Supplement for:

The first-principles treatment of the electron-correlation and spin-orbital effects in uranium mononitride nuclear fuels

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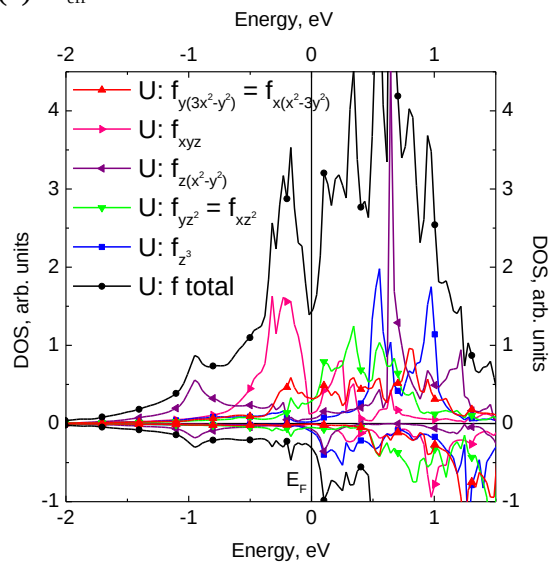
1. General information

In order to investigate nature of different contributions to the electronic structure of UN crystal we have calculated and plotted densities of states (DOSs) for a number of the different electronic states for various values of effective Hubbard parameter U_{eff}. These DOSs are presented here to support analysis provided in the main text of the paper. Because the total DOSs for antiferromagnetic (AFM) ordering of magnetic moments sums up densities for majority and minority spin orientations, the total DOSs does not allow us to distinguish contributions from electrons with different spin orientations. To separate these contributions we calculated DOSs projected on atoms located in a single [001] crystallographic plane containing atoms with the same magnetic polarization. The DOSs for electrons with majority spin orientation are plotted as positive values, those for electrons with minority spin orientation are plotted with negative values (their sign was changed). SOI was not included to any of DOSs calculations presented in this Supplement. These calculations were performed by means of the tetrahedron method (Ref. 32 in the main text).

(a) U_{eff}=0.875 eV



(b) U_{eff}=1.875 eV

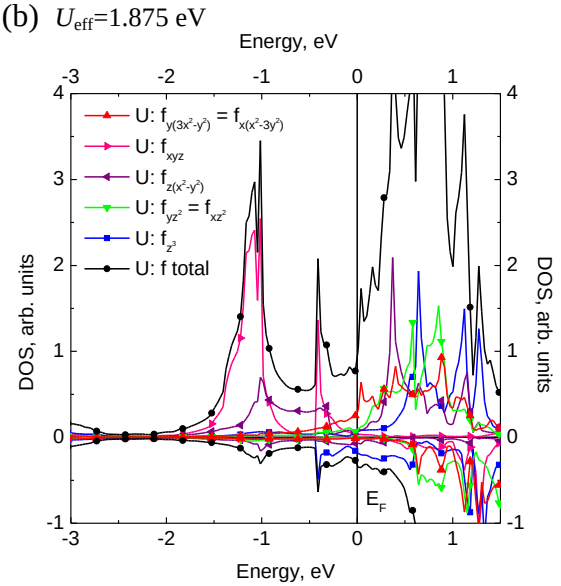
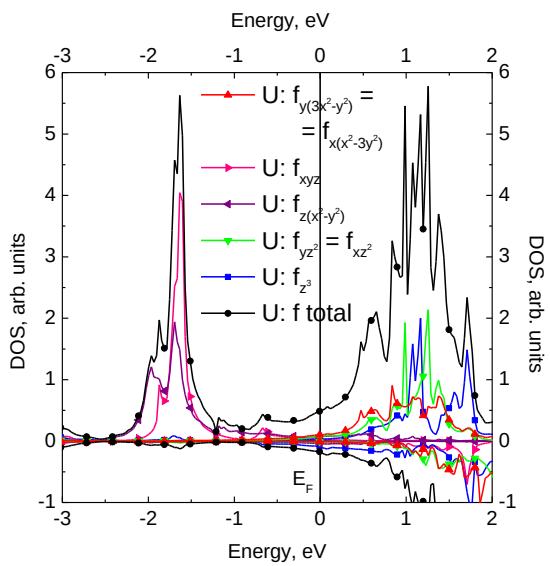


Figure S1. The DOSs projected at U5*f* orbitals of one of U atoms for various values of Hubbard parameter $U_{eff} = U - J$ ((a) 0.875 eV, (b) 1.875 eV, and (c) 2.875 eV) for the ground state of UN. The resolution was 0.03 eV between neighbor points.

(c) U_{eff}=2.875 eV



2. Analysis of DOSs for various U_{eff}

The changes in the electronic structure of UN crystal as a function of the effective Hubbard parameter U_{eff} were analyzed using DOSs calculated for AFM ground state for fixed U_{eff} : 0.875 eV, 1.875 eV, and 2.875 eV. Since we set the exchange parameter J=0.125 eV, these values correspond to values of Hubbard parameter U=1 eV, 2 eV, and 3 eV. The unit cell for the lowest value U_{eff}=0.875 eV still retains a cubic shape, whereas for higher values of U_{eff} (1.875 eV and 2.875 eV) the optimized unit cell in the ground AFM state becomes compressed (a>c) tetragonal. Fig. 3 in the main text shows a comparison of the DOSs calculated for the three mentioned values of U_{eff} . The spin polarization of UN crystal occurs due to difference in occupation of U5*f* orbitals by electrons with majority and minority spin orientations. Fig. S1 contains DOSs projected on these orbitals. The presented plots are enlarged to allow better interpretation of the most essential region of DOSs near the Fermi energy covering the highest occupied bands. The difference in occupation of these bands by electrons with different spin orientation can be easily seen. The analysis of these DOSs is provided in the main text.

3. Analysis of DOSs for the ground and metastable states

Figures S2-S5 contain a detailed decomposition of DOSs for both UN states (compressed and elongated unit cells) and both magnetic orders (AFM and FM). These DOSs were calculated with U_{eff}=1.875 eV (U=2 eV).

The lowest in energy and wide band seen at all these figures is formed by a mixture of N2*p* and U *spd* orbitals. Its width is about 4 eV. Contributions of N's and U's orbitals are essentially the same. The U *6s* orbitals define uranium atom contribution on the lower side of the band. The largest contribution of U6*p* orbitals is at the higher side of the band, where it is of the same magnitude as contributions of each of U *5d* orbitals. The largest contributions of U5d_{xz}, U5d_{yz} and U5$d_{x^2-y^2}$ orbitals are close to both sides of the band. The contributions of U5d_{xy} and U5d_{z^2} orbitals peak at the middle of the band, where it defines the U atom's contribution. There is no noticeable spin polarization within this band: DOSs for electrons with majority and minority spin orientations seems to be the same. While the position of this band for the AFM ground state remains the same as U_{eff} was varied, the positions of this band are noticeably different in different compressed and elongated states for both magnetic orders. Taking the position of the band in the AFM-compressed state as a reference, we obtain that it shifts in the AFM-elongated state up by roughly 0.27 eV, in the FM-compressed state up by 0.35 eV, and in the FM-elongated state up by 0.58 eV.

The energy band located above the described one has essentially U5*f* character with a small admixture of U5*d* orbitals in all states. The N2*p* orbitals present only in a very small amount in the AFM compressed state.

There are two peaks below the Fermi energy formed by U5f_{xyz} orbitals in the AFM compressed state (Fig. S2) on the majority spin side of DOS. One is at ~ -1.0 eV and another one is at ~ -0.4 eV. Below these peaks and between them one can find a significant contribution from U5$f_{z(x^2-y^2)}$ orbitals with a peak at -1.0 eV right below the lowest-energy peak for U5f_{xyz} orbitals. Two small peaks just above the Fermi level are formed by U5$f_{y(3x^2-y^2)}$ (U5$f_{x(x^2-3y^2)}$) orbitals. The following DOS has contributions from all U5*f* orbitals except U5f_{xyz} ones.

There is a narrow high peak below the Fermi energy for the AFM elongated state (Fig. S3) at -0.74 eV and a wider band at the Fermi level. Both of these peaks contain mostly U5$f_{y(3x^2-y^2)}$, U5$f_{x(x^2-3y^2)}$, U5f_{xz^2} and U5f_{yz^2} orbitals with some contribution from U5$f_{z(x^2-y^2)}$ orbitals. U5f_{xyz} orbitals contribute only in the peak at 0.72 eV above Fermi energy and there is no significant contribution into DOS of these orbitals below the Fermi energy.

A 1.1 eV - wide band is present at the Fermi level in the DOS for the FM compressed state (Fig. S4). It begins at -1. eV below the Fermi level and the last peak in this band lies just 0.1 eV above the Fermi level. This band is dominated by U5f_{xyz} orbitals. However, it contains also contributions from U5$f_{z(x^2-y^2)}$ and U5f_{z^3} orbitals.

The DOS for the FM elongated state (Fig. S5) also contains 1.2 eV – wide band which begins at -0.63 eV under Fermi level. Similarly to similar AFM state, this band is mostly formed by U5$f_{y(3x^2-y^2)}$, U5$f_{x(x^2-3y^2)}$, U5f_{xz^2} and U5f_{yz^2} orbitals. It also contains contribution from U5f_{z^3} orbitals at the lower boundary of the band. And this band does not contain any significant contributions from U5f_{xyz} and U5$f_{z(x^2-y^2)}$ orbitals.

Comparing DOSs obtained for all four states, one can see that the compressed states differ from the elongated states by the nature of bands occupied by the electron with majority spin orientation. The occupied bands in the former states are formed by U5f_{xyz} orbitals with participation of U5$f_{z(x^2-y^2)}$ orbitals. The occupied bands in the later states are formed by U5$f_{y(3x^2-y^2)}$, U5$f_{x(x^2-3y^2)}$, U5f_{xz^2} and U5f_{yz^2} orbitals. This is consistent with a shape of spin density distributions in Fig. 4 in the main text of the paper.

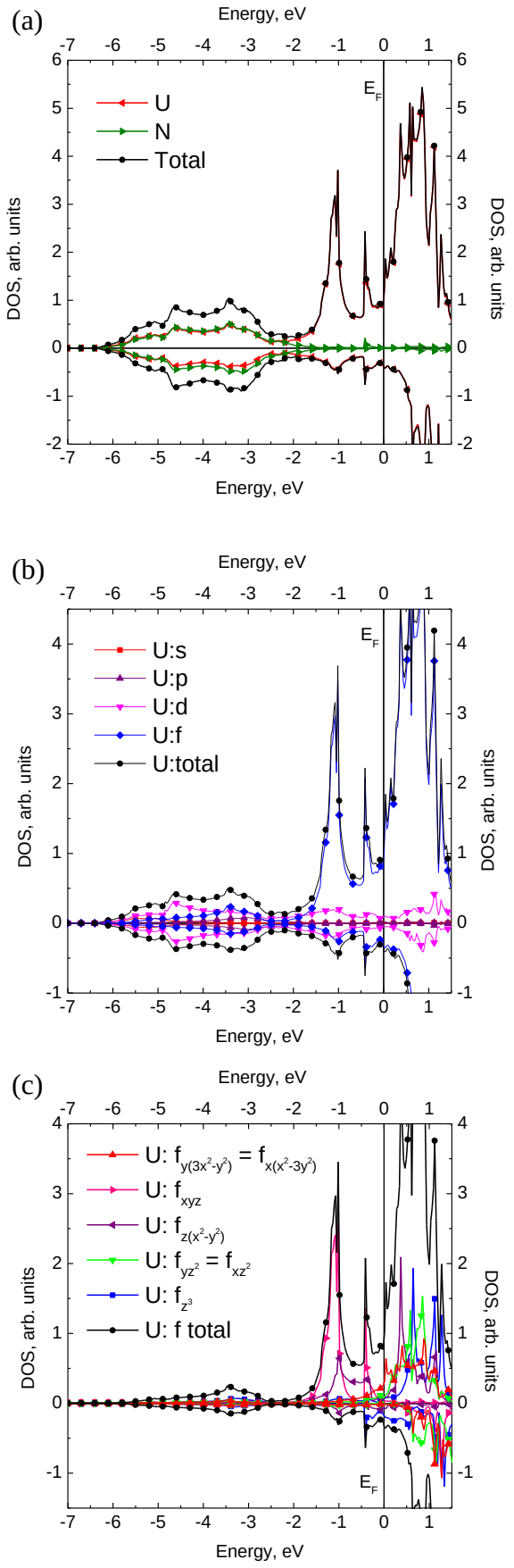


Figure S2. The projected DOS calculated for AFM "compressed" (a>c) state (ground state, Figure 4a) for U_{eff}=1.875 eV. The Fermi energy is taken as zero. SOI effects were neglected. The DOS was re-calculated with the tetrahedron method (Ref. 32 in the main text). (a) Decomposition of the DOS into DOSs projected to one of U atoms and one of N atoms in the unit cell. (b) Decomposition of the DOS projected at the U atom into the densities projected on s-, p-, d- and f-orbitals. (c) Decomposition of the total U5*f* DOS into the densities projected on all U5*f* orbitals. (d) Contributions of DOSs projected to U6s, U6p, and U5d orbitals. (e) Decomposition of the DOS projected at the N atom into densities projected on N2*s*- and N2*p*-orbitals.

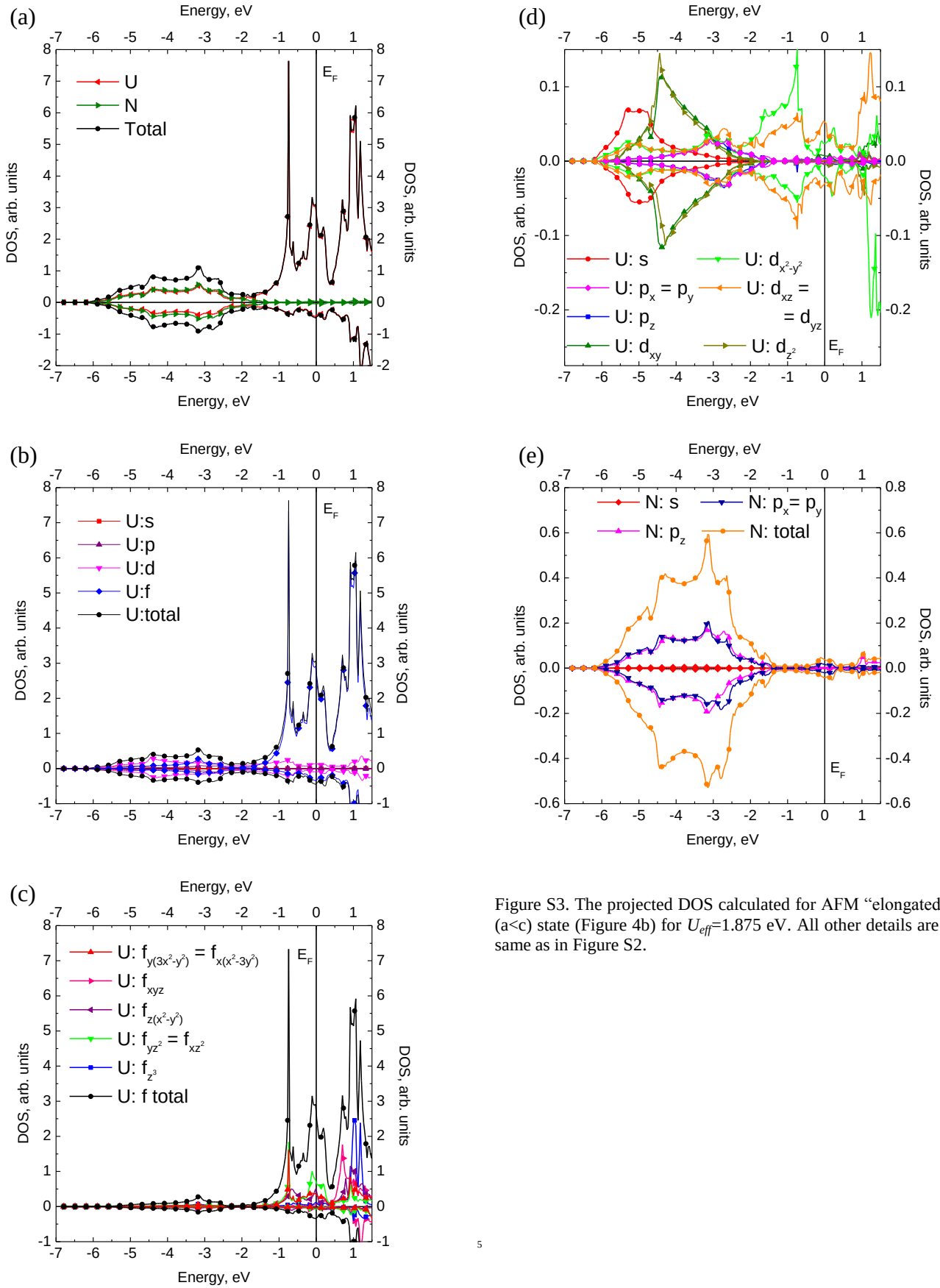


Figure S3. The projected DOS calculated for AFM "elongateded" (a<c) state (Figure 4b) for U_{eff}=1.875 eV. All other details are the same as in Figure S2.

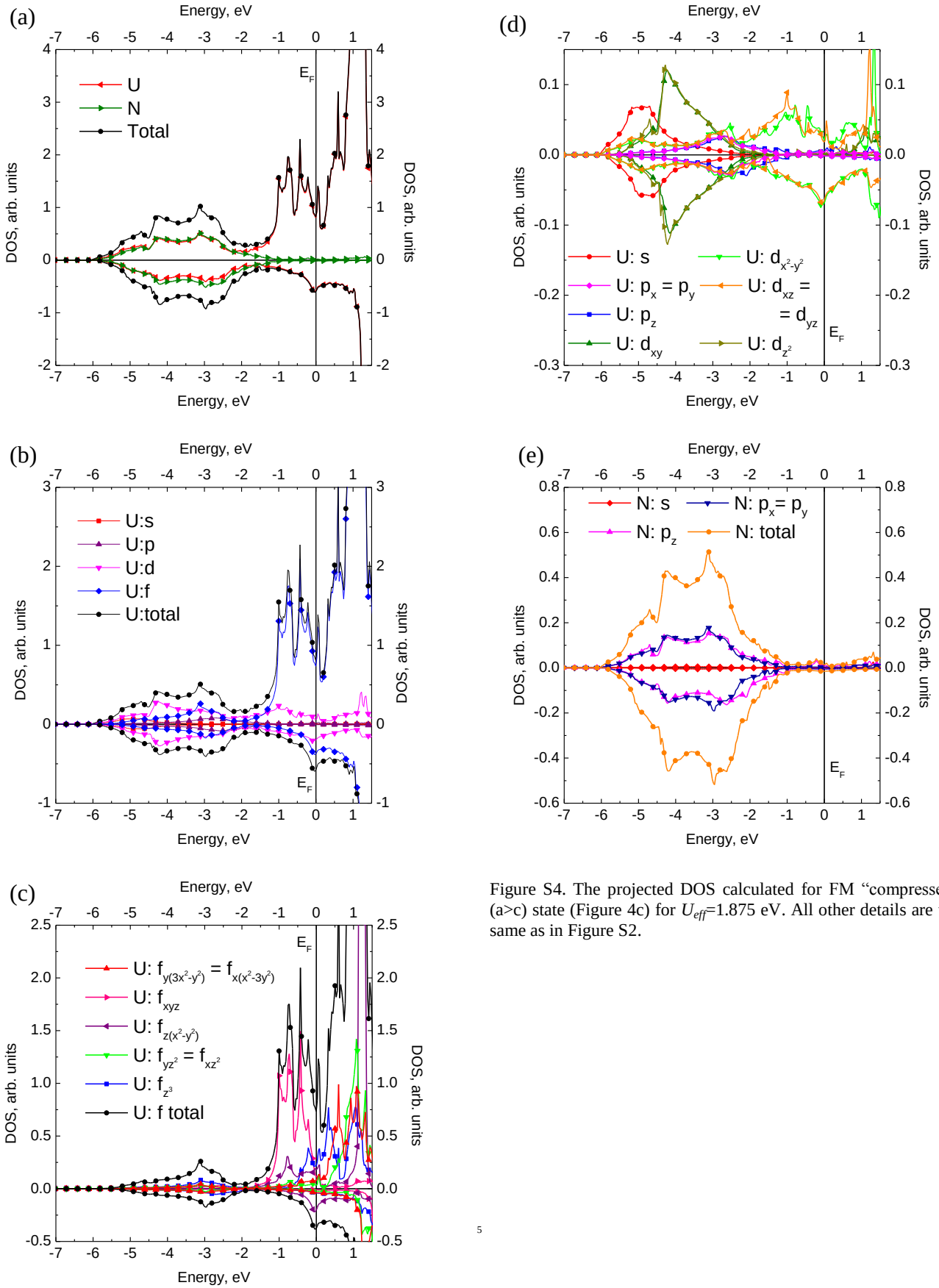


Figure S4. The projected DOS calculated for FM "compressed" (a>c) state (Figure 4c) for U_{eff}=1.875 eV. All other details are the same as in Figure S2.

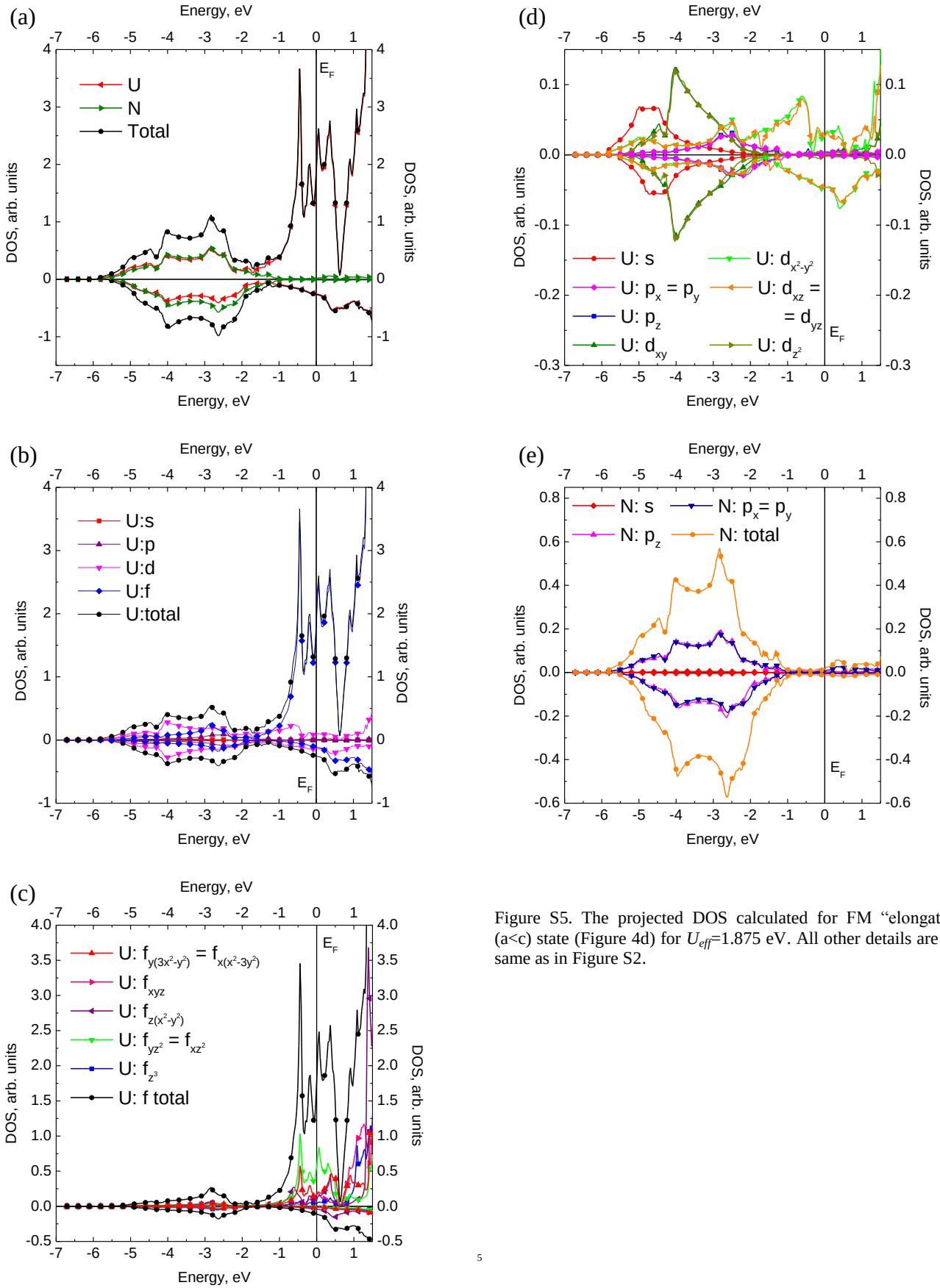


Figure S5. The projected DOS calculated for FM "elongated" (a<c) state (Figure 4d) for U_{eff}=1.875 eV. All other details are the same as in Figure S2.