DFT Study of Defects in Paramagnetic Cr_2O_3

SUPPORTING INFORMATION

AFM state

The standard defect formation energies in AFM Cr_2O_3 are shown in Table 1 with correction energies. The middle of forbidden band at 0 K is 6.96 eV. The pseudo total energy of Cr_2O_3 is -6073.29 eV per formula unit. The energy of Cr metal obtained by equation fitting is -2375.83 eV per atom.

Table 1. Effective Charge (q), Alignment Energy (E_{align}), Finite-Size Elastic Correction Energy ($E_{\mathrm{corr,elas}}$), Finite-Size Electrostatic Correction Energy ($E_{\mathrm{corr,elec}}$) and Standard Defect Formation Energy (E_{f}^{0}) for defect in 2 × 2 × 2 supercell of AFM Cr_2O_3.

Defect	q	E_{algin} (eV)	$E_{\mathrm{corr,elas}}$ (eV)	$E_{\mathrm{corr,elec}}$ (eV)	E_{f}^{0} (eV)
V_{Cr}'''	-3	0.91	-0.27	1.56	0.26
V_{Cr}''	-2	0.61	-0.10	0.69	0.32
V_{Cr}'	-1	0.30	-0.01	0.17	0.65
$V_{Cr}^{\times}$	0	0.00	-0.01	0.00	1.25
$V_{O}^{\times}$	0	0.00	0.00	0.00	5.42
$V_{O}^{\bullet}$	1	-0.04	-0.03	0.17	5.87
$V_{O}^{\bullet\bullet}$	2	-0.17	-0.09	0.69	6.76
O_{i}''	-2	0.08	-0.25	0.69	5.66
O_{i}'	-1	0.02	-0.10	0.17	4.76
$O_{i}^{\times}$	0	0.00	-0.02	0.00	4.49
$Cr_{i}^{\times}$	0	0.00	-0.15	0.00	10.78
$Cr_{i}^{\bullet}$	1	0.11	-0.06	0.17	9.61
$Cr_{i}^{\bullet\bullet}$	2	0.18	-0.05	0.69	8.66
$Cr_{i}^{\bullet\bullet\bullet}$	3	0.22	-0.12	1.56	7.94

Figure 1, Figure 2, Figure 3 and Figure 4 show the DOS spectra in defective AFM Cr_2O_3 of Cr vacancies, O vacancies, O interstitials and Cr interstitials, respectively. The spectra are very similar to that of bulk Cr_2O_3 with a band gap near 3.3 eV, except that some intensive discrete states (marked in red) are created near the valence or conduction band, which reduces the effective band gaps.

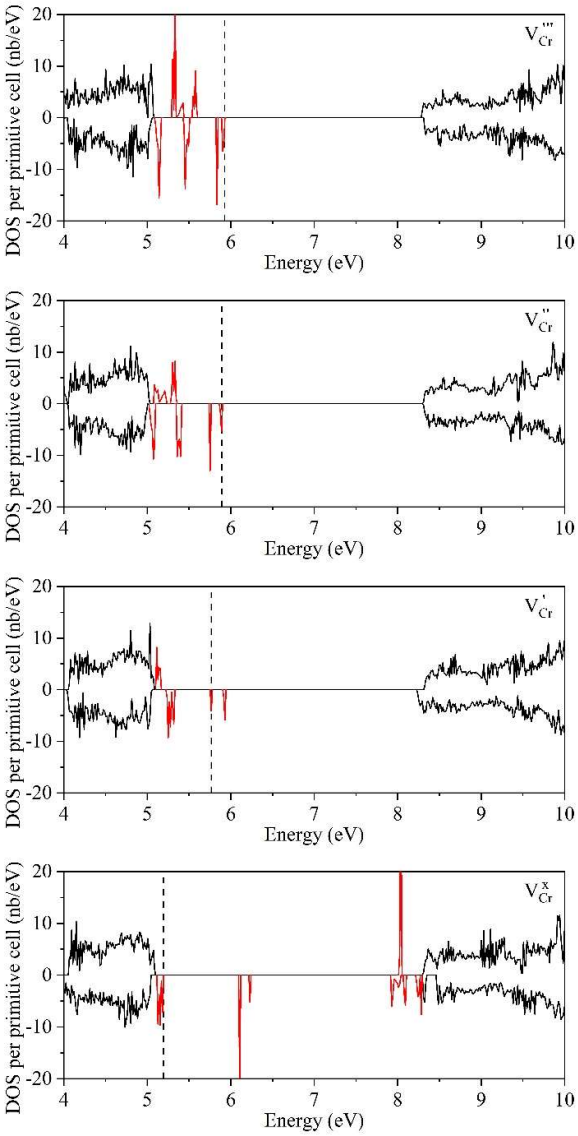


Figure 1. Density of states in defective AFM Cr_2O_3 with Cr vacancies. The Fermi energy is marked by the vertical dashed line. The states induced by the defect are marked in red.

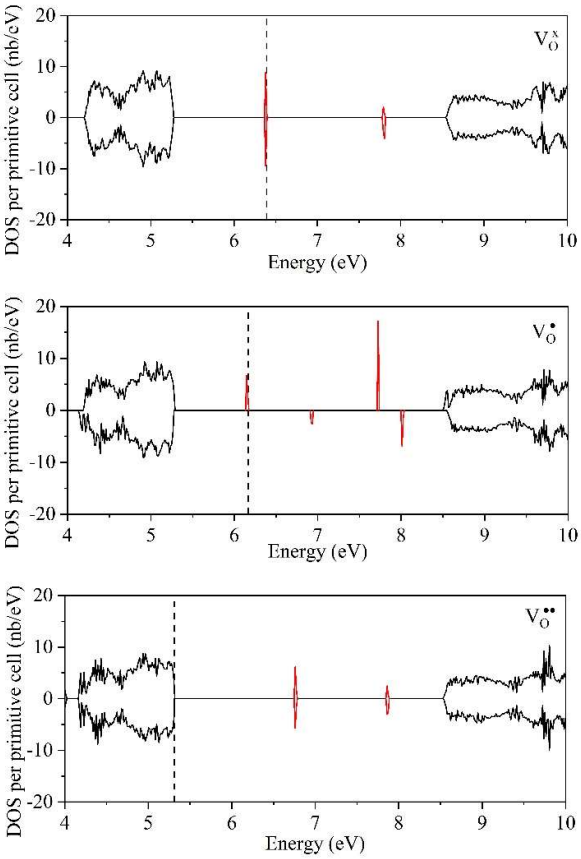


Figure 2. Density of states in defective AFM Cr_2O_3 with O vacancies. The Fermi energy is marked by the vertical dashed line. The states induced by the defect are marked in red.

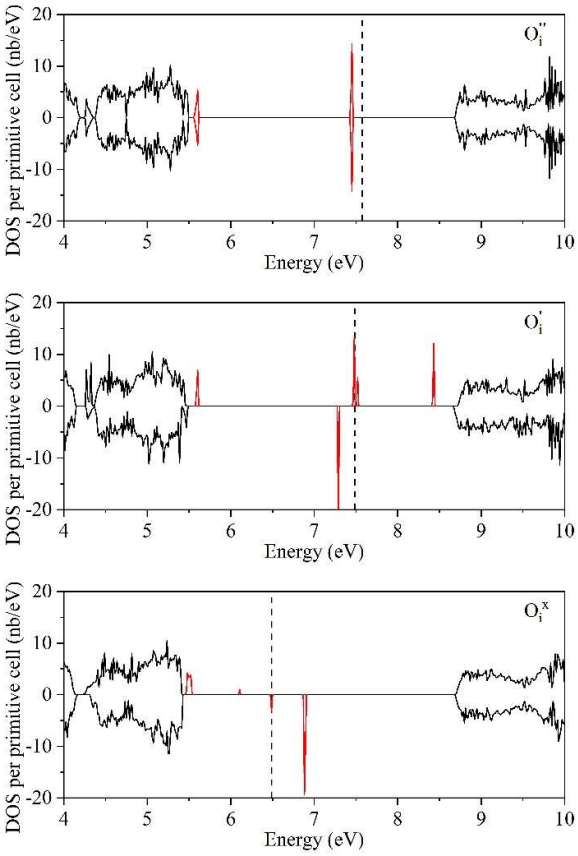
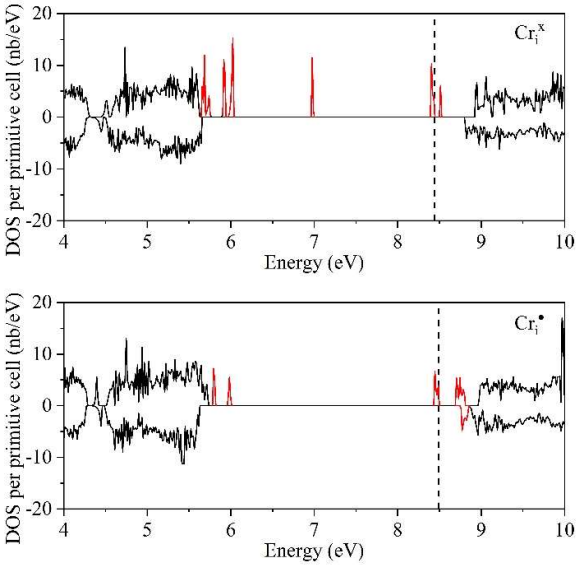


Figure 3. Density of states in defective AFM Cr_2O_3 with O interstitials. The Fermi energy is marked by the vertical dashed line. The states induced by the defect are marked in red.



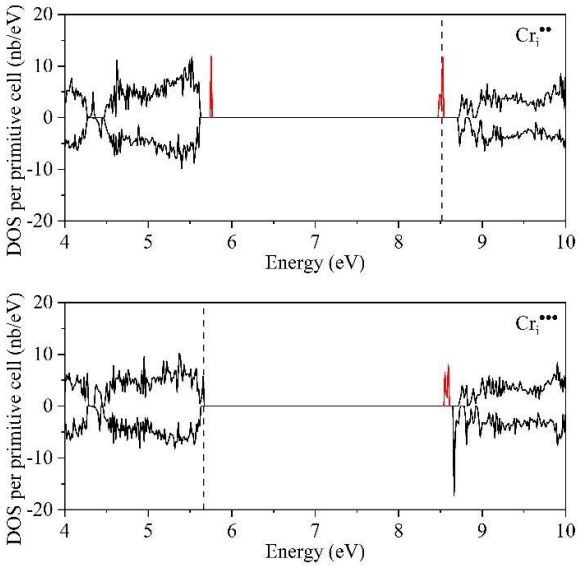


Figure 4. Density of states in defective AFM Cr_2O_3 with Cr interstitials. The Fermi energy is marked by the vertical dashed line. The states induced by the defect are marked in red.

PM state

The standard defect formation energy in PM Cr_2O_3 are shown in Table 2 with correction energies. The electrostatic correction energy, alignment energy and atomic chemical potential are the same as in AFM Cr_2O_3. The elastic correction energies of defect with different SQS configurations at different sites are nearly the same and shown in Table 2. The corrected energy of bulk PM Cr_2O_3 with 4 SQS configurations after cell-fixed relaxation is nearly the same (-6073.24 eV). The thermal average value at 700 °C of the middle of the band gap is 7.05 eV and this value is chosen to be the reference Fermi level in PM Cr_2O_3.

Table 2. Effective Charge (q), Finite-Size Elastic Correction Energy ($E_{\mathrm{corr,elas}}$) and Standard Defect Formation Energy (E_{f}^0) for defect in 2 × 2 × 2 supercell of PM Cr_2O_3.

	q	$E_{\mathrm{corr,elas}}$ (eV)	SQS	E_{f}^0 (eV)			
V_{Cr}'''	-3	-0.30	1	-0.16	-0.12	-0.14	-0.12
			2	-0.13	-0.14	-0.19	-0.17
			3	-0.10	-0.11	-0.17	-0.12
			4	-0.13	-0.15	-0.19	-0.13
V_{Cr}''	-2	-0.12	1		-0.09	-0.00	-0.09
V_{Cr}'	-1	-0.02	1	0.55	0.29		0.29
$V_{Cr}^{\times}$	0	-0.01	1	1.31	1.05	1.16	1.05
$V_O^{\times}$	0	0.00	1	5.38	5.40	5.45	5.40
			2	5.42	5.41	5.44	5.36
$V_O^{\bullet}$	1	-0.02	1	5.92	5.94	5.84	5.94
			2	5.83	5.98	5.93	5.90
$V_O^{\bullet\bullet}$	2	-0.08	1	6.98	6.93	6.97	6.93
			2		7.01	6.98	6.97
$Cr_i^{\bullet\bullet\bullet}$	3	-0.08	1	8.81	8.20	8.29	8.22

PM state of Cr_2O_3 in this work is simulated by SQS structures generated by Cr atom positions relaxed in AFM state shown in Table 3. The pair-correlation of Cr spins in the SQS vanished between neighbors within 4.2 Å. Table 3 shows these structures with the values of magnetic moment after relaxation

keeping cell shape and dimension fixed as for defect calculations. The initial Cr magnetic moment is set to be 3 μ_B. The spin directions do not change after relaxation. The atom sites used to calculate vacancy formation energies are in bold. The interstitial sites used in the calculations are in the middle of atoms 8 and 9, of atoms 18 and 19, of atoms 28 and 29 and of atoms 48 and 49.

Table 3. Spin distribution of AFM and SQS Cr_2O_3 in reduced rhombohedral coordinates in which the length is 10.895 Å and the angle is 55.133° for the three axis. The positive and negative signs of magnetic moment after relaxation represents respectively the up and down spin directions oriented along [111] direction in rhombohedral coordinates.

Number	Atom	Position			Magnetic moment (μ_B)				
					AFM	SQS-1	SQS-2	SQS-3	SQS-4
1	**O**	**0.375**	**0.223**	**0.027**	**0.00**	**0.00**	**0.00**	**-0.01**	**0.00**
2	O	0.027	0.375	0.223	0.00	0.00	0.02	0.02	0.02
3	O	0.223	0.027	0.375	0.00	-0.02	0.00	0.01	-0.01
4	O	0.125	0.277	0.473	0.00	0.00	-0.01	0.00	0.00
5	O	0.473	0.125	0.277	0.00	0.00	0.01	0.00	0.00
6	O	0.277	0.473	0.125	0.00	0.00	0.02	0.00	0.02
7	**Cr**	**0.076**	**0.076**	**0.076**	**2.73**	**2.74**	**-2.75**	**2.71**	**2.75**
8	Cr	0.174	0.174	0.174	-2.73	2.75	-2.74	-2.74	2.76
9	Cr	0.326	0.326	0.326	2.73	2.74	2.73	-2.73	-2.75
10	Cr	0.424	0.424	0.424	-2.73	2.74	-2.74	2.73	2.71
11	**O**	**0.875**	**0.223**	**0.027**	**0.00**	**0.01**	**-0.01**	**0.01**	**0.00**
12	O	0.527	0.375	0.223	0.00	-0.01	0.00	0.00	0.00
13	O	0.723	0.027	0.375	0.00	0.00	0.00	0.00	-0.01
14	O	0.625	0.277	0.473	0.00	0.02	0.00	-0.01	0.00
15	O	0.973	0.125	0.277	0.00	-0.02	0.01	0.00	-0.02
16	O	0.777	0.473	0.125	0.00	0.02	-0.01	0.02	0.02
17	**Cr**	**0.576**	**0.076**	**0.076**	**2.73**	**-2.75**	**-2.74**	**-2.76**	**2.74**
18	Cr	0.674	0.174	0.174	-2.73	2.72	-2.75	2.73	-2.72
19	Cr	0.826	0.326	0.326	2.73	-2.73	-2.73	-2.72	-2.75
20	Cr	0.924	0.424	0.424	-2.73	2.72	-2.73	-2.76	-2.76
21	**O**	**0.375**	**0.723**	**0.027**	**0.00**	**0.00**	**0.00**	**0.00**	**-0.01**
22	O	0.027	0.875	0.223	0.00	0.00	0.01	0.00	-0.02
23	O	0.223	0.527	0.375	0.00	-0.02	0.00	0.00	0.00
24	O	0.125	0.777	0.473	0.00	-0.02	0.00	-0.02	0.00
25	O	0.473	0.625	0.277	0.00	0.01	-0.01	0.01	0.01
26	O	0.277	0.973	0.125	0.00	-0.01	0.01	0.01	-0.02
27	**Cr**	**0.076**	**0.576**	**0.076**	**2.73**	**2.74**	**-2.77**	**2.73**	**-2.74**
28	Cr	0.174	0.674	0.174	-2.73	-2.73	-2.76	-2.72	-2.75
29	Cr	0.326	0.826	0.326	2.73	2.75	-2.72	-2.73	2.77
30	Cr	0.424	0.924	0.424	-2.73	2.75	2.73	-2.75	2.75
31	O	0.875	0.723	0.027	0.00	0.01	0.00	0.00	0.00
32	O	0.527	0.875	0.223	0.00	-0.01	0.00	0.02	-0.01
33	O	0.723	0.527	0.375	0.00	0.00	0.01	0.02	0.02
34	O	0.625	0.777	0.473	0.00	0.00	-0.01	-0.01	0.01
35	O	0.973	0.625	0.277	0.00	0.00	0.02	0.00	0.01
36	O	0.777	0.973	0.125	0.00	0.00	0.02	0.00	0.00
37	Cr	0.576	0.576	0.076	2.73	-2.75	2.74	-2.77	-2.75
38	Cr	0.674	0.674	0.174	-2.73	-2.76	2.74	-2.76	-2.74

39	Cr	0.826	0.826	0.326	2.73	-2.72	-2.75	-2.71	2.73
40	Cr	0.924	0.924	0.424	-2.73	2.74	2.71	2.74	2.74
41	**O**	**0.375**	**0.223**	**0.527**	**0.00**	**-0.01**	**0.00**	**0.00**	**0.00**
42	O	0.027	0.375	0.723	0.00	0.01	-0.02	0.01	0.00
43	O	0.223	0.027	0.875	0.00	0.00	0.00	0.00	-0.01
44	O	0.125	0.277	0.973	0.00	-0.02	0.01	0.00	-0.02
45	O	0.473	0.125	0.777	0.00	0.02	0.00	-0.01	0.00
46	O	0.277	0.473	0.625	0.00	-0.02	0.00	-0.02	0.00
47	**Cr**	**0.076**	**0.076**	**0.576**	**2.73**	**2.75**	**2.74**	**2.72**	**2.74**
48	Cr	0.174	0.174	0.674	-2.73	-2.72	2.74	-2.73	-2.73
49	Cr	0.326	0.326	0.826	2.73	2.73	2.72	2.76	2.74
50	Cr	0.424	0.424	0.924	-2.73	-2.72	-2.74	2.75	-2.73
51	O	0.875	0.223	0.527	0.00	0.00	0.01	0.01	0.01
52	O	0.527	0.375	0.723	0.00	0.00	0.00	-0.02	0.00
53	O	0.723	0.027	0.875	0.00	0.02	0.00	0.00	0.00
54	O	0.625	0.277	0.973	0.00	0.00	0.01	0.00	0.00
55	O	0.973	0.125	0.777	0.00	0.00	-0.01	0.00	0.00
56	O	0.777	0.473	0.625	0.00	0.00	-0.02	-0.01	0.02
57	Cr	0.576	0.076	0.576	2.73	-2.74	-2.72	2.75	2.74
58	Cr	0.674	0.174	0.674	-2.73	-2.75	2.74	2.76	-2.71
59	Cr	0.826	0.326	0.826	2.73	-2.74	2.74	-2.73	2.70
60	Cr	0.924	0.424	0.924	-2.73	-2.74	2.76	-2.75	-2.75
61	O	0.375	0.723	0.527	0.00	-0.01	0.00	0.01	-0.01
62	O	0.027	0.875	0.723	0.00	0.01	0.00	0.00	0.00
63	O	0.223	0.527	0.875	0.00	0.00	0.00	-0.02	0.00
64	O	0.125	0.777	0.973	0.00	0.00	0.02	0.00	0.01
65	O	0.473	0.625	0.777	0.00	0.00	-0.01	-0.02	0.02
66	O	0.277	0.973	0.625	0.00	0.00	-0.01	0.00	0.00
67	Cr	0.076	0.576	0.576	2.73	2.75	2.75	2.73	-2.72
68	Cr	0.174	0.674	0.674	-2.73	2.76	-2.72	2.77	2.74
69	Cr	0.326	0.826	0.826	2.73	2.72	-2.74	2.75	2.73
70	Cr	0.424	0.924	0.924	-2.73	-2.74	2.74	-2.74	2.75
71	O	0.875	0.723	0.527	0.00	0.00	-0.01	0.00	-0.01
72	O	0.527	0.875	0.723	0.00	0.00	0.00	0.00	-0.02
73	O	0.723	0.527	0.875	0.00	0.02	-0.02	0.01	0.00
74	O	0.625	0.777	0.973	0.00	0.02	-0.02	0.02	0.01
75	O	0.973	0.625	0.777	0.00	-0.01	0.00	-0.01	0.00
76	O	0.777	0.973	0.625	0.00	0.01	0.00	-0.02	0.00
77	Cr	0.576	0.576	0.576	2.73	-2.74	2.74	2.74	-2.74
78	Cr	0.674	0.674	0.674	-2.73	2.73	2.75	2.74	-2.74
79	Cr	0.826	0.826	0.826	2.73	-2.75	2.75	-2.73	2.74
80	Cr	0.924	0.924	0.924	-2.73	-2.75	-2.74	2.73	-2.72

In this work, PM state of Cr metal is tried to be simulated by SQS structures generated by Cr atom positions relaxed in AFM state shown in Table 4. The pair-correlation of Cr spins in the SQS almost vanished between neighbors within 5.0 Å. Table 4 shows these structures with the values of magnetic moment after relaxation keeping cell shape and dimension fixed. The initial Cr magnetic moment is set to be 4 μ_B. The spin directions do not change after relaxation.

Table 4. Spin distribution of AFM and SQS Cr metal in Cartesian coordinates in which the commensurate length is 9.490 Å for the three axis. The positive and negative signs of magnetic moment after relaxation represents respectively the up and down spin directions oriented along [001] direction in Cartesian coordinates.

Number	Position			Magnetic moment (μ_B)			
				AFM	SQS1	SQS2	SQS3
1	0.000	0.000	0.000	3.35	-3.53	3.53	-3.47
2	0.167	0.167	0.167	-3.35	-3.43	3.57	3.52
3	0.333	0.000	0.000	3.35	-3.52	3.51	3.54
4	0.500	0.167	0.167	-3.35	-3.54	-3.52	-3.43
5	0.667	0.000	0.000	3.35	-3.49	-3.43	3.55
6	0.833	0.167	0.167	-3.35	3.49	3.45	-3.50
7	0.000	0.333	0.000	3.35	-3.55	3.57	3.49
8	0.167	0.500	0.167	-3.35	-3.49	3.45	3.49
9	0.333	0.333	0.000	3.35	3.50	-3.46	-3.50
10	0.500	0.500	0.167	-3.35	3.55	3.49	-3.49
11	0.667	0.333	0.000	3.35	-3.56	-3.35	-3.61
12	0.833	0.500	0.167	-3.35	3.49	3.39	3.47
13	0.000	0.667	0.000	3.35	3.48	-3.49	-3.50
14	0.167	0.833	0.167	-3.35	-3.44	3.44	3.50
15	0.333	0.667	0.000	3.35	-3.49	3.48	3.47
16	0.500	0.833	0.167	-3.35	-3.55	3.46	3.47
17	0.667	0.667	0.000	3.35	3.49	-3.44	-3.49
18	0.833	0.833	0.167	-3.35	-3.46	3.42	-3.50
19	0.000	0.000	0.333	3.35	3.48	3.56	3.44
20	0.167	0.167	0.500	-3.35	-3.45	-3.53	3.58
21	0.333	0.000	0.333	3.35	3.48	-3.48	3.52
22	0.500	0.167	0.500	-3.35	-3.50	3.53	-3.45
23	0.667	0.000	0.333	3.35	-3.51	-3.46	3.49
24	0.833	0.167	0.500	-3.35	3.54	3.51	3.52
25	0.000	0.333	0.333	3.35	3.49	3.51	3.49
26	0.167	0.500	0.500	-3.35	3.53	-3.47	-3.45
27	0.333	0.333	0.333	3.35	3.47	3.48	3.46
28	0.500	0.500	0.500	-3.35	-3.50	-3.52	-3.47
29	0.667	0.333	0.333	3.35	-3.52	-3.42	-3.57
30	0.833	0.500	0.500	-3.35	-3.49	-3.50	-3.50
31	0.000	0.667	0.333	3.35	3.43	-3.45	3.49
32	0.167	0.833	0.500	-3.35	-3.48	3.49	-3.43
33	0.333	0.667	0.333	3.35	-3.54	-3.44	-3.50
34	0.500	0.833	0.500	-3.35	3.53	3.48	3.51
35	0.667	0.667	0.333	3.35	3.48	3.52	-3.53
36	0.833	0.833	0.500	-3.35	3.60	-3.49	-3.45
37	0.000	0.000	0.667	3.35	3.49	3.51	3.46
38	0.167	0.167	0.833	-3.35	-3.49	3.53	3.45
39	0.333	0.000	0.667	3.35	-3.53	-3.56	3.48
40	0.500	0.167	0.833	-3.35	-3.48	3.53	-3.49
41	0.667	0.000	0.667	3.35	3.47	3.51	-3.54
42	0.833	0.167	0.833	-3.35	-3.47	3.43	3.52

43	0.000	0.333	0.667	3.35	3.47	-3.53	-3.46
44	0.167	0.500	0.833	-3.35	3.54	-3.53	-3.46
45	0.333	0.333	0.667	3.35	-3.52	3.51	3.41
46	0.500	0.500	0.833	-3.35	-3.51	-3.55	-3.45
47	0.667	0.333	0.667	3.35	3.43	-3.47	3.52
48	0.833	0.500	0.833	-3.35	-3.46	3.48	-3.54
49	0.000	0.667	0.667	3.35	3.51	-3.58	3.44
50	0.167	0.833	0.833	-3.35	3.46	-3.45	-3.45
51	0.333	0.667	0.667	3.35	3.53	-3.55	3.42
52	0.500	0.833	0.833	-3.35	3.44	-3.50	3.51
53	0.667	0.667	0.667	3.35	3.48	-3.59	-3.54
54	0.833	0.833	0.833	-3.35	3.53	-3.50	-3.55