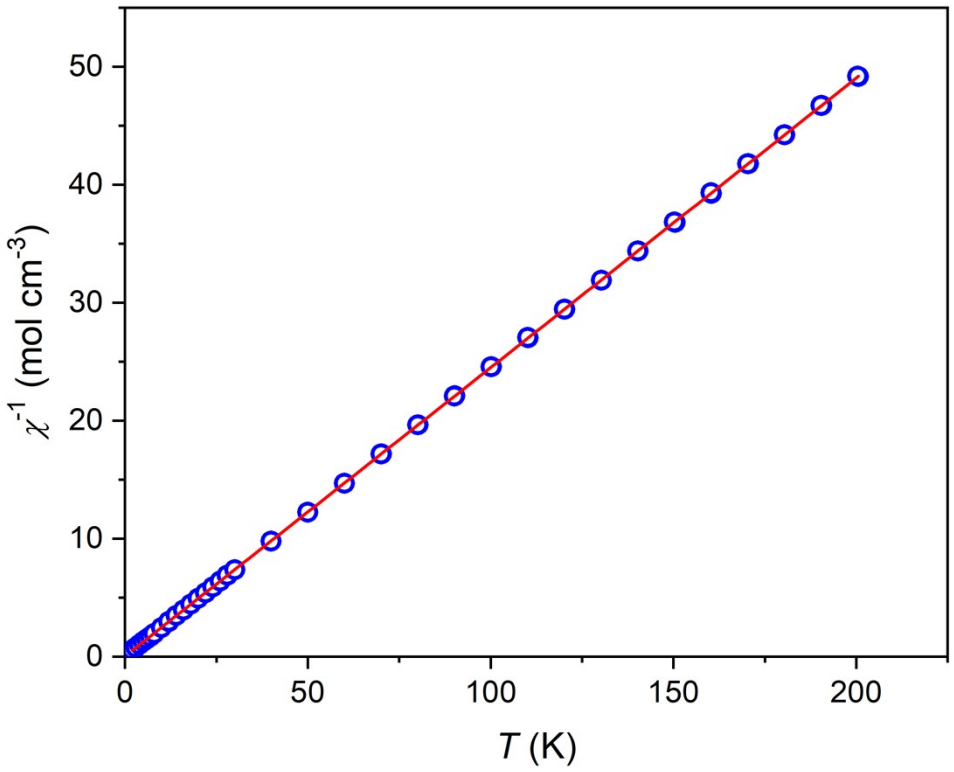
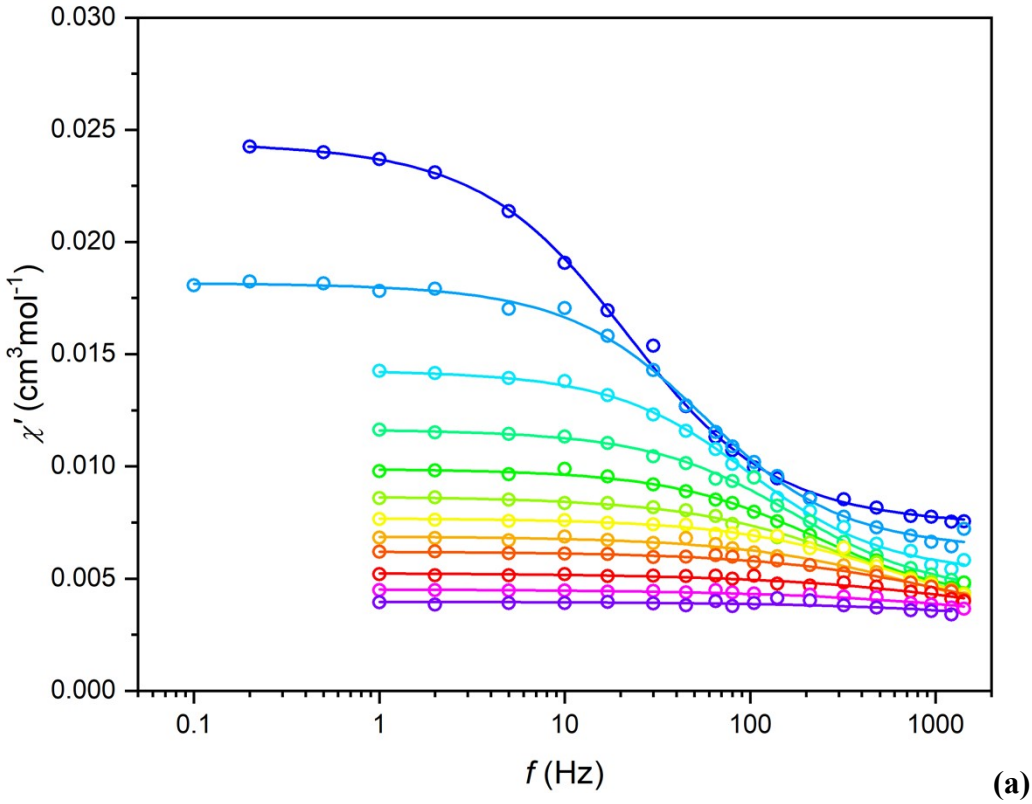
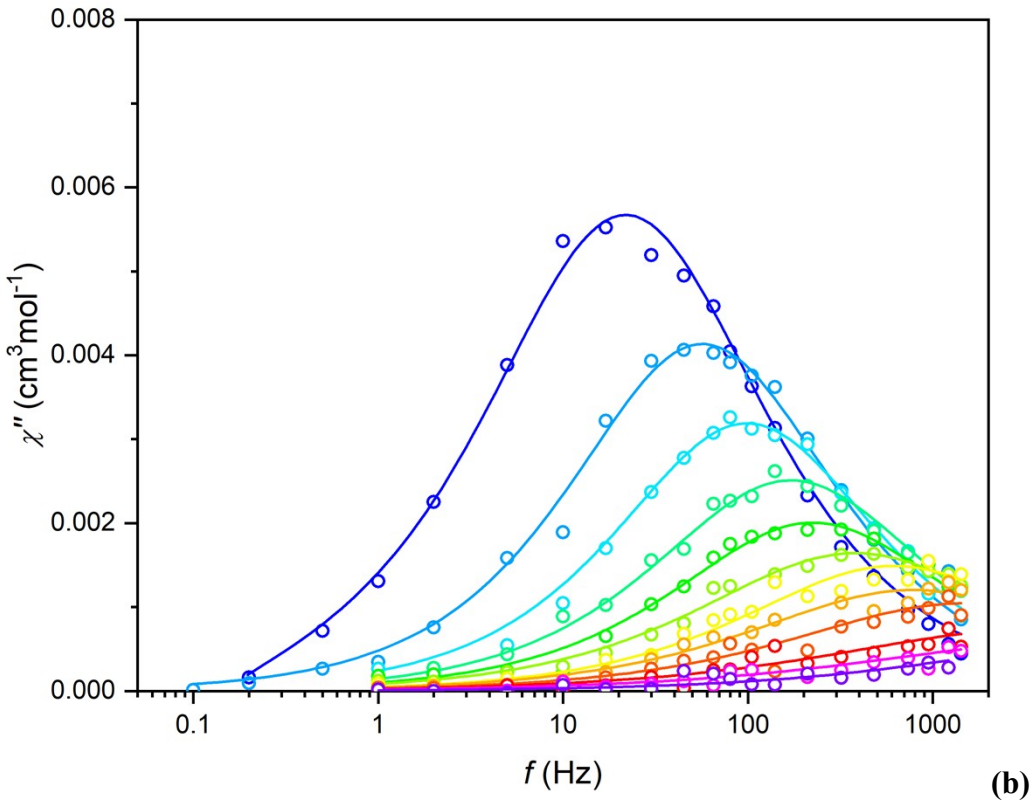


Figure S5. Temperature dependence of reciprocal susceptibility per mol of Fe in CAF25. Symbols – experimental data. Line – fit with the Curie-Weiss law.

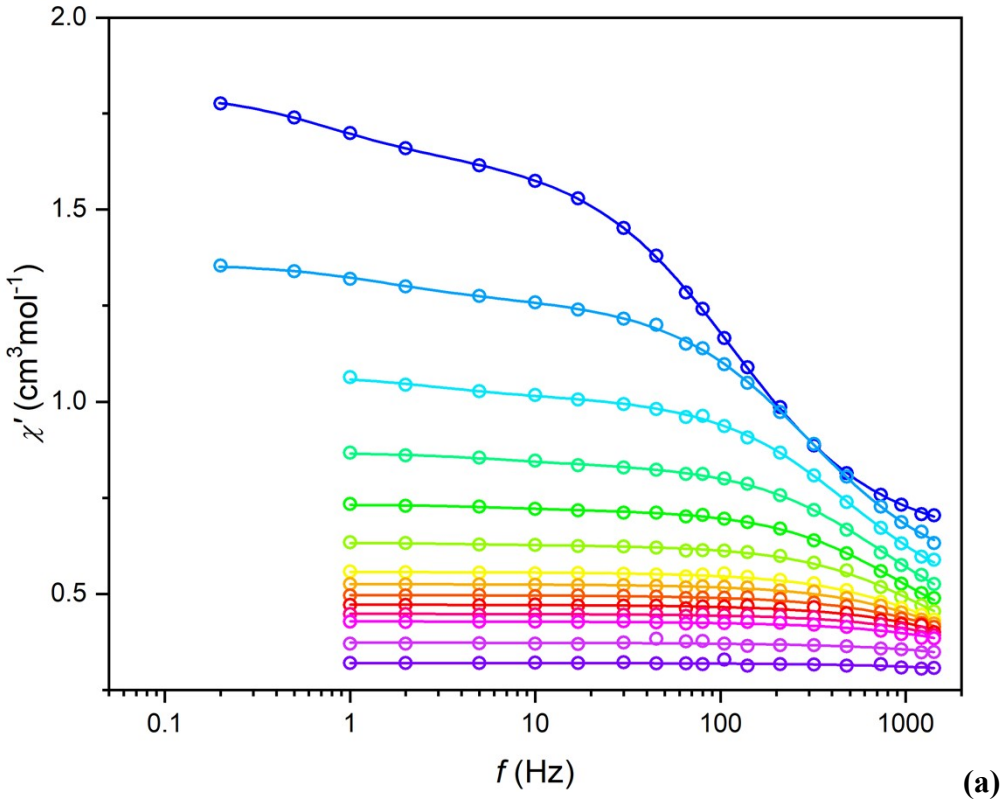


(a)

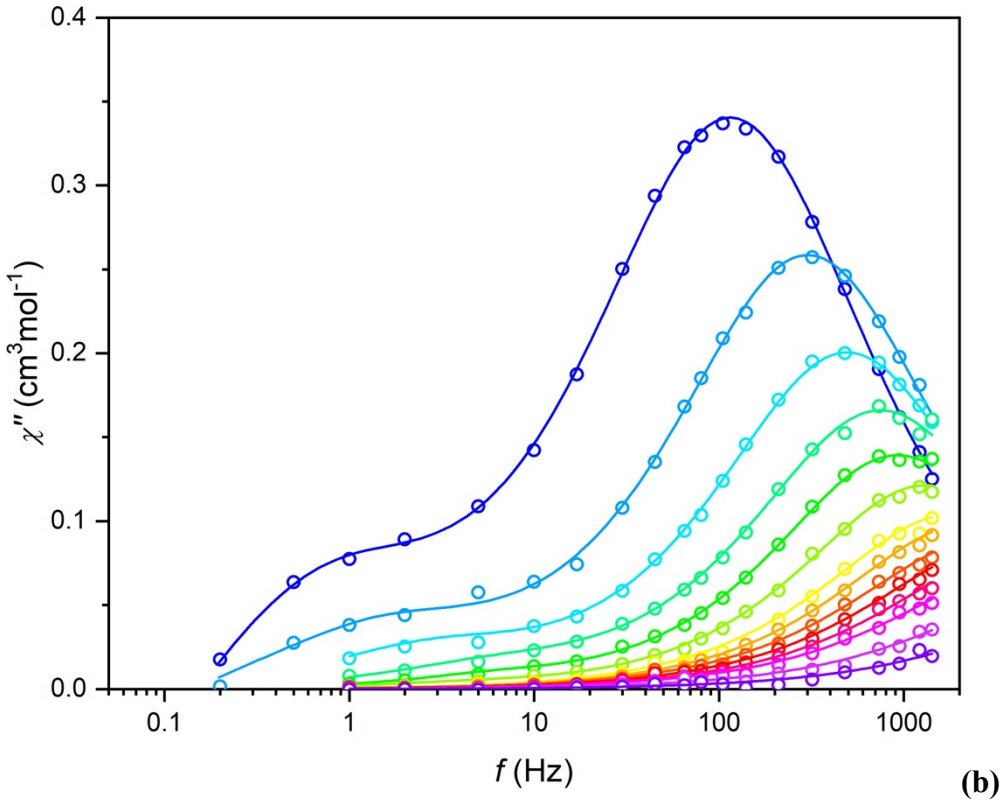


(b)

Figure S6. Frequency dependence of ac susceptibility per mol of $Ca_{12}Al_{14}O_{33}$ in CAF0 at temperatures 2 – 10 K (1 K step), 12 K, 14K (color codes, blue-yellow-red-violet) under a dc magnetic field of 4 kOe. Symbols – experimental points, lines – fitting. (a) – in-phase susceptibility χ', (b) – out-of-phase susceptibility χ''.

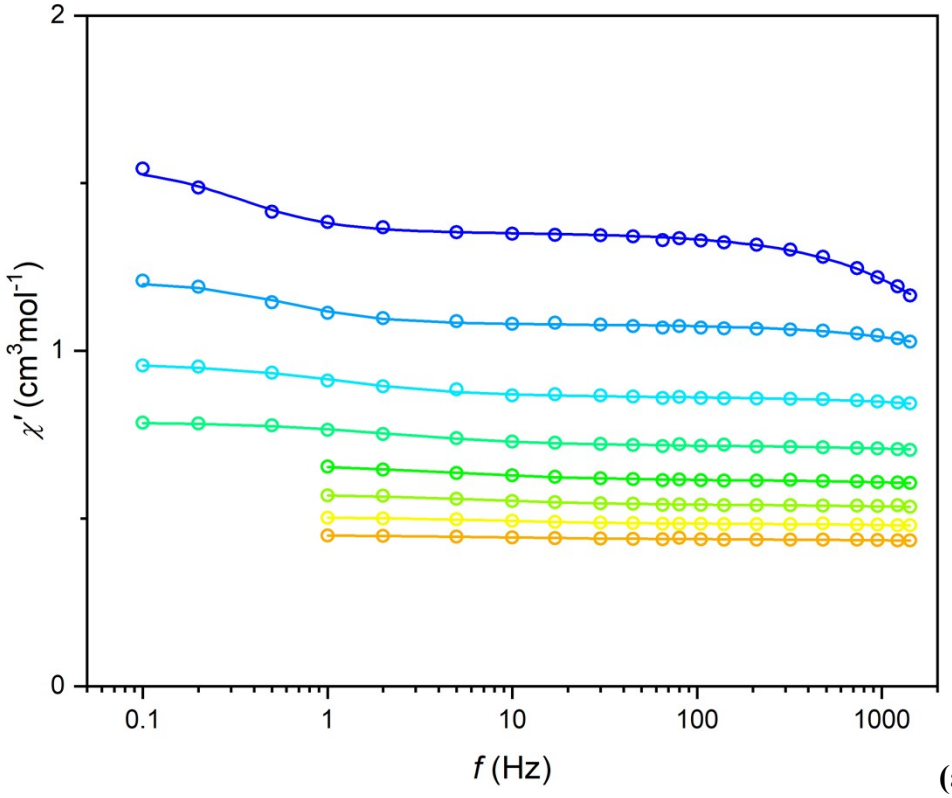


(a)

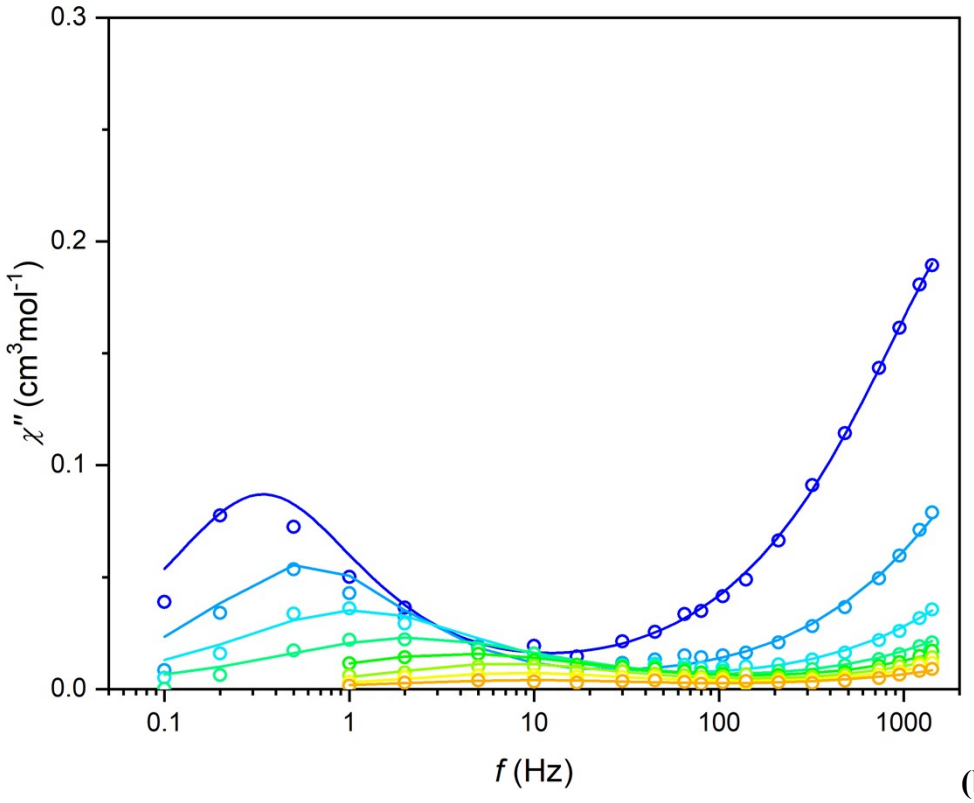


(b)

Figure S7. Frequency dependence of ac susceptibility per mol of Fe in CAF5 at temperatures 2 – 7 K (1 K step), 8.0 – 10.5 K (0.5 K step), 12 K, 14K (color codes, blue-yellow-red-violet) under a dc magnetic field of 4 kOe. Symbols – experimental points, lines – fitting. (a) – in-phase susceptibility χ', (b) – out-of-phase susceptibility χ''.



(a)



(b)

Figure S8. Frequency dependence of ac susceptibility per mol of Fe in CAF25 at temperatures 2 – 9 K (1 K step, color codes, blue-yellow-orange) under a dc magnetic field of 4 kOe. Symbols – experimental points, lines – fitting. (a) – in-phase susceptibility χ', (b) – out-of-phase susceptibility χ''.

Electronic structure data

Table S10. Crystal field parameters in Wybourne notation derived using the program CONCORD for Fe^{3+} using experimental atomic coordinates of the coordination polyhedron (from Table S8) for full tetrahedron O1+3O2 (**I**), for O1 only (**II**), for 3O2 only (**III**) (*z*-axis along trigonal axis).

Parameter	**I**, value (cm^{-1})	**II**, value (cm^{-1})	**III**, value (cm^{-1})
B_{20}	38578.30	76521.66	-37943.36
B_{22}	0	0	0
B_{40}	8669.67	17694.85	-9025.18
B_{42}	0	0	0
B_{43}	-20068.82	0	-20068.82
B_{44}	0	0	0

Table S11. Modeling of the Fe^{3+} electronic structure with the CONDON program using crystal field parameters listed in Table S10. Energies and magnetic moments of all electronic states (Kramers doublets) derived from the $3d^5$ configuration.

Energy (cm^{-1})		$-\mu_z$ (μ_B)	$-\mu_x$ (μ_B)
0	(M_s = -5/2)	-4.995	-0.1431
5.821E-11	(M_s = 5/2)	4.995	-0.1428
3.262	(M_s = -3/2)	-2.997	-0.3829
3.262	(M_s = 3/2)	2.997	-0.2635
4.869	(M_s = -1/2)	-0.9988	-2.472
4.869	(M_s = 1/2)	0.9988	3.405
6399		-4.428	-0.02746
6399		4.428	0.0234
6523		-2.392	-0.01565
6523		2.392	0.01531
6683		-0.3653	5.318E-4
6683		0.3653	5.956E-4
6857		-1.662	-0.01014
6857		1.662	0.01296
9800		-0.7375	-0.5423
9800		0.7374	0.5394
9833		-1.461	0.00102
9833		1.461	0.00137
10830		-1.094	-1.941
10830		1.093	1.939
11030		-3.185	8.987E-4
11030		3.184	9.001E-4
11870		-0.9604	-1.704
11870		0.9602	1.705

12720	-4.015	-0.00441
12720	4.015	0.00204
12970	-2.05	-3.111E-4
12970	2.05	-2.622E-4
13230	-0.1338	-0.5622
13230	0.1337	0.5633
13500	-1.824	-0.521
13500	1.824	0.5228
13600	-0.8865	-2.062
13600	0.8868	2.019
13610	-2.666	0.02129
13610	2.667	0.0218
19830	-0.7639	-6.821E-4
19830	0.7638	-6.19E-4
19960	-1.398	-0.2263
19960	1.398	0.2273
20890	-0.7172	-1.345
20890	0.7146	1.338
20930	-1.417	-0.0011
20930	1.417	-8.636E-4
21020	-0.9473	-1.415
21020	0.9497	1.418
21030	-3.39	-0.00392
21030	3.39	0.00826
21650	-1.279	-1.138
21650	1.279	1.138
22210	-1.337	-8.277E-4
22210	1.337	-6.619E-4
22330	-0.5982	-0.2863
22330	0.5982	0.2876
22770	-0.9032	-1.014
22770	0.9033	1.014
23710	-0.917	-1.092
23710	0.9169	1.092
24680	-2.9	-0.00344
24680	2.9	-0.00343
24750	-0.9783	-1.918
24750	0.9783	1.925
25610	-3.408	-0.1034
25610	3.406	-0.1031
25620	-5.446	0.04746
25620	5.417	0.1328
25630	-0.6443	-1.605
25630	0.6659	1.622
25660	-0.8953	-1.676
25660	0.9023	1.684
25760	-2.511	6.213E-4
25760	2.512	6.292E-4
26160	-0.1774	-0.00424
26160	0.1774	0.00451
26670	-1.054	-0.8156

26670	1.053	0.8157
27620	-2.039	-0.3375
27620	2.039	0.3369
27940	-0.3266	-0.0017
27940	0.3266	-0.00163
27990	-1.93	-0.03423
27990	1.93	0.02184
28020	-0.487	-1.562
28020	0.4565	1.494
28030	-0.09221	0.0358
28030	0.09237	0.03724
28060	-2.368	-1.509
28060	2.4	1.519
28560	-0.7046	-1.134
28560	0.705	1.136
29270	-3.04	-0.00382
29270	3.04	-0.0038
29330	-1.014	-1.937
29330	1.014	1.944
29890	-1.123	-1.127
29890	1.124	1.127
31400	-2.105	-5.704E-4
31400	2.105	-5.379E-4
31600	-0.05876	-0.1631
31600	0.05869	0.164
32480	-0.9203	-1.812
32480	0.9204	1.809
32620	-2.791	0.00177
32620	2.791	0.00178
33260	-2.68	-0.00895
33260	2.68	-0.00634
33270	-0.3098	0.00733
33270	0.3098	0.00775
34210	-2.47	-0.00258
34210	2.47	0.00226
34760	-0.6183	8.89E-5
34760	0.6182	9.253E-5
35450	-0.4924	-1.183
35450	0.4883	1.183
35620	-1.596	-1.054
35620	1.6	1.054
37180	-1.09	-0.1453
37180	1.09	0.1427
37240	-0.5061	0.00101
37240	0.5063	0.00122
37730	-0.8483	-1.214
37730	0.8478	1.214
38360	-1.574	-0.117
38360	1.574	0.1077
38380	-3.683	0.00476
38380	3.683	0.00513

38640	-2.12	-0.4227
38640	2.119	0.4182
38760	-0.1313	-0.3657
38760	0.1314	0.3639
38880	-1.813	6.057E-4
38880	1.813	0.00122
39000	-3.783	0.00155
39000	3.783	0.003
40060	-1.172	-1.127
40060	1.172	1.128
41320	-0.9854	-1.87
41320	0.9855	1.813
41330	-2.954	0.02798
41330	2.954	0.02877
42310	-0.8993	-1.084
42310	0.8998	1.084
43800	-1.003	-0.4758
43800	1.003	0.474
44010	-0.9435	1.54E-4
44010	0.9434	2.347E-4
44420	-0.4385	-2.668E-4
44420	0.4385	-2.572E-4
44510	-0.9826	-0.4031
44510	0.9826	0.4042
44840	-2.325	-0.03815
44840	2.326	0.03876
46180	-0.9541	-0.9206
46180	0.9541	0.9205
46570	-0.04907	-7.585E-4
46570	0.04916	-7.082E-4
46700	-2.038	-0.0332
46700	2.038	0.03484
49420	-2.062	-6.675E-4
49420	2.061	-6.297E-4
49570	-3.838	-0.01569
49570	3.837	0.0169
51500	-2.76	-0.01883
51500	2.759	-0.01891
51520	-0.897	-1.934
51520	0.8964	1.971
51830	-2.075	-0.2136
51830	2.075	0.2101
51860	-0.8578	-0.1073
51860	0.8579	0.1034
51900	-1.076	0.00286
51900	1.076	0.00308
52160	-0.1738	-0.1217
52160	0.1737	0.1208
52450	-1.838	3.182E-4
52450	1.838	3.514E-4
52750	-3.825	-0.00283

52750	3.825	0.00466
53650	-1.103	-2.016
53650	1.104	2.006
53710	-3.273	0.00516
53710	3.274	0.00518
54160	-1.86	-0.9701
54160	1.859	0.97
54770	-0.1148	-0.07988
54770	0.1155	0.07925
54870	-1.296	-0.01212
54870	1.296	-0.00922
54880	-0.1937	-0.683
54880	0.194	0.7045
55220	-0.6222	-0.1315
55220	0.6228	0.1312
55450	-1.188	4.119E-4
55450	1.188	4.388E-4
56580	-0.923	-0.9446
56580	0.9231	0.9449
59670	-0.3563	-0.00446
59670	0.3563	-0.00422
59690	-2.36	-0.02332
59690	2.36	0.03177
61030	-1.261	-0.0012
61030	1.261	-9.5E-4
61260	-0.7463	-3.787E-4
61260	0.7463	-3.461E-4
61340	-0.4557	-1.056
61340	0.4543	1.057
61500	-2.546	-0.1073
61500	2.546	0.108
61740	-4.663	-0.1071
61740	4.663	0.1093
62880	-1.326	-1.105
62880	1.327	1.105
64670	-1.884	-5.102E-4
64670	1.884	-3.923E-4
64890	-0.09962	-0.1408
64890	0.09963	0.1416
66480	-1.072	-0.7696
66480	1.072	0.7699
68790	-0.261	-0.02739
68790	0.2611	0.02709
69350	-1.762	1.661E-4
69350	1.762	1.682E-4
71600	-1.267	-0.9671
71600	1.266	0.967
73530	-0.7361	-0.9532
73530	0.7368	0.9532
75330	-1.31	-0.00526
75330	1.309	-0.00478

75350	-0.6448	-0.00139
75350	0.6447	0.0114
78170	-0.06805	-0.06224
78170	0.0675	0.0617
78430	-1.289	3.402E-4
78430	1.289	3.997E-4
79770	-0.3502	-0.04522
79770	0.3508	0.04488
80220	-3.045	2.307E-4
80220	3.045	2.391E-4
81160	-0.9942	-0.9787
81160	0.9942	0.9787
88380	-1.004	-0.9722
88380	1.004	0.9722
98320	-0.8963	-2.32E-4
98320	0.8963	-2.165E-4
98710	-2.891	-5.991E-4
98710	2.891	0.00106
101600	-0.9983	-1.041
101600	0.9983	1.041
116100	-1.936	-2.931E-4
116100	1.936	-1.756E-4
116400	-0.06707	-0.04757
116400	0.06707	0.0481