

Role of $4f$ states in infinite-layer NdNiO₂: Supplemental Material

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I. CALCULATION METHODS

Our calculations with WIEN2K were based on the generalized gradient approximation (GGA)[1]. The effects of correlation were treated with the GGA+U approach in the fully localized limit. In the GGA+U calculations presented here, we focused on the results of the Hubbard $U = 8(5)$ eV and Hund's coupling $J = 1(0.7)$ eV for the Nd $4f$ (Ni $3d$), except where noted. Our conclusions weren't affected by varying the value of U by 1–2 eV.

In WIEN2K, the basis size was determined by $R_{mt}K_{max} = 8$; checking $R_{mt}K_{max}=9$ gave no noticeable difference. The APW radii were chosen as Nd 2.50, Ni 1.98, and O 1.70, in atomic units. Convergence was checked with dense k -meshes up to $29 \times 29 \times 34$ to treat the highly localized $4f$ orbitals carefully.

II. FERMI SURFACE OF Nd_{0.8}Sr_{0.2}NiO₂ IN RIGID BAND APPROXIMATION

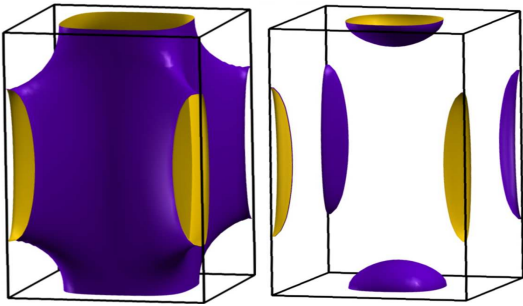


FIG. 1: Fermi surfaces of $x=0.20$ Sr hole doped NdNiO₂, in the rigid band approximation, for case AFM0 (non-magnetic Ni) as defined in the main text. The region shown is the folded zone corresponding to AFM $4f$ alignment. Surfaces have been separated into left and right sub-panels for clarity. These surfaces can be compared with the bottom panel of Fig. 3 in the main text, which provides the surfaces in the virtual crystal approximation. The Γ -centered electron pocket has been emptied, while the k_z dispersion is increased substantially. (The undoped case is also given in the top panel of Fig. 3 in the main text.)

III. GGA+U ELECTRONIC STRUCTURE OF FERROMAGNETIC STATE

We provide here and below fatband plots indicating band character for all Ni $3d$ and Nd $5d$ orbitals, for both FM and AFM1 magnetic alignments (fully aligned moments; both Ni and Nd moments antialigned). The differences, also compared to the information in the main text for non-magnetic Ni, indicate how the various characters are shifted by relative magnetic alignment. Although ordering does not occur down to the lowest temperature measured, the differences give an indication of the effects of spin fluctuations. Some of the points to notice are included in the captions.

The spin-resolved fatband plots of separate Ni $3d$ and Nd $5d$ orbitals in the range of -4 eV to 4 eV for FM alignment of all moments are displayed in Fig. 2. Some aspects to note follow. The electron pocket band at the Γ point (fully spin polarized for this FM alignment) has strong Nd $5d_{z^2}$ character as noted by others, but it is mixed with significant Ni $3d_{z^2}$ character near the Γ point. For the electron pocket at $A = (\pi, \pi, \pi)$ there is admixture of Ni $3d_{xz}/3d_{yz}$ character with the Nd $5d_{xy}$ orbitals. The hole bands at the M and A points have the primary $d_{x^2-y^2}$ character as occurs in cuprates.

Figure 3 displays the GGA+U orbital- and atom-projected densities of states (PDOSs) for FM alignment. The Nd $4f$ -orbital resolved DOSs obtained from GGA+U+SOC are given in the bottom right panel of Fig. 3. The main effect of SOC is to produce, via introduced anticrossings, individual flat bands giving rise to separated DOS peaks for each orbital $|j.m_j\rangle$.

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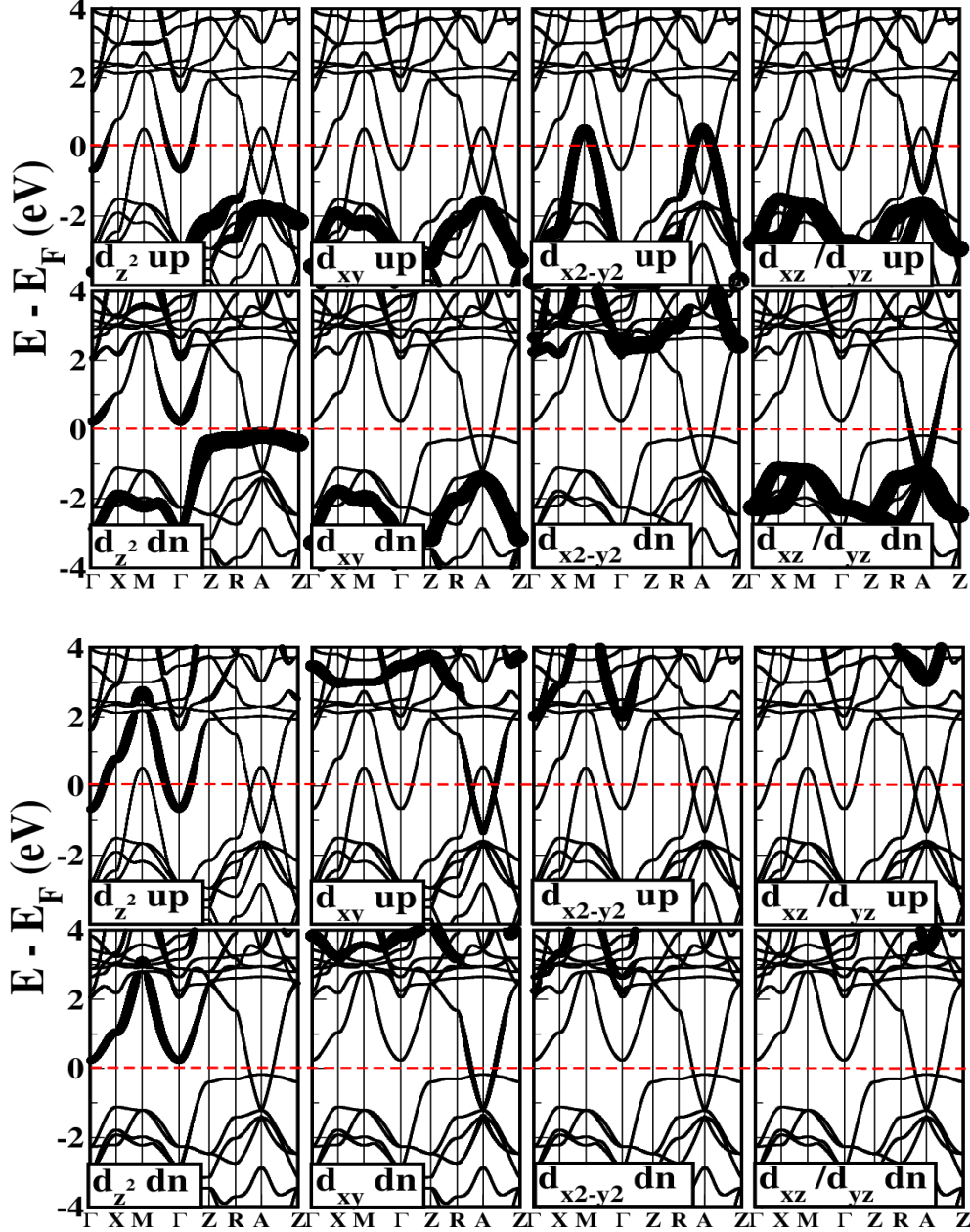


FIG. 2: Top: Fatband plots for all Ni $3d$ orbitals for FM alignment, with the GGA+U functional (see main text and section above for methods and values of interactions). Majority (up) bands are given in the upper panels, minority (down) in the lower panels. Note that there is some Ni d_{z^2} character for both spin directions in the Γ centered electron pocket. There is very strong Ni d_{z^2} character almost at E_F in the minority bands along the zone edge $Z - R - A - Z$.

Bottom: Fatband plots for all Nd $5d$ orbitals corresponding to those of Ni $3d$, above. Majority (up) bands are in the upper panels, minority (down) bands are in the lower panels. Strong Nd $5d$ character (d_{z^2}) is confined to the electron pockets Pk1 at Γ . There is lesser Nd contribution (d_{xy}) to the electron pocket Pk2 at A .

IV. GGA+U ELECTRONIC STRUCTURES OF ANTIFERROMAGNETIC STATES

To consider antiferromagnetic (AFM) states, a $\sqrt{2} \times \sqrt{2}$ supercell is necessary. As mentioned in the main text, we

considered three AFM states and a fully aligned configuration:

- * AFM0: nonmagnetic Ni and AFM ordered Nd
- * AFM1: both AFM ordered Ni and Nd ions
- * AFM2: AFM ordered Ni and FM ordered Nd
- * FM: both sublattices completely aligned.

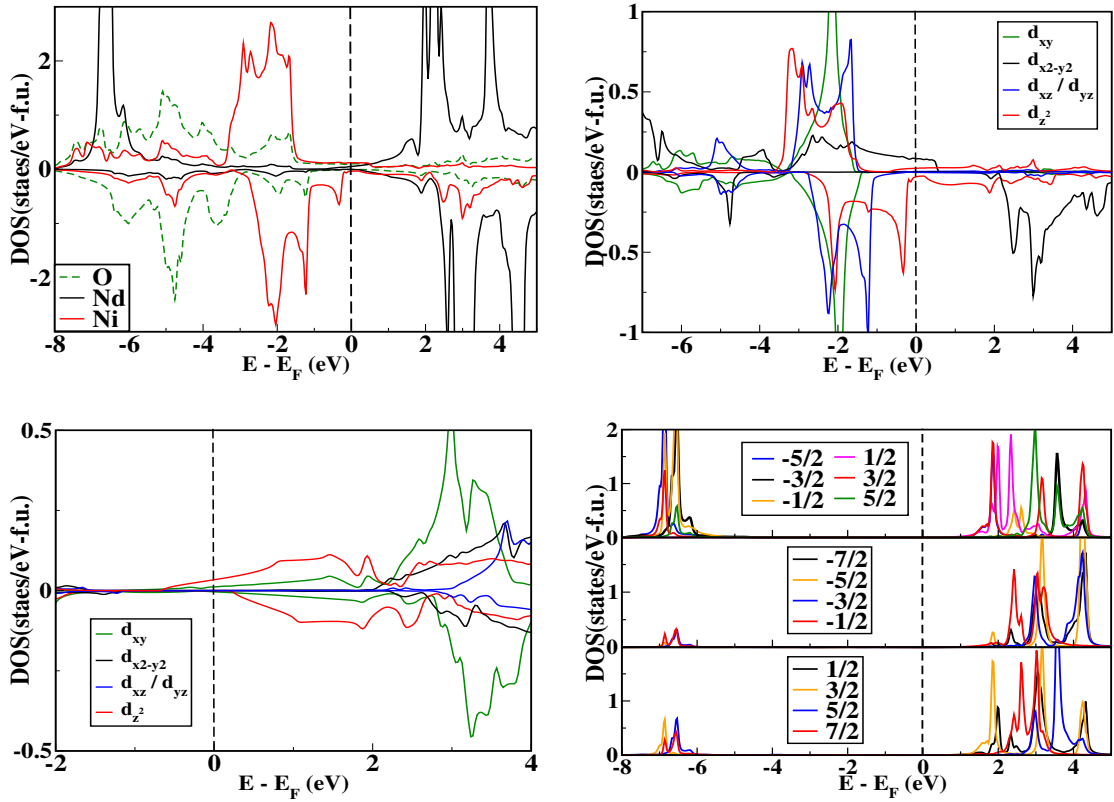


FIG. 3: FM projected densities of states (PDOSs) in GGA+U. Top left: atom PDOS. Top right: Ni 3d orbital PDOS. Bottom left: Nd 5d orbital PDOS. Bottom right: FM orbital-resolved DOSs of Nd 4f orbitals in the $|j, m_j\rangle$ basis, using GGA+U+SOC. The occupied orbitals are mostly $|5/2, -5/2\rangle$, $|5/2, -3/2\rangle$, and $|5/2, -1/2\rangle$ characters. Minor mixing with $|5/2, 5/2\rangle$, $|5/2, 3/2\rangle$ orbitals lead to an orbital moment of $-2.6 \mu_B$.

Here we provide additional information of AFM1 and AFM2, both of which have AFM Ni layers. For the AFM0 state, see the main text.

In GGA+U, similar to the FM cases, the magnitude of the local spin moments are $3 \mu_B$ for Nd and around $1.2 \mu_B$ for Ni. In AFM2, the FM ordered Nd moment induces a very small difference between up and down Ni moments of $0.03 \mu_B$, indicating the weakness but non-vanishing of the magnetic Nd-Ni coupling as noted by others.

Figure 4 shows the band structures along lines in the AFM zone and atom-PDOSs of AFM1 and AFM2. (In the band structure plots, the *prime* symbol is omitted for simplicity.) Both band structures are characterized by a near gap as a cuprate would display, except for a band dispersing upward from $Z' - R'$ and downward from $a' - Z'$ along the $k_z = \pi$ plane. No such dispersion is observed on the $k_z = 0$ plane $\Gamma - X' - M' - \Gamma$. The Fermi level is fixed not by half-filling of this band but by the lower conduction band, which is flat along $Z' - R' - A' - Z'$. The dispersion band is of ambiguous mixed character while the flat band has very strong Ni d_{z^2} character.

In GGA, a magnetic Ni ion leads to a 120 meV energy gain compared to non-magnetic Ni. This exaggerated tendency toward magnetic ordering and the magnitude of

the magnetic moment is a known deficiency of (semi)local density functional methods, with much of the problem attributed to the lack of effects of spin fluctuations in the functional.

The energies of AFM1, AFM2, and FM, obtained with the same functional, can be compared. The energy of AFM2 (FM Nd) is slightly lower than that of AFM1 (AFM Nd), by 7 meV for $U=0$ and by only 1 meV (at the edge of computational precision) with $U=5$ eV on Ni, reflecting a slight tendency toward FM ordering of the 4f moments. The energy difference between FM and AFM2 provides the difference between AFM and FM Ni moments; AFM alignment is favored by 116 (25) meV/Ni in GGA(+U). This energy difference contains information about Ni-Ni in-plane exchange coupling, and would give a value of the nearest neighbor coupling if all others were negligible. Liu *et al.* have derived values of coupling for a few neighbors, concluding that the values depend strongly on the value of U^{Ni} that are used.[2]

Results of AFM1 and AFM2 show similarity as expected, with differences in the band structures appearing as small spin-splitting of bands, most evident in the Nd $5d$ electron-pocket band at Γ . Curiously, this band becomes incredibly flat along the zone-top lines $Z - R - A - Z$, pinning the Fermi level. The flatness leads to a sharp peak at the Fermi level with the associated tendency toward instabilities of various kinds, and might contribute to the lack of such ordering.

We display the simpler band structure of AFM1, with the fatband plots of Ni $3d$ and Nd $5d$ presented separately in Figs. 5 and 6, respectively. The flat band at the Fermi

level is seen to be very strongly Ni d_{z^2} in character. The corresponding orbital-projected DOSs are given in Fig. 7, where the Ni d_{z^2} peak is very prominent at the Fermi level – purely of a single character.

We also considered the effects of SOC in the GGA+U+SOC to analyze the Nd $4f$ configuration, leading to the Nd orbital moment of $-4.45 \mu_B$. Figure 8 shows the PDOS of Nd $4f$ orbitals in the $|j, m_j\rangle$ basis. Figure 9 shows the band structure and atom-projected DOS, when applying U and J only to the Nd $4f$ orbitals in the AFM1 alignment.

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- [1] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
 [2] Z. Liu, Z. Ren, W. Zhu, Z. F. Wang, and J. Yang, Elec-

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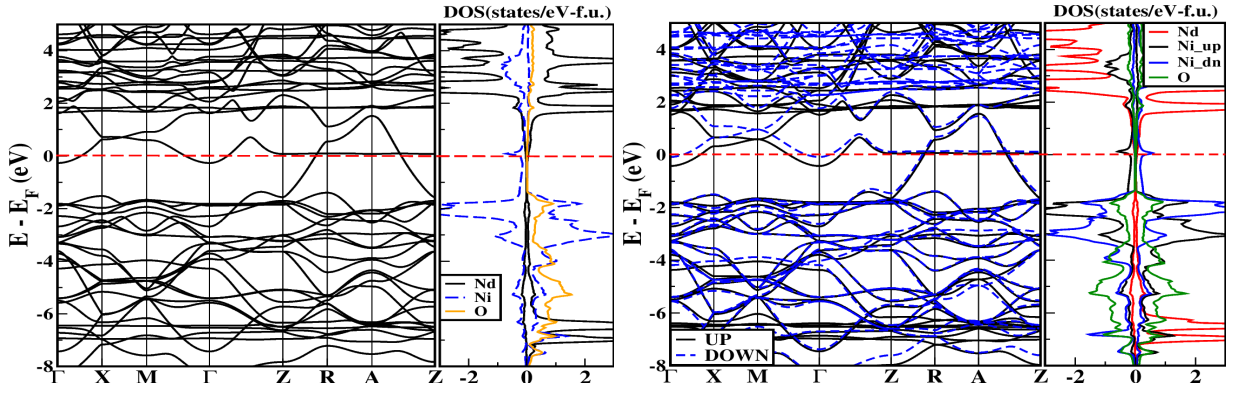


FIG. 4: GGA+U band structures and atom-projected DOSs of (left) AFM1 and (right) AFM2. In the AFM2 state, a small spin-imbalance in the antiferromagnetic ordered Ni ions is induced by the FM ordered Nd ions (see the region near E_F). Note that in both cases a flat band along $Z - R - A - Z$ pins the Fermi level.

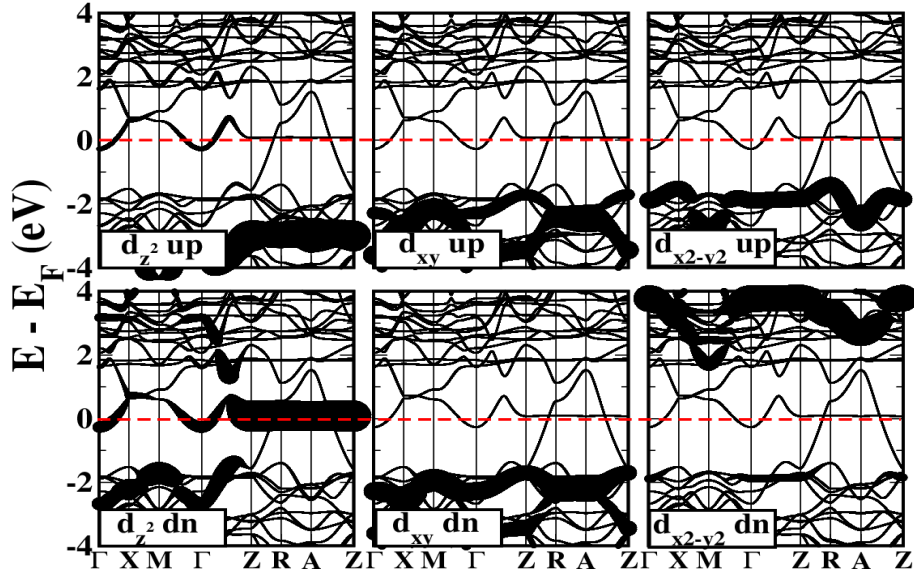


FIG. 5: AFM1 full fatband plots of Ni 3d orbitals in GGA+U. The fully occupied d_{xz}/d_{yz} orbitals are not shown here.

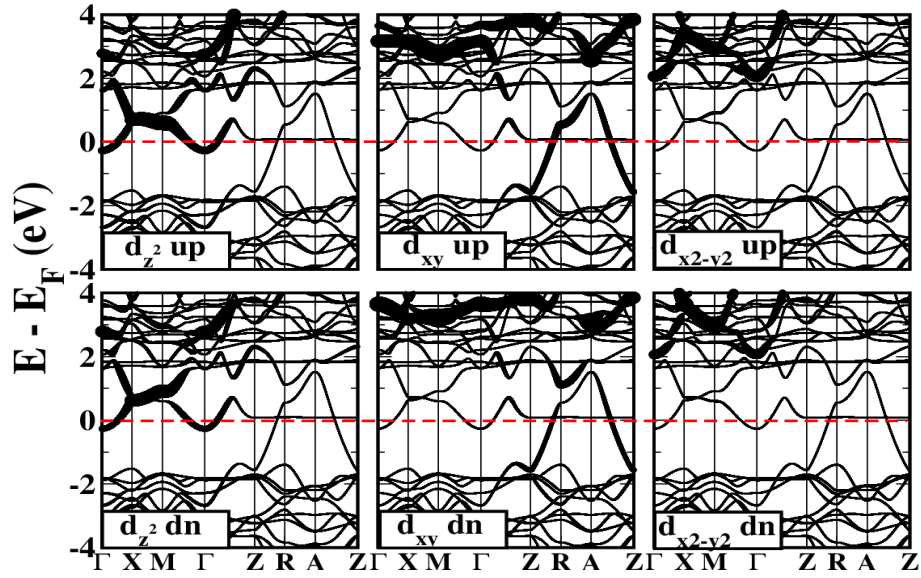


FIG. 6: AFM1 full fatband plots of Nd 5d orbitals in GGA+U. The fully unfilled d_{xz}/d_{yz} orbitals are not shown here.

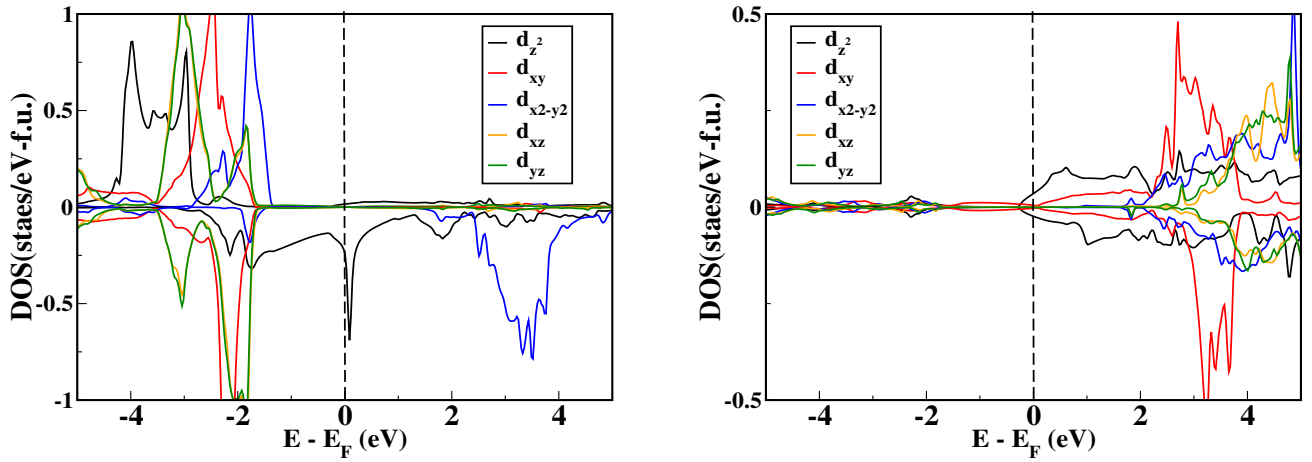


FIG. 7: AFM1 orbital-projected densities of states of (left) Ni 3d and (right) Nd 5d orbitals in GGA+U.

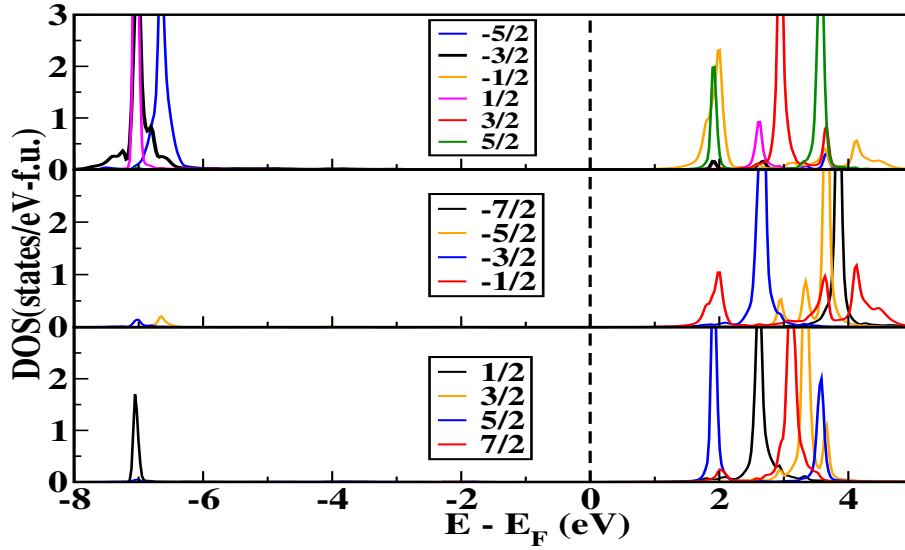


FIG. 8: AFM1 orbital-resolved DOSs of Nd 4f orbitals in the $|j, m_j\rangle$ basis, using the GGA+U+SOC. The occupied orbitals have mostly $|5/2, -5/2\rangle$, $|5/2, -3/2\rangle$, and $|5/2, +1/2\rangle$ character, leading to the 4f orbital moment of $-4.45 \mu_B$. Other configurations of similar energy might be obtained as self-consistent solutions, in which case the orbital moment would differ.

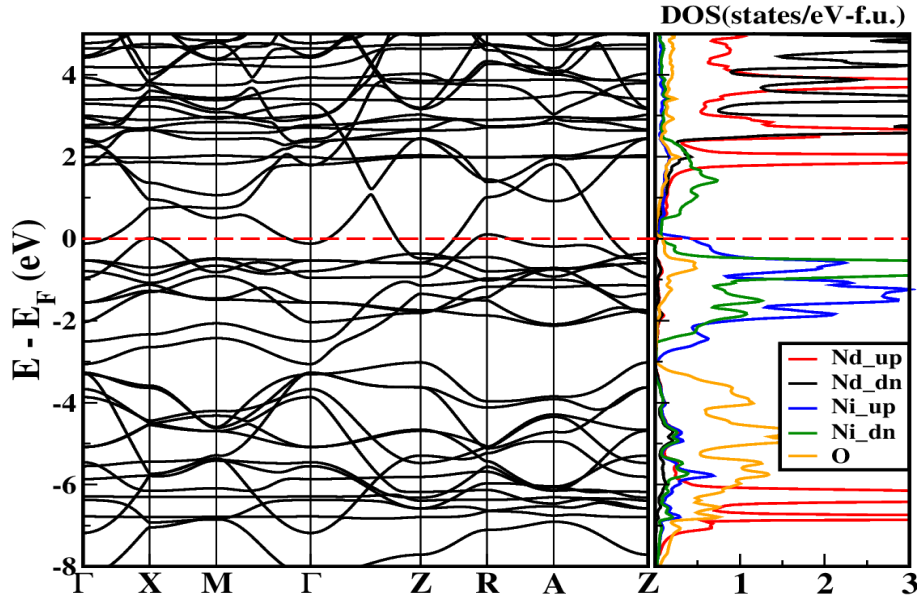


FIG. 9: AFM1 band structure and atom-projected DOSs in GGA+U, applying $U = 8$ eV and $J = 1$ eV only to the Nd 4f orbital. The magnitudes of the local spin moments are Nd $3 \mu_B$ and Ni $0.65 \mu_B$. Compared with that of applying U to both Ni and Nd orbitals (see Fig. 4), a clear distinction appears on the $k_z = \pi$ plane (along the $Z-R-A-Z$ line), in addition to a few hole Fermi surface. In this case, the Ni $3d_{z^2}$ orbital, which is dispersionless in this plane, is fully occupied, and an electron band appears at the Z-point.