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Electronic Supplementary Information

The Influence of (Al, Fe, Mg) Impurities on Triclinic Ca_3SiO_5: Interpretations from DFT Calculations

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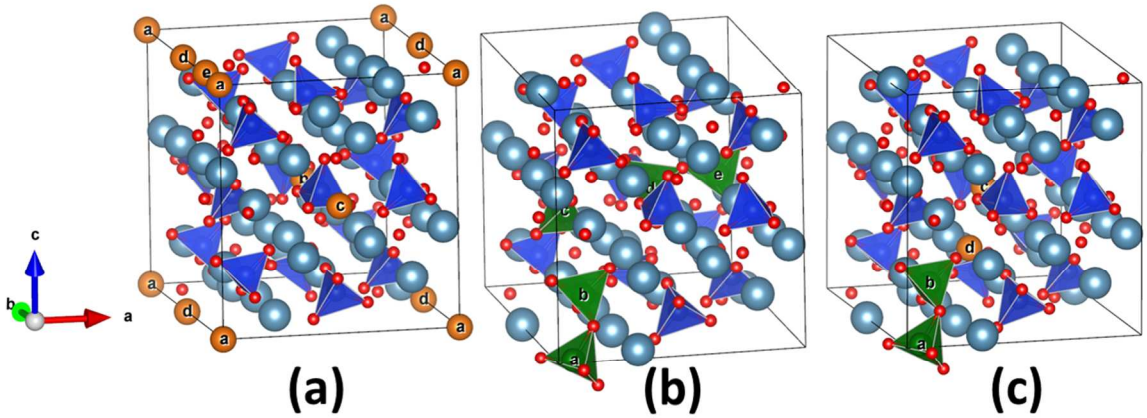

Figure ES1: Crystal structures of Tl-Ca_3SiO_5 containing impurities. Calcium (Ca), silicon (Si), magnesium (Mg), aluminum (Al) and oxygen atoms (O) are represented as gray, blue, orange, green and red spheres, respectively. The blue and gray tetrahedra represent Si and Al tetrahedra respectively. (a) Mg replacement (Cases: 2-6); (b) Al replacement (Cases: 7-10); (c) mixed Mg and Al insertions (Cases 11 and 12). The substitutions by Fe impurities are similar to Al atom substitutions in Figure 2(b). In all figures, the letters 'a-e' are used to label different atoms corresponding to different substitution sites (see text for details).

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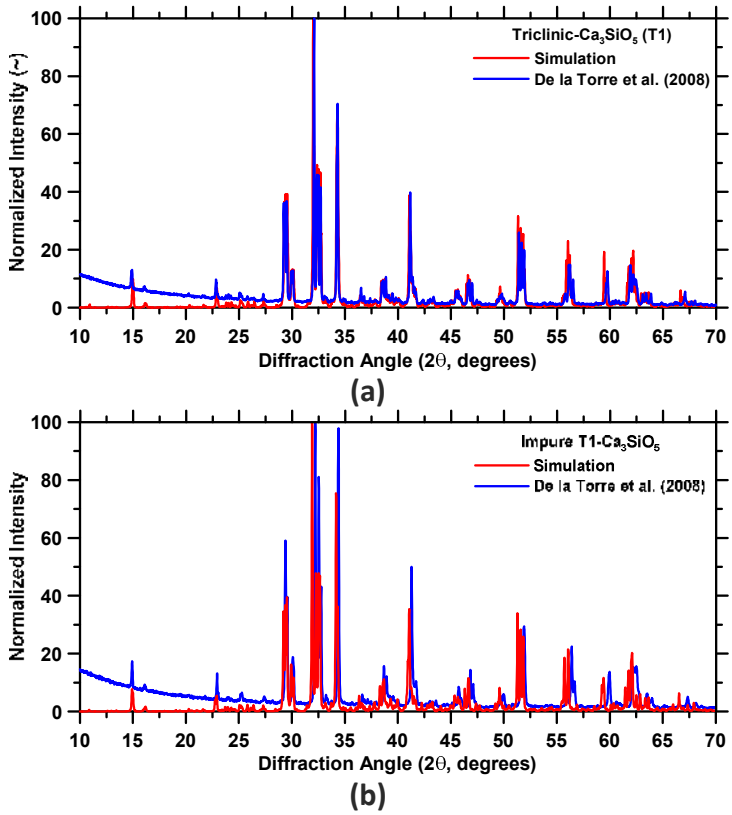

Figure ES2: A comparison of the simulated and experimental x-ray patterns of: (a) pure (Checkpoint # 1) and (b) impure variants of TI-Ca_3SiO_5 (Checkpoint # 2). The simulated patterns are at the most offset 0.30° offset with respect to the experimentally measured patterns.[11] This difference is explained by the slightly different equilibrium cell dimensions obtained from the DFT calculations with respect to experiments (see Table 1).

Table ES1: Interplanar spacing (d), Miller indices (h,k,l) and diffraction angles (2θ) for the major x-ray peaks noted in Figure ES2 (b)

Simulated Structural Parameters					Experimental (from De la Torre e al. 2008)				
d (Å)	h	k	l	2θ	d (Å)	h	k	l	2θ
3.0507	-1	-4	3	29.2494	3.0362	-1	-4	3	29.3932
2.9787	-2	-2	4	29.973	2.9691	-2	-2	4	30.0727
2.8126	3	0	3	31.7888	2.7755	3	0	3	32.1741
2.6204	-1	0	5	34.1888	2.6058	-1	0	5	34.3874
2.1943	-1	0	6	41.1001	2.1860	0	0	6	41.2649
1.7708	-4	6	1	51.5667	1.7696	-6	3	1	51.6064
1.7630	1	-8	2	51.8144	1.7594	-3	7	0	51.9293
1.6382	-2	4	6	56.0929	1.6228	1	4	6	56.6736
1.5541	-5	-6	5	59.4242	1.5422	5	-3	6	59.9282
1.5076	2	1	8	61.4505	1.4915	-4	-8	1	62.1908
1.5007	-6	6	0	61.7610	1.4898	-6	6	0	62.2659

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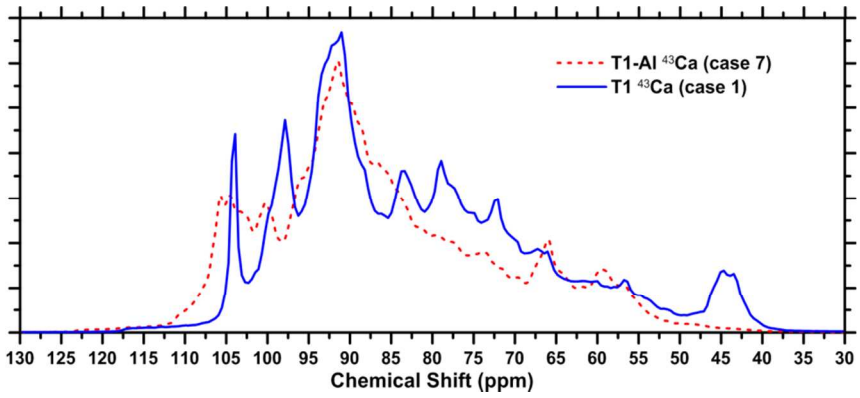
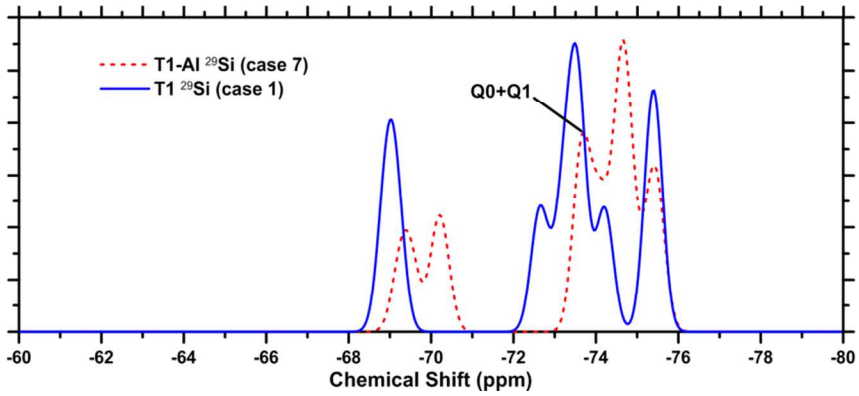
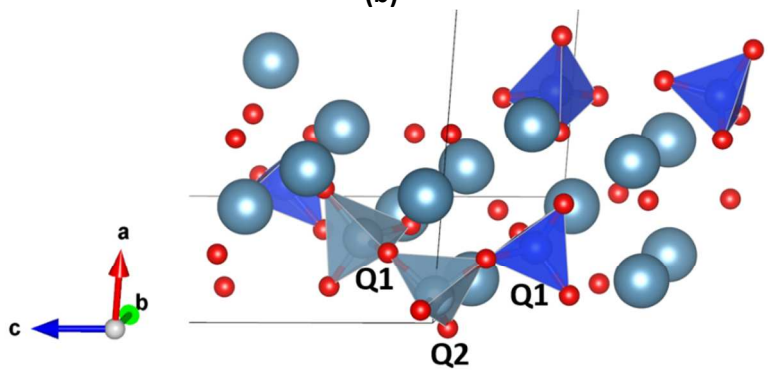


(a)



(b)



(c)

Figure ES3: Calculated NMR spectra for: (a) ^{43}Ca and (b) ^{29}Si for selected impurity scenarios. Solid blue and red dotted lines correspond to pure TI (Case 1) and TI with Al impurities (Case 7). (c) Shows the arrangement of tetrahedra in T1 containing Al impurities (Case 7). Ca, Si, Al and O atoms are represented as gray, blue, small gray and red spheres, respectively.

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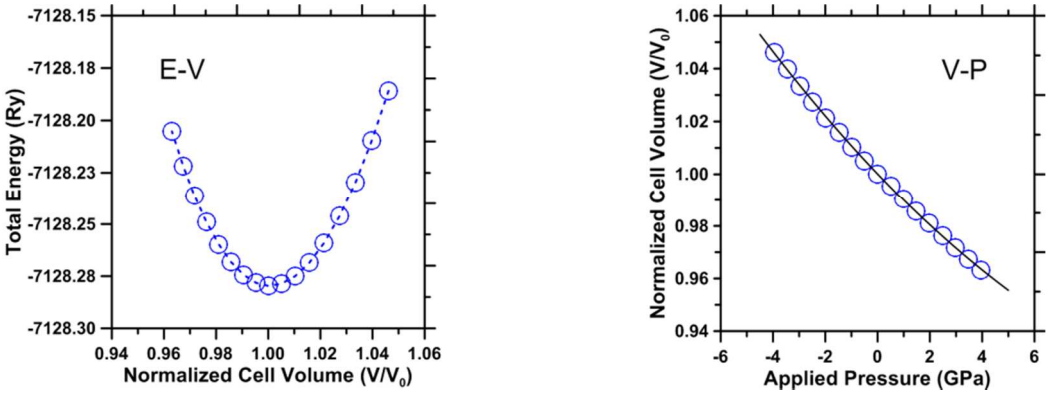
Table ES2: Calculated parameters for variants of TI-Ca_3SiO_5 containing Al, Fe, Mg species.

P	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6	Case 7	Case 8	Case 9	Case 10	Case 11	Case 12	Case 13	Case 14	Case 15	Case 16
a (Å)	11.73	11.72	11.71	11.69	11.69	11.63	11.75	11.72	11.77	11.80	11.74	11.73	11.70	11.74	11.74	11.75
b(Å)	14.28	14.27	14.27	14.25	14.25	14.24	14.27	14.28	14.25	14.23	14.25	14.23	14.27	14.29	14.29	14.30
c(Å)	13.73	13.69	13.70	13.67	13.69	13.62	13.69	13.68	13.71	13.67	13.66	13.70	13.70	13.72	13.72	13.70
α°	104.80	104.80	104.72	104.73	104.80	104.73	104.52	104.59	104.90	104.61	104.52	104.56	104.61	104.51	104.51	104.54
β°	94.35	94.32	94.32	94.28	94.27	94.42	94.23	94.11	94.34	94.22	94.18	94.24	94.29	94.28	94.27	94.23
γ°	90.12	90.12	90.01	90.07	90.03	89.90	89.80	90.08	90.18	89.87	89.87	89.80	89.89	89.76	89.80	89.83
V(Å^3)	2215.45	2206.95	2207.07	2196.25	2197.75	2173.61	2215.51	2209.92	2215.41	2213.77	2206.47	2205.88	2207.46	2222.64	2221.73	2223.19
ρ (g/cMIII)	3.081	3.080	3.080	3.083	3.081	3.091	3.061	3.077	3.070	3.059	3.070	3.071	3.124	3.102	3.104	3.102
$-E_C$ (kJ/mol)	5299.60	5290.75	5290.49	5281.67	5281.62	5265.36	5295.53	5292.78	5295.03	5290.72	5286.69	5284.99	5248.99	5265.29	5264.26	5263.43
$-\Delta H_{fe}$ (kJ/mol)	2674.16	2667.66	2667.40	2660.93	2660.89	2649.32	2669.92	2667.17	2669.41	2664.93	2663.42	2661.73	2607.63	2623.93	2622.89	2622.07
$-\Delta H_{fo}$ (kJ/mol)	109.37	105.82	105.57	102.05	102.00	96.35	99.86	97.11	99.35	89.59	96.31	94.62	83.27	99.57	98.54	97.71



(a) **(b)**

Figure ES4: (a) Total energy (Ry) versus the normalized equilibrium cell volume and (b) the normalized equilibrium cell volume versus the applied pressure in the range -4 GPa - 4 GPa.

(a) **(b)**

Figure ES5: An illustration of the bond lengths and bond angles described in Table 3. (a) Si, Ca and O atoms are represented as blue, green and red spheres, respectively. (b) Ca is represented as a green sphere, and Ca and O atoms are on the same plane. This figure also represents the case of Mg substituting at Ca sites.

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Table ES3: The calculated directional stiffness constants (in GPa) for pure and impure TI-Ca_3SiO_5.

	Case1	Case2	Case4	Case5	Case6	Case7	Case10	Case11	Case13	Case14
C_{11}	166.47	167.17	168.44	165.89	164.68	157.50	156.41	156.15	164.80	155.58
C_{12}	56.32	56.27	57.64	56.07	57.20	56.99	57.48	58.10	57.40	56.72
C_{13}	60.63	60.53	60.61	60.55	60.60	60.58	59.02	59.94	63.09	60.01
C_{14}	-0.31	-0.33	-0.02	-0.33	-0.15	-1.70	-1.53	-1.40	-0.78	-1.36
C_{15}	-9.60	-9.60	-10.26	-9.52	-10.18	-7.35	-8.77	-7.94	-9.28	-7.16
C_{16}	0.02	-0.57	-0.94	-0.33	0.41	0.67	0.96	0.39	-0.24	0.49
C_{22}	196.78	196.77	194.88	196.47	197.58	193.62	186.40	192.52	192.79	190.78
C_{23}	70.15	71.28	73.16	71.44	74.71	71.11	71.16	72.40	73.69	72.24
C_{24}	0.50	0.30	0.58	0.61	1.66	0.54	1.32	0.93	0.40	0.60
C_{25}	-7.73	-8.05	-8.20	-7.71	-8.31	-6.62	-7.00	-6.69	-7.56	-6.91
C_{26}	0.09	0.58	1.82	0.40	1.25	1.44	1.07	0.85	1.51	1.93
C_{33}	172.91	171.59	169.19	171.37	169.64	167.05	163.10	165.61	168.93	163.97
C_{34}	0.70	0.66	0.81	0.91	0.18	0.26	0.70	0.56	1.12	0.56
C_{35}	-4.50	-4.60	-3.94	-4.34	-4.24	-3.21	-2.93	-2.62	-4.42	-3.39
C_{36}	-0.80	-1.43	-1.66	-0.58	-2.16	-0.55	-0.88	-0.69	-0.72	-0.67
C_{44}	64.90	65.33	66.23	65.22	68.01	65.67	64.36	66.36	63.62	63.47
C_{45}	-1.75	-2.62	-2.68	-1.75	-3.18	-1.43	-1.17	-1.43	-2.22	-1.97
C_{46}	-3.19	-3.34	-3.54	-2.91	-3.27	-1.95	-2.64	-2.24	-3.03	-2.07
C_{55}	61.49	60.76	60.73	60.48	60.78	59.07	57.43	58.92	58.96	55.46
C_{56}	-0.18	0.00	0.33	0.01	0.46	-1.20	-0.34	-0.58	-0.74	-0.59
C_{66}	48.45	48.80	49.24	47.11	50.46	48.63	48.90	49.23	47.43	47.15

Table ES4: The maximum isosurface value of the charge density (MIV, e/Å^3) for pure and impure TI-Ca_3SiO_5

Polytype	MIV at VBM (e/Å^3)	MIV at CBM (e/Å^3)
Pure TI (Case 1)	0.084902	0.001715
TI-Mg (Case 4)	0.081823	0.001806
TI-Al (Case 7)	0.077469	0.002460
TI-Fe (no spin) (Case 13)	0.165750	0.199470
TI-Fe (AF) (Case 14)	0.222030	0.373920

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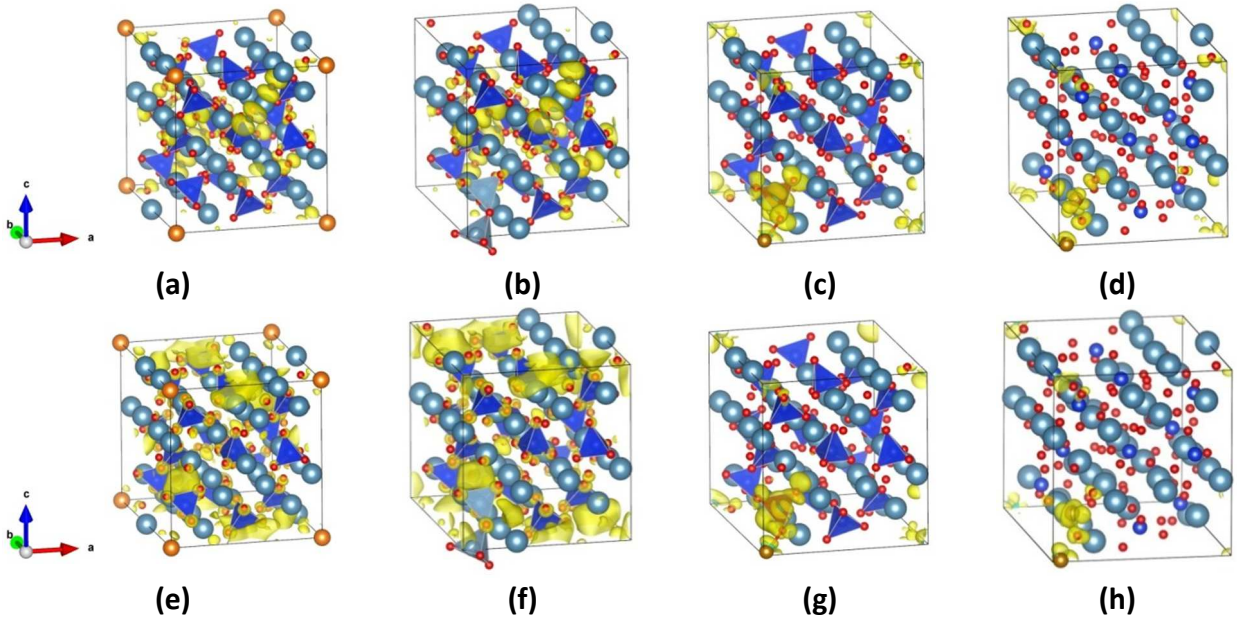

Figure ES6: Partial charge density of the VBM (a, b, c, d) and CBM (e, f, g, h) of impure TI-Ca_3SiO_5. From left to right, the reported cells correpond to Cases 4, 7, 13, and 14, respectively. Ca, Si and O atoms are represented as gray, blue and red spheres, respectively. Mg, Al and Fe atoms are represented as orange, small gray, brown spheres, respectively.

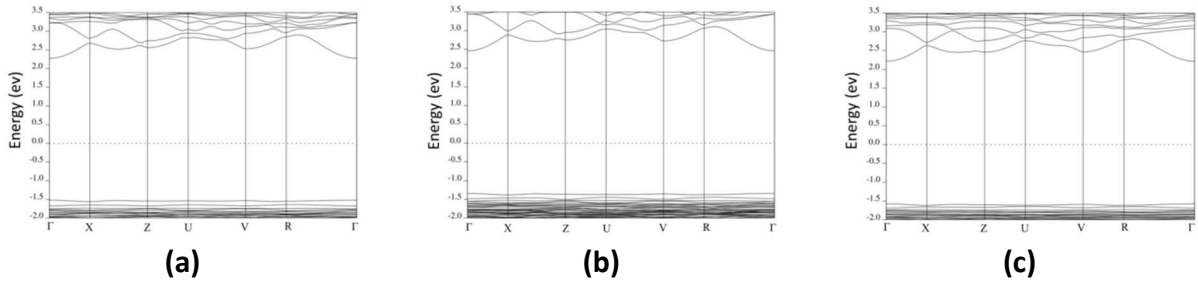

Figure ES7: Band structures of pure and impure TI-Ca_3SiO_5. (a) Pure TI-C_3S; (b) Case 4 with Mg impurities; (c) Case 7 with Al impurities. The Fermi energy corresponds to 0.0 eV. K-points path for bands structure:

Γ = (0,0,0), X=(0.5,0,0), Z=(0,0,–0.5), Y=(0.5,0,–0.5), ς=(0,0.5,–0.5), P=(0.5,0.5,–0.5).

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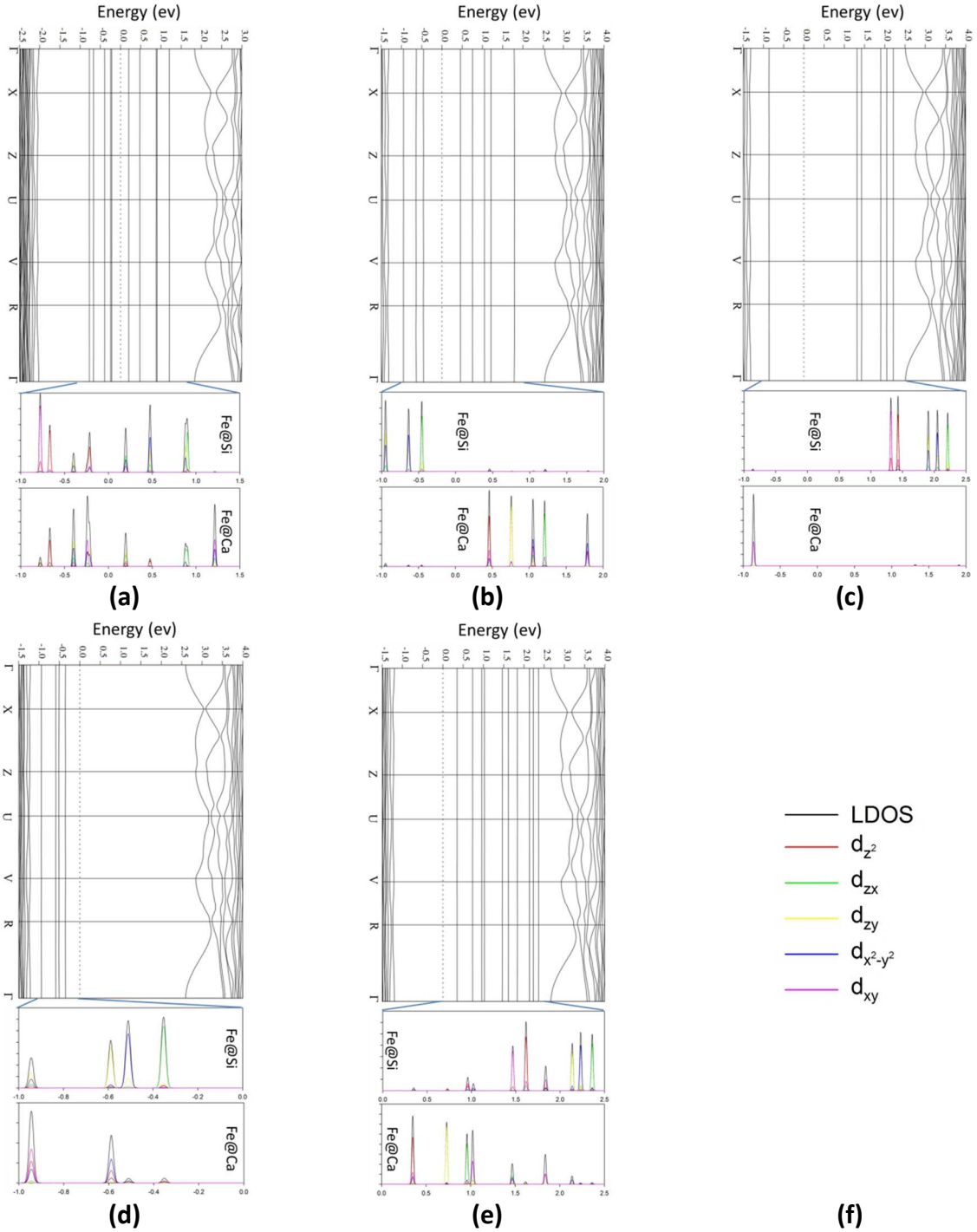

Figure ES8: Band structure and projected density of state (PDOS) of the Fe-3d orbital in TI-C_3S containing Fe impurities. (a) Case 13 (spin-unpolarized), Case 14, AF (b) spin-up electrons and (c) spin-down electrons; Case 15, FM (d) spin-up electrons and (e) spin-down electrons, (f) color code for different orbitals. The lines between band structures and PDOS correspond to the amplified PDOS area in band structures.

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Table ES5: Magnetic moments (μB) of Fe and O atoms in the Fe-doped TI-C_3S system.

	FM	AF
Fe at Si site	3.8152	3.7241
Fe at Ca site	3.8745	-3.8181
O1	0.3980	-0.0691
O2	0.3046	0.2923
O3	0.2822	0.2773
O4	0.3013	-0.2756
O5	0.2953	-0.2591
O6	0.2984	0.2901
O7	0.1684	-0.1586