1. Detailed derivation of the tight-binding models

Here we show the detailed derivation of using a 1D-chain model with $d_{xy}$ bonding orbitals and the nearest $\sigma$-interaction with second-order perturbation methods regarding the deviation of Na distribution from the uniformity perturbation to derive the Fermi level instability. The distribution of sodium ions in the 1D-chain $N_i = N_0 + \delta N_i$ is the degree of freedom. $N_0$ represents the uniform distribution and the fluctuation $\delta N_i$ can be understood as an average value of the grand canonical ensemble where the Na occupation at each site is either 0 or 1, with the average that can change continuously. Its Fourier transformation is as follow:

$$\delta N_i = \frac{1}{N} \sum_k \delta V_k e^{ikx_i}$$  \hspace{1cm} (S1)

The instability of NDW can be studied through the energy functional to $\delta N_i$, which could be expanded to the second-order (the first order diminishes because the total number of sodium ions is a constant):
\[
\delta E[\delta N] = \frac{1}{2} \sum_{ij} V_{ij} \delta N_i \delta N_j = \frac{1}{2N^2} \sum_{ij} V_{ij} (x_i - x_j) \sum_{k_1,k_2} \delta N_{k_1} \delta N_{k_2} e^{i(k_1 x_i + k_2 x_j)}
\]

\[
= \frac{1}{2N^2} \sum_{k_1,k_2} \delta N_{k_1} \delta N_{k_2} \sum_{i-j} e^{i(k_1 - k_2)} (x_i - x_j)/2 V_{ij} (x_i - x_j) \sum_{i+j} e^{i(k_1 + k_2)} (x_i + x_j)/2
\]

\[
= \frac{1}{2N} \sum_{k_1,k_2} \delta N_{k_1} \delta N_{k_2} \sum_{i-j} e^{i(k_1 - k_2)} (x_i - x_j) \delta_{k_1,-k_2}
\]

\[
= \frac{1}{2N} \sum_k \delta N_k \delta N_{-k} \sum_{i-j} e^{i k(x_i-x_j)} V_{ij} (x_i - x_j)
\]

\[
= \frac{1}{2N} \sum_k \left[ \frac{1}{N} \sum_i e^{ikr_i} V(r_i) \right] \left| \delta N_k \right|^2
\]

(S2)

Define \( f_k = \frac{1}{N} \sum_i e^{ikr_i} V(r_i) \), then we have the 2\textsuperscript{nd} order expansion in the momentum space:

\[
\delta E = \frac{1}{2} \sum_k f_k \left| \delta N_k \right|^2
\]

(S3)

To determine the coefficients \( V_{ij} \) and \( f_k \), we can calculate through the 2\textsuperscript{nd} order perturbation theory regarding the deviation of Na density from the uniform \( \delta N_i \) as the perturbation to derive the electronic energy:

\[
\tilde{H}_e = \tilde{H}_{e0} + \delta \tilde{H}_e
\]

\[
= \left[ \sum_i \epsilon_0 c_i^+ c_i + \sum_{ij} t_0 c_i^+ c_j + U \right. \sum_i n_{i\uparrow} n_{i\downarrow}
\]

\[
+ \left. \sum_i \delta \epsilon_i c_i^+ c_i + \frac{1}{2} \sum_i \delta t_{i,i+1} (c_i^+ c_{i+1} + c_{i+1}^+ c_i) \right]
\]

(S4)

Where the variation \( \delta \epsilon_i \) and \( \delta t_{i,i+1} \) is expanded for \( N_i \) to the first order with coefficients \( \partial \epsilon \) and \( \partial t \), which are \( \delta \epsilon_i = (\partial \epsilon) N_i \), \( \delta t_{i,i+1} = \partial t \).

Parameters used in Fig. 4(b) and 4(c) are \( t_0 = 2, \partial t = 0.5, \partial \epsilon = 0.7 \), where \( \partial \epsilon \) is the modulation to orbital energy when inducing 1 Na ion on either side. Coefficients are set as \( \epsilon_0 = e_1 = 0.22, t_0 = 1, t_N = 0.15, m \omega / t_d = 5 \) in Fig. 4(e). Parameters are set as \( t_0 = 1.5, t_N = 0.5, t_d = 1, e_0 = 0.05, e_1 = 0.1, m \omega^2 = 10 \) in Fig. 6. These values are determined through the comparison with the DFT calculations.

The 0\textsuperscript{th} order condition corresponds to a totally uniform sodium environment, where \( \epsilon_i \) and \( t_{i,i+1} \) are constants:
\[ E_0(k) = \epsilon_0 - t_0 \cos(kd), \quad \psi_0(k) = \frac{1}{\sqrt{N}} \sum_i e^{ikx_i} \phi_i(x) \] (S5)

And then, we can calculate the 2\textsuperscript{nd} order band energy

\[
\delta E(k) = \langle \psi_k | \delta H_e | \psi_k \rangle + \sum_{k'} \left| \left[ \psi_k \left| \delta \hat{H}_e | \psi_{k'} \right. \right] \right|^2 \frac{E_0(k) - E_0(k')}{E_0(k) - E_0(k')}
= 0 + \frac{1}{N^2} \sum_{k', \text{vac}} \left| \sum_i \left[ \psi_k \right| \delta \hat{H}_e | \psi_{k'} \right] \right|^2 \frac{E_0(k) - E_0(k')}{E_0(k) - E_0(k')}
\]

(S6)

The corresponding change of the total energy is therefore

\[
\Delta E = \sum_{k, \text{occ}} \delta E(k) = \frac{1}{N^2} \sum_{k, \text{occ}} \left( \sum_{k', \text{vac}} + \sum_{k', \text{occ}} \right) \left| \sum_i \left[ \psi_k \right| \delta \hat{H}_e | \psi_{k'} \right] \right|^2 \frac{E_0(k) - E_0(k')}{E_0(k) - E_0(k')}
= 0 + \frac{1}{N^2} \sum_{k, \text{occ}} \sum_{k', \text{vac}} \left| \sum_i \left[ \psi_k \right| \delta \hat{H}_e | \psi_{k'} \right] \right|^2 \frac{E_0(k) - E_0(k')}{E_0(k) - E_0(k')}
\]

(S7)

The last two equations show the electronic part of \( V_{ij} \) and \( f_k \) through direct comparisons. Including the screened Coulomb interaction between sodium ions, we have:

\[
V_{ij} = \frac{2}{N^2} \sum_{k, \text{occ}} \sum_{k', \text{vac}} \frac{e^{i(k' - k)(x_i - x_j)} \left| \partial \epsilon \left( e^{ik'd} + e^{-ikd} \right) \partial t \right|^2 \delta N_i}{\epsilon_0(k) - \epsilon_0(k')} + v_{ij}
\]

\[
f_k = \frac{2}{N^2} \sum_{k' \in \text{vac}, k = k' \in \text{occ}} \frac{\left| \partial \epsilon \left( e^{ik'd} + e^{-i(k' - k)d} \right) \partial t \right|^2 \delta N_k}{\epsilon_0(k' - k) - \epsilon_0(k')} + V_c(k)
\]

(S8)

for coefficients in real space \((V_{ij})\) and reciprocal space \((f_k)\) in Fig. 4c and Fig. 4b, respectively. The screened Coulomb potential is that \( V_c(r) = e^{-r/\delta}/r \). The Coulomb potential \( V_c(k) \) is its Fourier transformation cut-off at a large wave vector limit.
2. Supplementary figures

**Figure S1.** Structure models for the O3, P2 and P3 stackings. In the models, gray, red and yellow balls refer to TM ions, O ions and Na ions. ABCABC, ABBAAB and ABBCCA describes the periodic oxygen stacking types. The periodicity can be inferred from the number of 3 or 2 included in the notations, while the shape of NaO₆, can be inferred from the letter of P or O, where O is for octahedral shape and P is for prismatic shape.

<table>
<thead>
<tr>
<th>Lattice Type</th>
<th>NaₓTiO₂</th>
<th>NaₓVO₂</th>
<th>NaₓCrO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit Cell</td>
<td>Monoclinic</td>
<td>Hexagonal</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>(a) = 5.260, (b) = 3.037, (c) = 5.697, (\beta) = 107.927°</td>
<td>(a) = 2.865, (c) = 11.260</td>
<td>(a) = 5.189, (b) = 2.981, (c) = 5.868, (\beta) = 105.923°</td>
<td></td>
</tr>
<tr>
<td>Peak x Range</td>
<td>0.58 ~ 0.66</td>
<td>0.50 ~ 0.57</td>
<td>0.50 ~ 0.66</td>
</tr>
<tr>
<td>Superstructure Peak Index</td>
<td>1: (1, x, 1/2) ~3.1 Å</td>
<td>1: (1, x, 1) ~3.0 Å</td>
<td>1: (1, x, 0) ~3.5 Å</td>
</tr>
<tr>
<td></td>
<td>2: (1, x, -3/2) ~2.8 Å</td>
<td>2: (1, x, 3/2)</td>
<td>2: (1, x, -1) ~3.3 Å</td>
</tr>
<tr>
<td></td>
<td>3: (1, x, 3/2) ~2.3 Å</td>
<td></td>
<td>3: (1, x, 1) ~2.7 Å</td>
</tr>
<tr>
<td>NDW (\lambda) (Å)</td>
<td>(\frac{3.04}{x})</td>
<td>(\frac{2.87}{x})</td>
<td>(\frac{2.98}{x})</td>
</tr>
<tr>
<td>(\Delta k) (Å⁻¹)</td>
<td>(2.07x)</td>
<td>(2.19x)</td>
<td>(2.11(2x - 1))</td>
</tr>
</tbody>
</table>
Table S1. Comparison of properties of Na superstructures from the in-situ XRD measurements, including the type of Na sites, cell parameters, the composition range of moving superstructure peak in experiments, solved superstructure peak index as a function of x and the corresponding lattice plane distance, the NDW wavelength, and momentum change contributed by the scattering on the NDW. Note that the lattice type of O or P states that the NaO₆ local environment forms octahedral or prismatic geometry. O₃, P₃ or P₂ classifies the interlayer stacking by every 3 or 2 repeating unit cells along c, while O’3, P’3 or P’2 labels the existence of monoclinic distortion. [1] The fast and continuous evolution of the superstructure XRD peaks with changing Na compositions compared with the largely static background major hkl peaks can be understood as a two-component scattering. ∆k₀ on the underlying lattice with fixed momentum change of inverse lattice vector, and ∆k₁ on the Na superstructure NDW with momentum change of 2π/λₑᵧ, where λ is the wavelength of the NDW. From x = 2/3 to x = 1/2, λ continuously increases, leading to a gradually smaller momentum change due to scattering on the NDW and the continuous shift of the XRD peaks toward the lower angle observed in experiments. Superstructure peaks are typically observed for x around 0.5 with the superstructure interplanar distance around 3 Å, whose (hkl) labels are shown in Table 1. The evolution patterns of all the peaks share a unified expression of Miller indices (1, x, s), where s is integer or half integer.
**Fig. S2.** Illustration of the modulation of Na ions on Ti-Ti bonding. (a) shows the local potential, where the Na points directly to Ti is boxed in dashed lines. (b) shows the probability density of $d_{xy}$ orbitals, where the black arrows illustrate the oxygen movement direction pulled away from the Ti ions by Na ions.

![Graphs showing PDOS](image)

**Fig. S3.** Projected density of states (PDOS) of (a) O’3-Na$_{2/3}$TiO$_2$, (b) O’3-Na$_{1/2}$VO$_2$, (c) P’3-Na$_{1/2}$CrO$_2$, (d) P2-Na$_{1/2}$VO$_2$. The transition metal types and interlayer stackings are denoted in the figures. Most materials form dimers except P-2 Na$_x$VO$_2$ that forms the trimer. The calculated DOS are projected to TM ions in dimers and trimers as indicated by the legends. The splitting around the Fermi level is strong in Ti and V, but weak in Cr. The strong splitting in P2 and O3 Na$_x$VO$_2$ leads to the formation of small bandgaps.
Fig. S4 A typical band structure calculated from the 1D-model. The Fermi level of Ti falls in the lower-energy area of splitting, while the Cr falls to the higher-energy area.

References: