Supplement Materials

SUBSTITUTION EFFECTS IN SPIN-POLARIZED $(Cr_{4-x}Fe_X)_{0.5}AC$ (A = Ge, Si, Al) MAX PHASES

Natalja A. Fedorova[1,2], Alena V. Kovaleva[1], Julia S. Olshevskaya[3], Daria A. Ivanova[1], Victoria V. Kozak[1,2], Alexander A. Shubin[2], Anton S. Tarasov[1,2], Sergey N. Varnakov[1], Sergei G. Ovchinnikov[1, 2], Evgeniya M. Moshkina[1], Olga A. Maximova[1,2], Pavel V. Avramov[3**], and Felix N. Tomilin[1, 2*]

[1] Kirensky Institute of Physics, Federal Research Center KSC SB RAS, Krasnoyarsk, 660036 Russia
[2] Siberian Federal University, Krasnoyarsk, 660041 Russia
[3] Department of Chemistry, College of Natural Sciences, Kyungpook National University, 80 Daehak-ro, Buk-gu, Daegu, 41566 Republic of Korea
*****Correspondence: felixnt@gmail.com; paul.veniaminovich@knu.ac.kr

Abstract.

The use of spintronic devices with a tunable magnetic order on small scales is highly important for novel applications. The MAX phases containing transition metals and/or magnetic ion-substituted lattices attract a lot of attention. In this study, the magnetic and electronic properties of $(Cr_{4-X}Fe_X)_{0.5}AC$ (A = Ge, Si, Al) compounds were predicted and investigated within the density functional theory. It was established that single-substituted $(Cr_3Fe_1)_{0.5}AC$ (A = Ge, Si, Al) lattices are energetically favorable. An analysis of the magnetic states of the MAX phases demonstrated that their spin order changes upon substitution of iron atoms for chromium ones. It was found that mostly the $(Cr_{4-x}Fe_x)_{0,5}GeC$ and $(Cr_{4-x}Fe_x)_{0,5}AlC$ lattices acquire a ferrimagnetic state in contrast to $(Cr_{4-x}Fe_x)_{0,5}SiC$ for which the ferromagnetic spin-order dominates. It was pointed out that the atomic substitution could be an efficient way to tune the magnetic properties of proposed $(Cr_{4-X}Fe_X)_{0.5}AC$ (A = Ge, Si, Al) MAX phases.

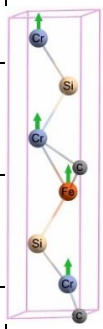
Keywords: MAX-phase; density functional theory; B3LYP; spintronics; magnetic and electronic properties.

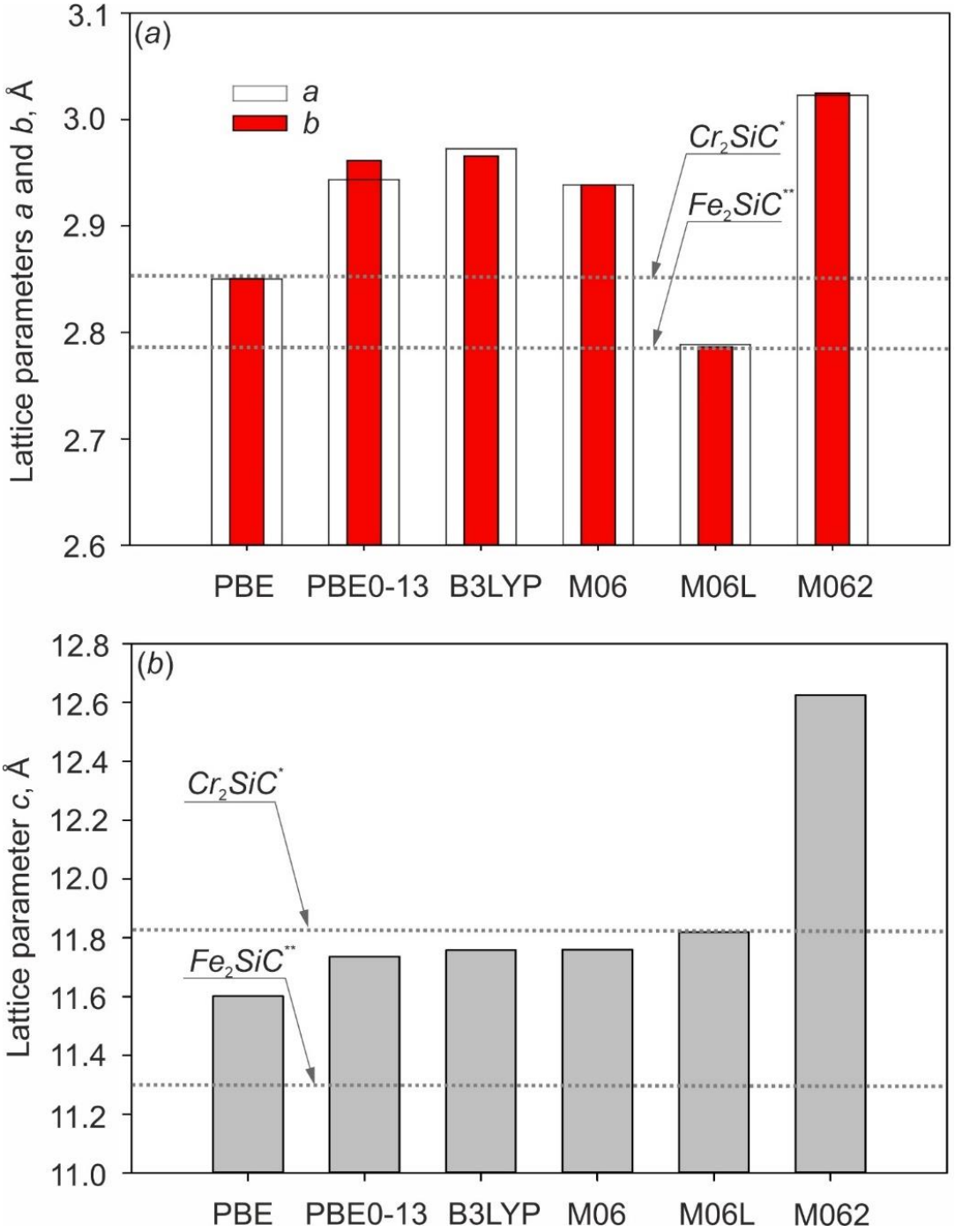
Table S1. Atomic and ionic radii*

Element	Atomic radius, Å	Ion charge	Ionic radius, Å
Fe	1.24	+2	0.82
		+3	0.67
Cr	1.25	+3	0.64

*- J. Emsley, The Elements, 3rd Edition, Oxford University Press, 1989, p. 264.

Table S2. Schematic of the ferromagnetic (FM), ferrimagnetic (FiM-*n*), and antiferromagnetic (AFM-*n*) ordering of the Cr and Fe magnetic moments in the $(Cr–Fe–Cr–Cr)_{0.5}SiC$ structure. Green and red arrows indicate the spins up and spin down directions on M atoms, respectively

M atom No. in the cell	Magnetic structure type											
		Formally possible for all the structures	Formally possible for only the unsubstituted structures						Formally possible for all the structures			
	FM	FM	AFM-1	AFM-2	AFM-3	AFM-4	AFM-5	AFM-6	FiM-1	FiM-2	FiM-3	FiM-4
4		↑	↑	↑	↓	↓	↑	↓	↑	↑	↑	↓
3		↑	↑	↓	↓	↑	↓	↑	↑	↑	↓	↑
2		↑	↓	↓	↑	↑	↑	↓	↑	↓	↑	↑
1		↑	↓	↑	↑	↓	↓	↑	↓	↑	↑	↑



Experiment:

*- Liao T., Wang J., Zhou Y. Chemical bonding and mechanical properties of M_2AC (M = Ti, V, Cr, A = Al, Si, P, S) ceramics from first-principles investigations // Journal of Materials Research. 2009. Vol. 24, № 2. P. 556–564.

**- Metadjer N. et al. Electronic and magnetic properties of Fe_2SiC // European Physical Journal B. Springer New York LLC, 2014. Vol. 87, № 10.

Figure S1. Comparison of unit cell parameters *a*, *b* (on the left), and *c* (on the right) obtained using different functionals.

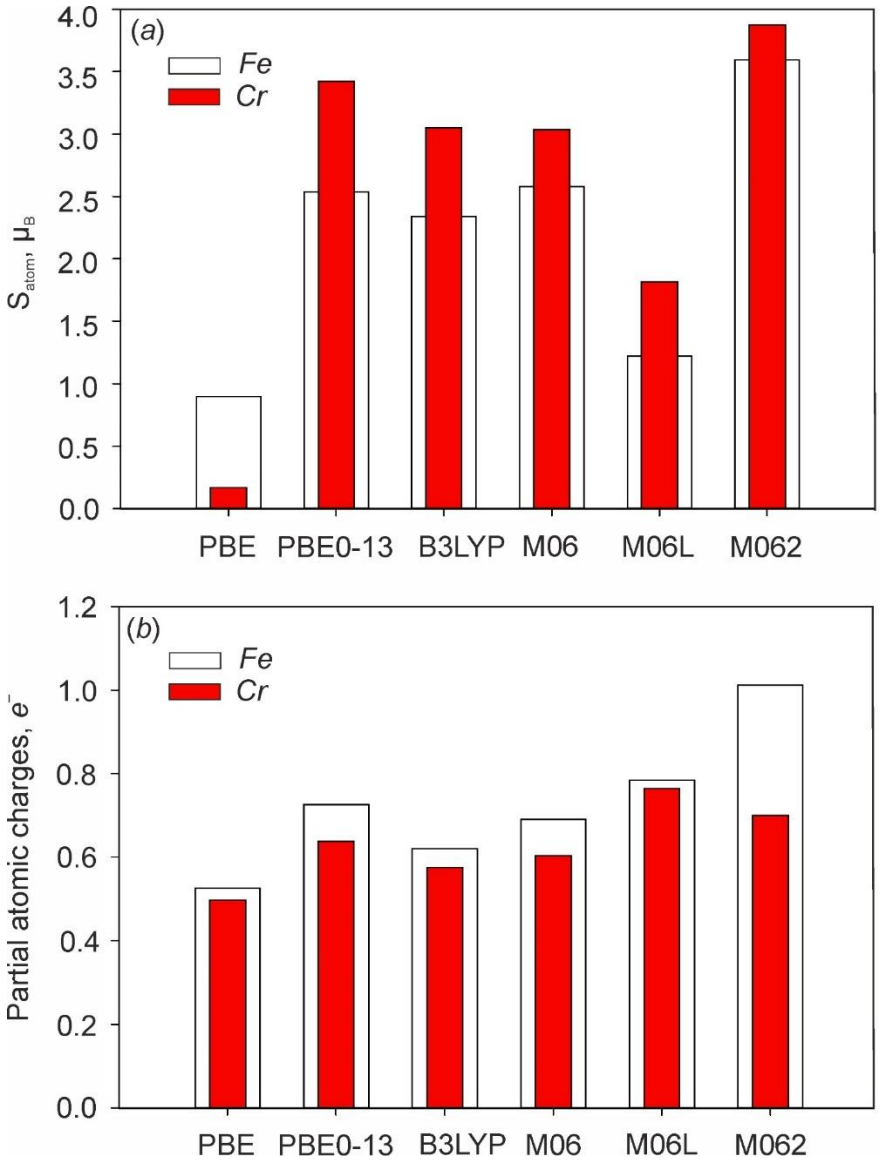
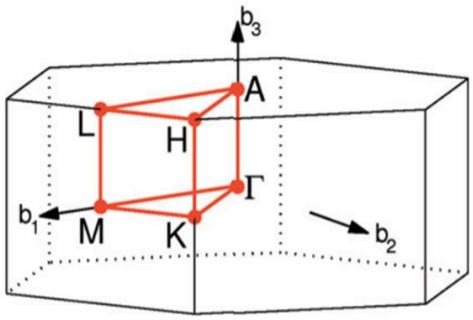


Figure S2. Iron and chromium partial charges in the CrFeSiC structure obtained using different functionals (up) and magnetic moment S_{atom} (μ_B) of nonequivalent atoms of the metals. Iron and chromium magnetic moments in the CrFeSiC structure obtained using different functionals (down).



Way: Γ-M-K-A-L-H-Γ

Figure S3. Brillouin zone of a hexagonal lattice.

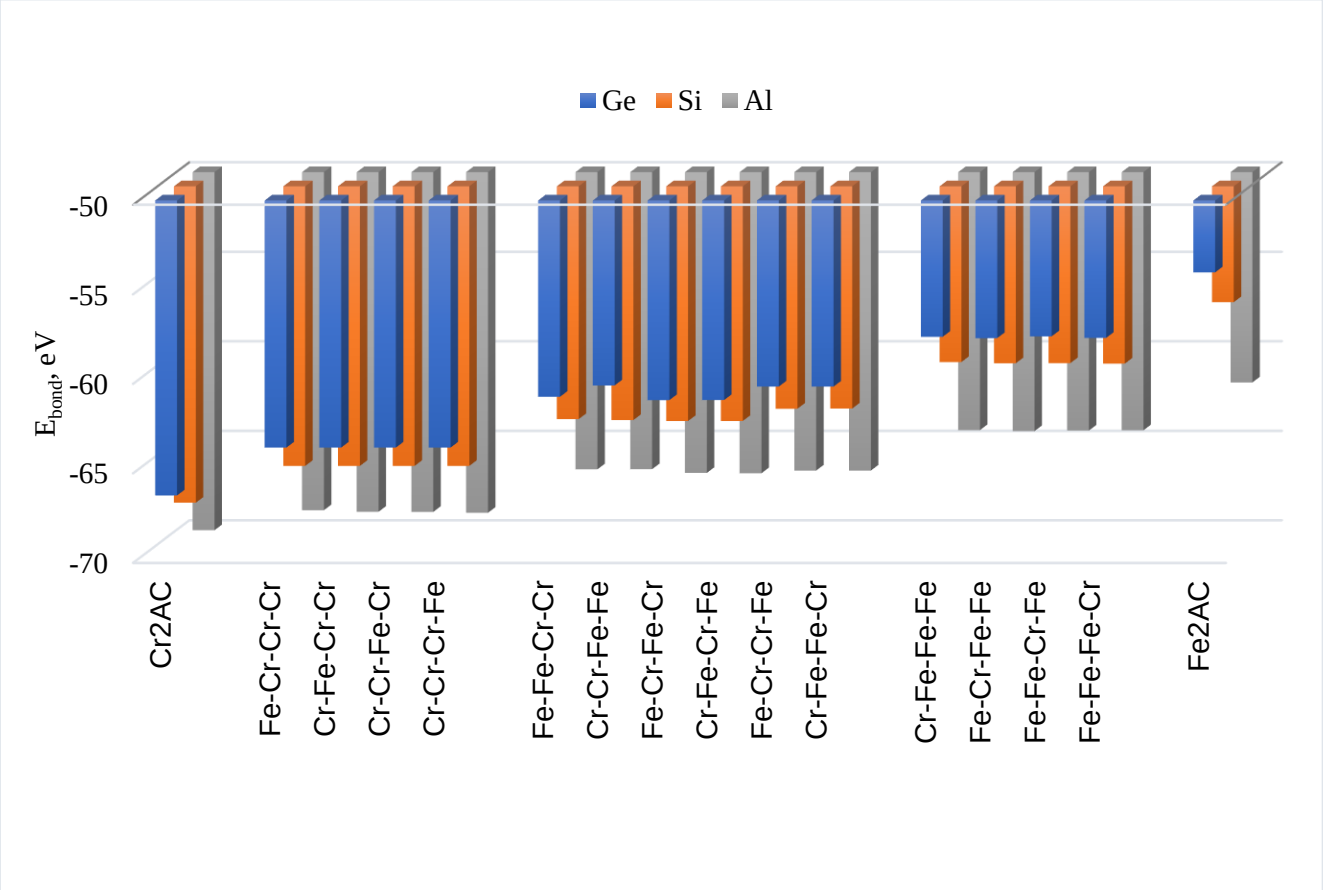


Figure S4. Binding energy change in the $(Cr_{4-x}Fe_x)_{0.5}AC$ (A = Ge, Si, Al) crystal lattices in the ferromagnetic state upon substitution of Fe atoms for Cr ones. Blue, orange, and gray histograms correspond to the phases with Ge, Si, and Al as the A element.

Total and partial density of states

Densities of states of the Cr_2AC, $(Fe–Cr–Cr–Cr)_{0.5}AC$, and Fe_2AC (A = Ge, Si, Al) structures. The presented energetically favorable structures in the germanium-based MAX phases are FM for Cr_2GeC, FiM for Fe_1Cr_3GeC, and FiM for Fe_2GeC. In silicon-based MAX phases, these are FiM for Cr_2SiC, FM for Fe_1Cr_3SiC, and FM for Fe_2SiC. In the aluminum-based MAX-phases, these are FiM for Cr_2AlC, AFM-6 (FiM) for Fe_1Cr_3AlC, and FiM for Fe_2AlC.

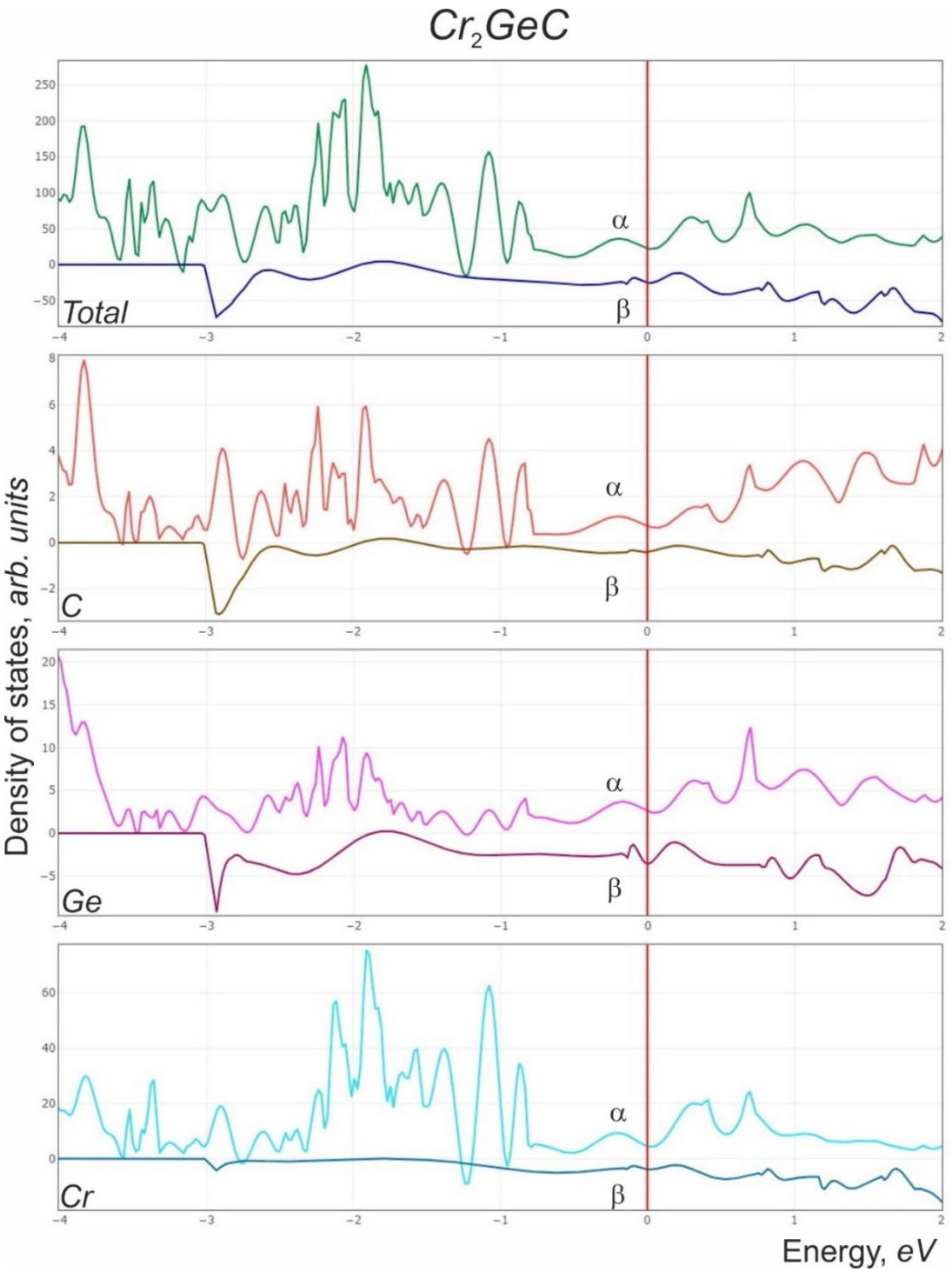


Figure S5. Densities of states of the Cr_2GeC. Partial densities of states of the M element of the first crystal lattice layer (blue), of the M element of the second crystal lattice layer (lilac), of the A element (dark blue), and of the element X = C (burgundy).

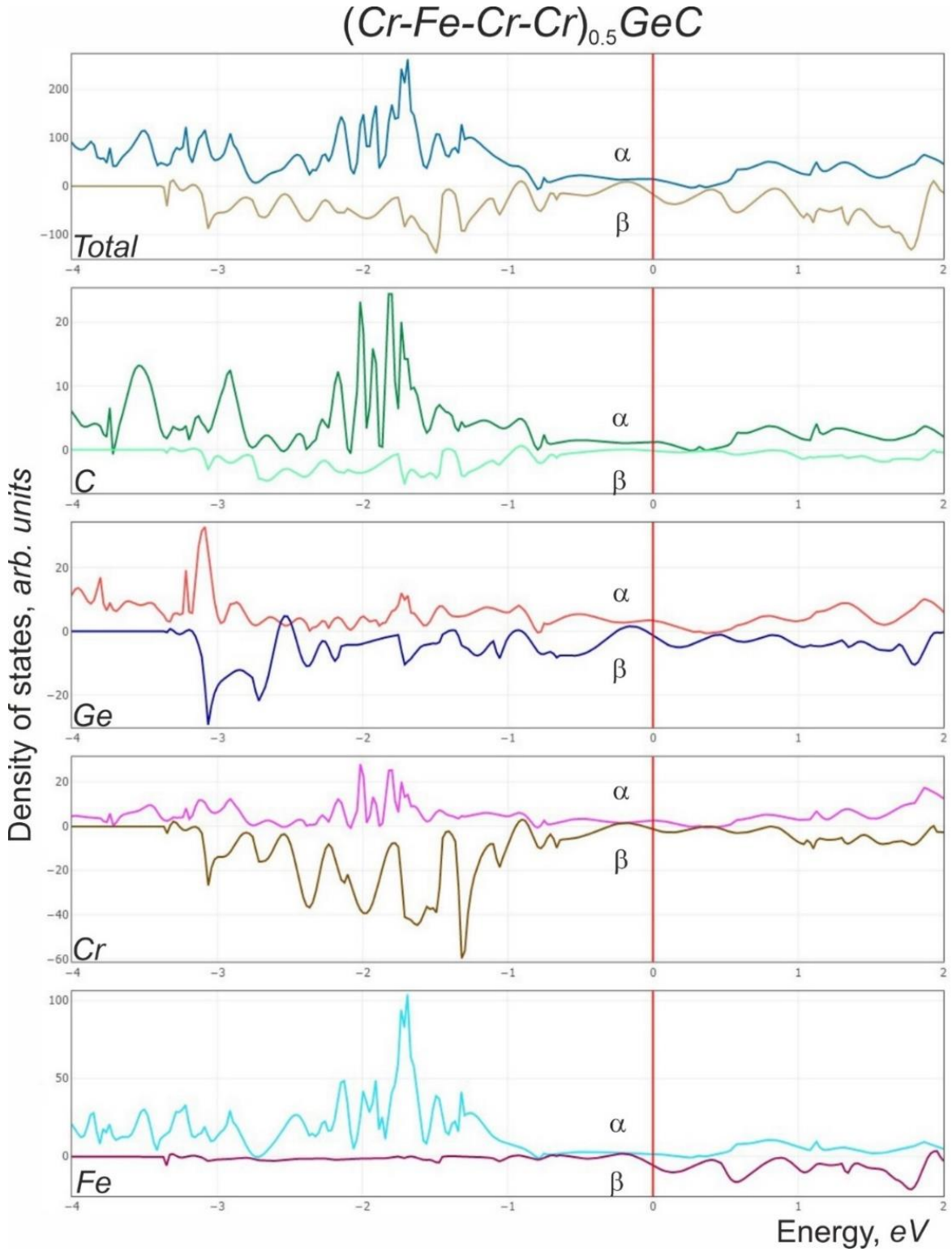


Figure S6. Densities of states of the (Cr-Fe-Cr-Cr)GeC.

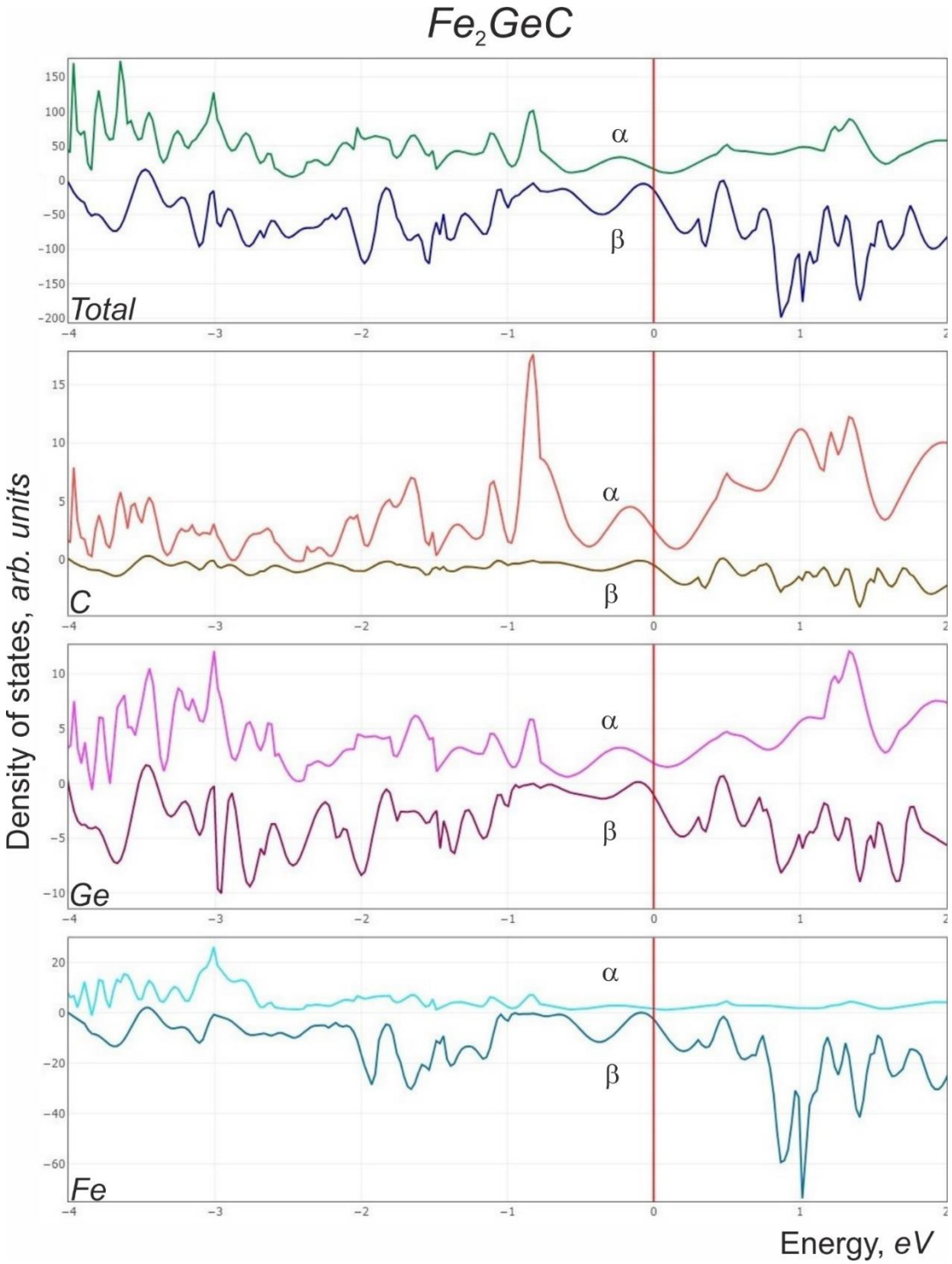


Figure S7. Densities of states of the Fe_2GeC.

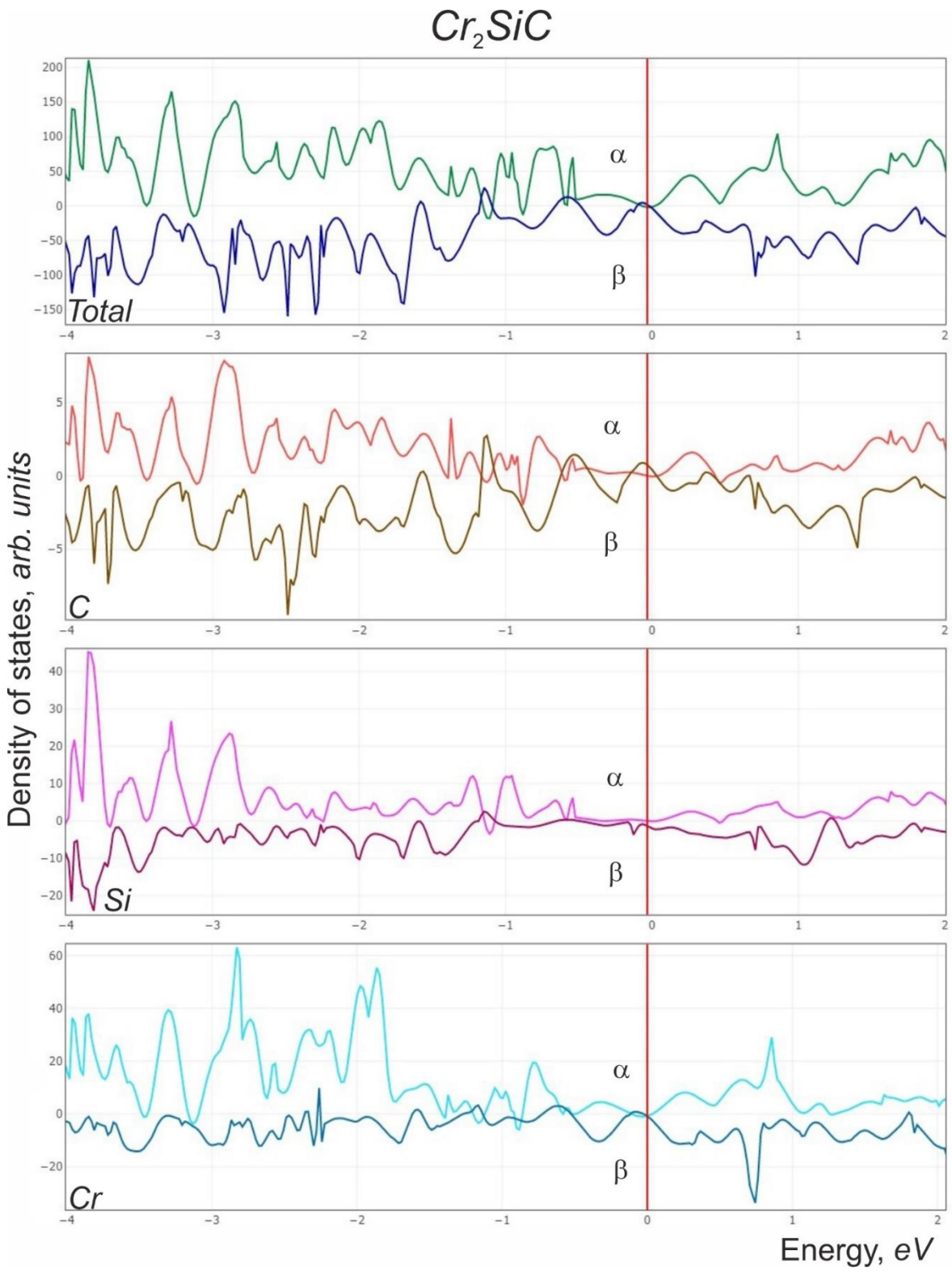


Figure S8. Densities of states of the Cr_2SiC.

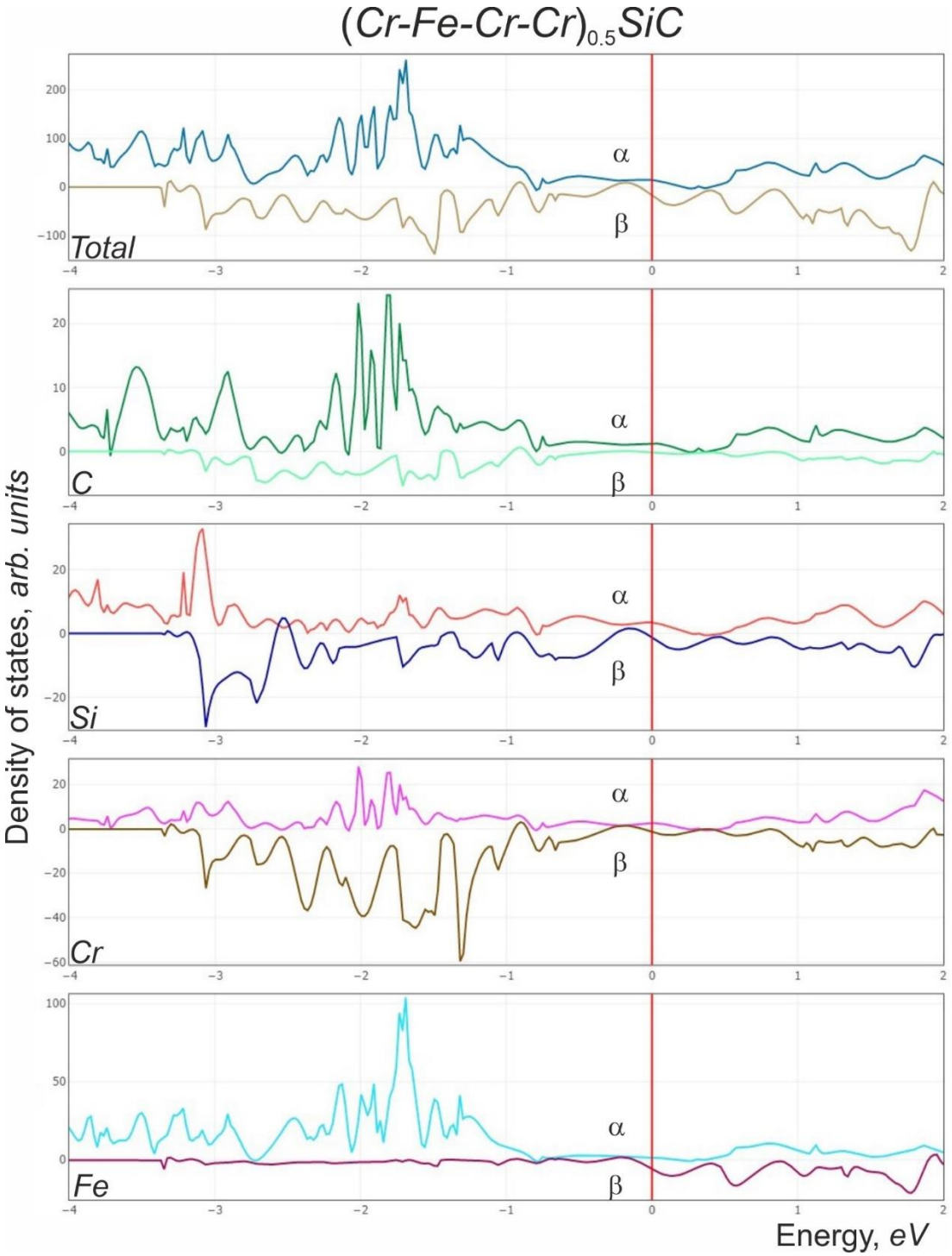


Figure S9. Densities of states of the (Cr-Fe-Cr-Cr)SiC.

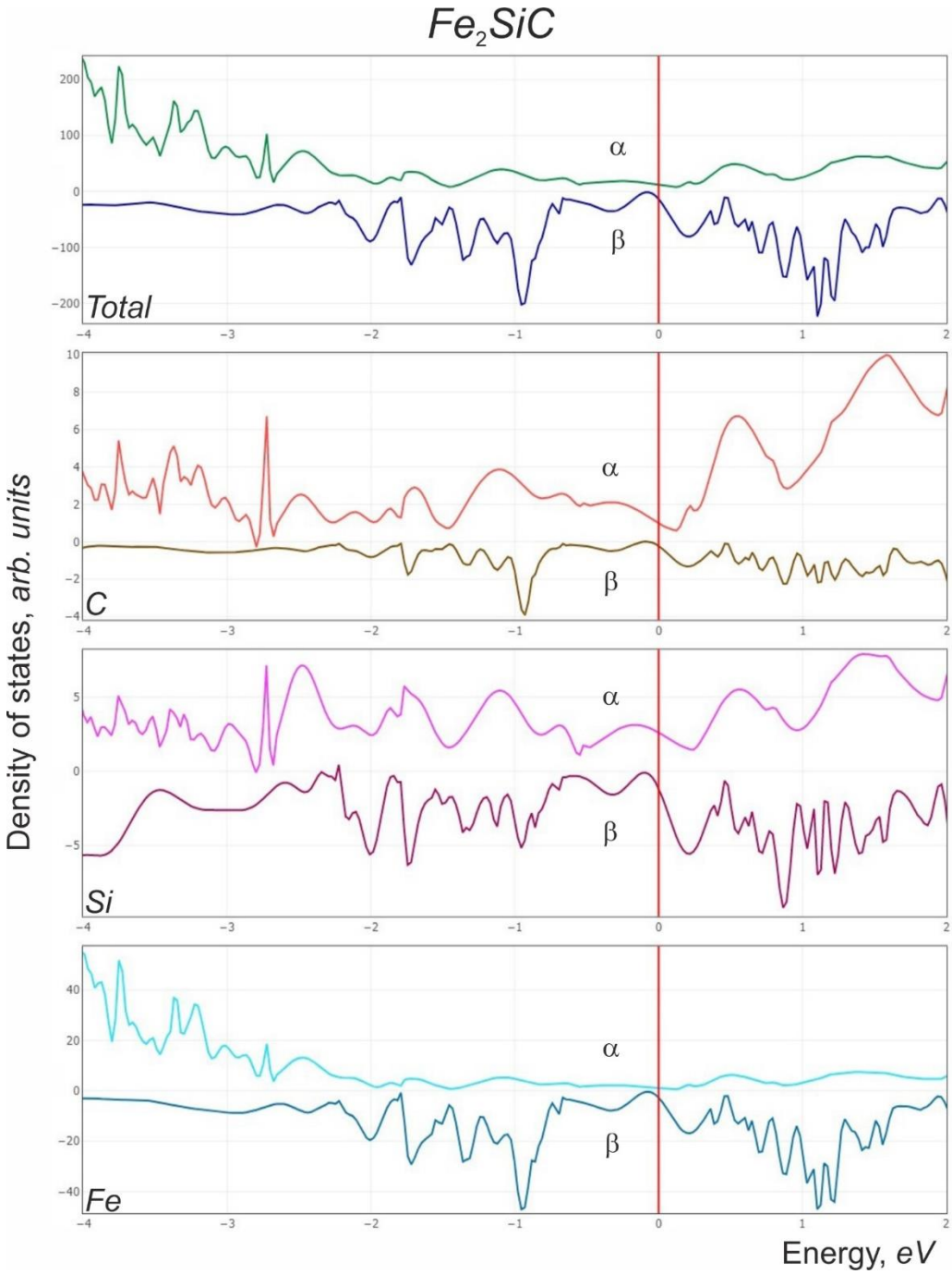


Figure S10. Densities of states of the Fe_2SiC.

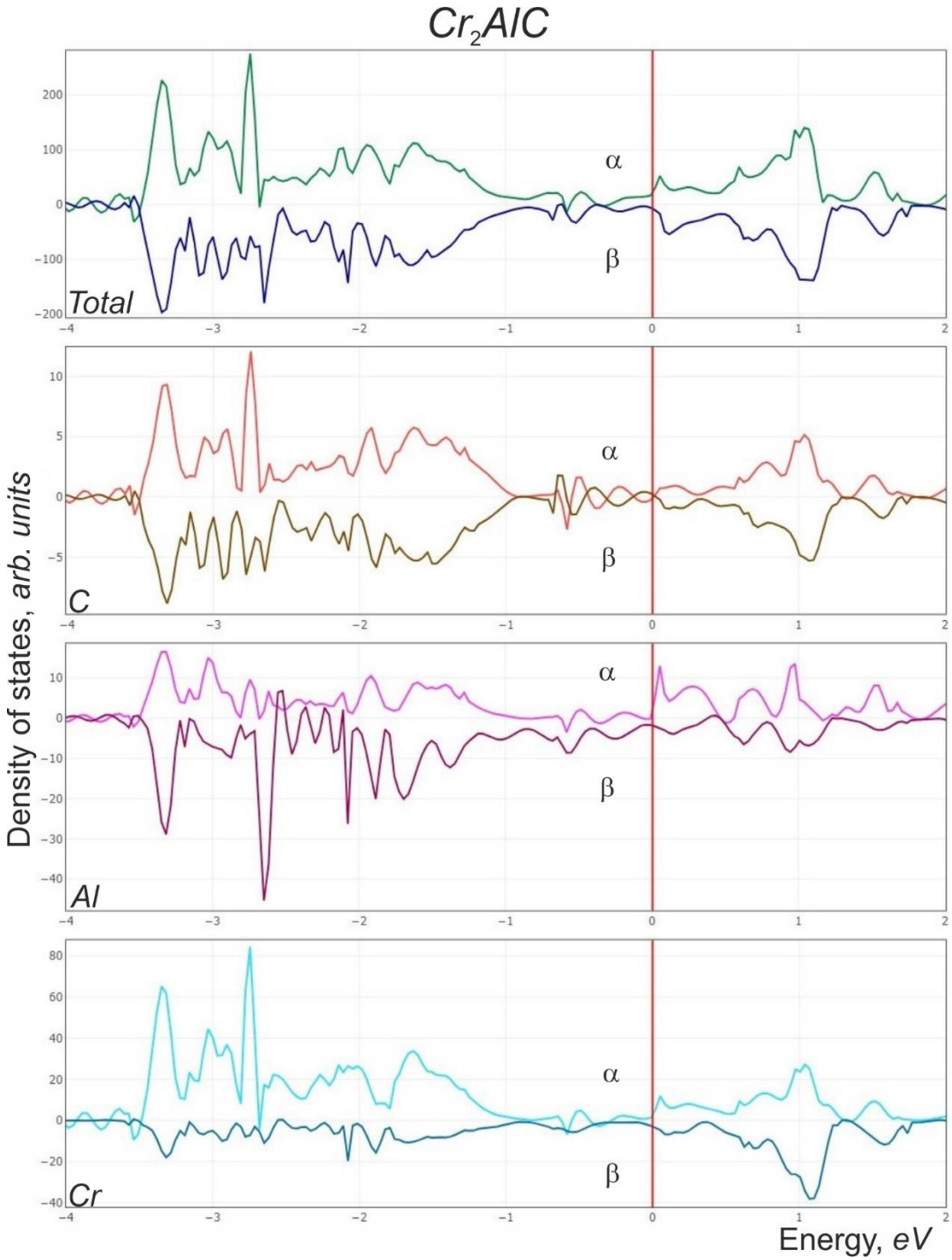


Figure S11. Densities of states of the Cr_2AlC

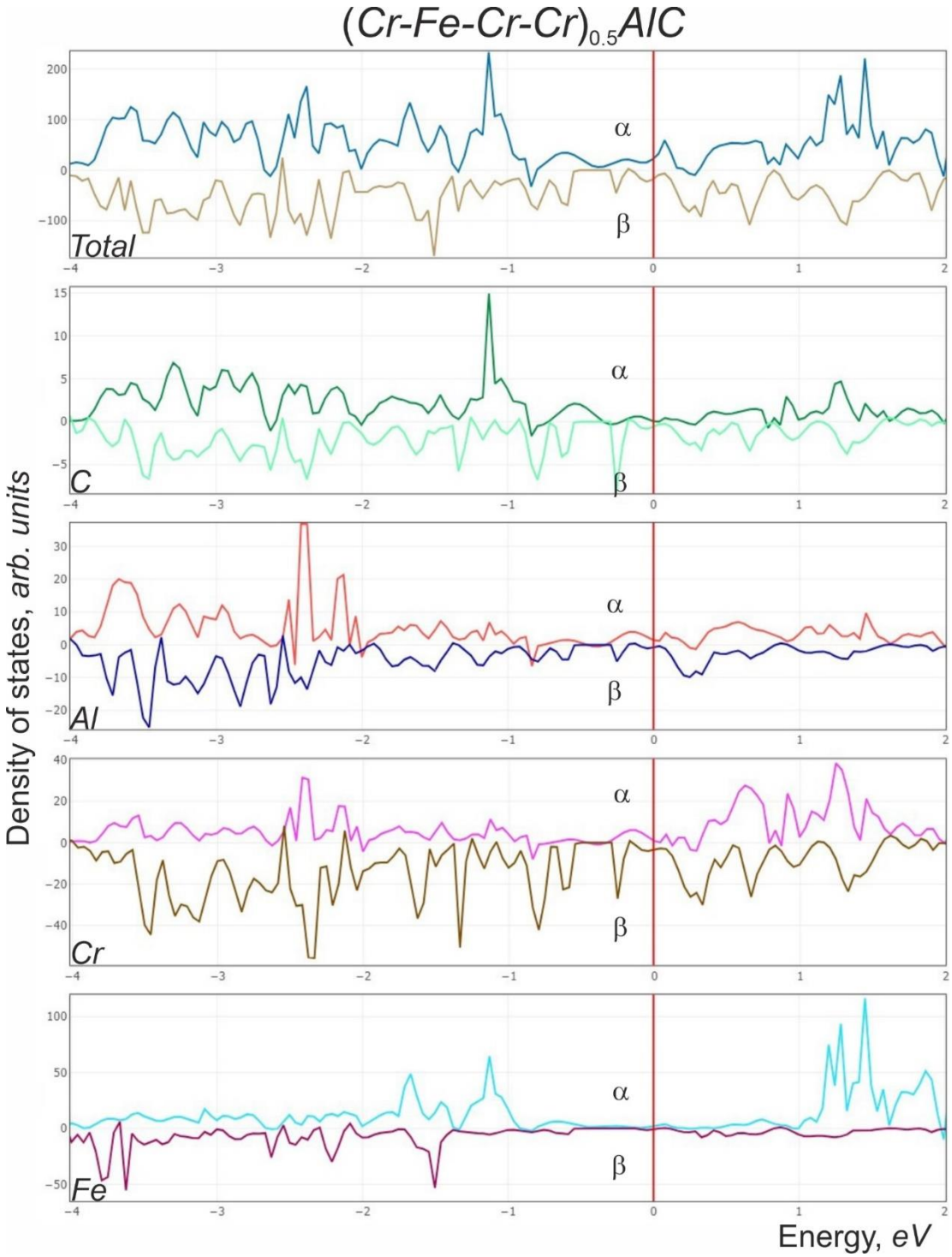


Figure S12. Densities of states of the (Cr-Fe-Cr-Cr)AlC

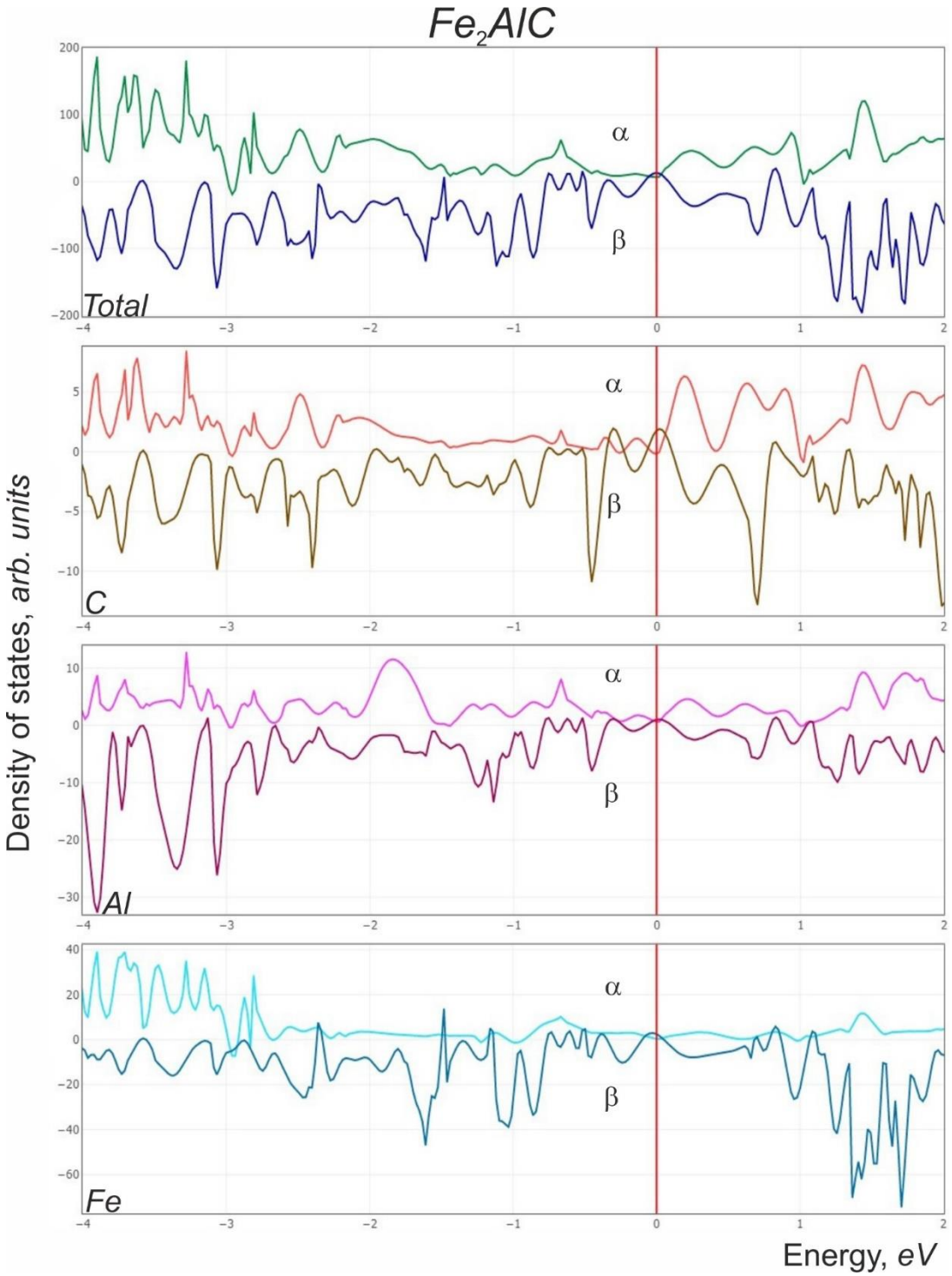


Figure S13. Densities of states of the Fe_2AlC