Electronic supplementary information (ESI) for

In-gap states and strain-tuned band convergence in layered structure trivalent iridate $K_{0.75}Na_{0.25}IrO_2$

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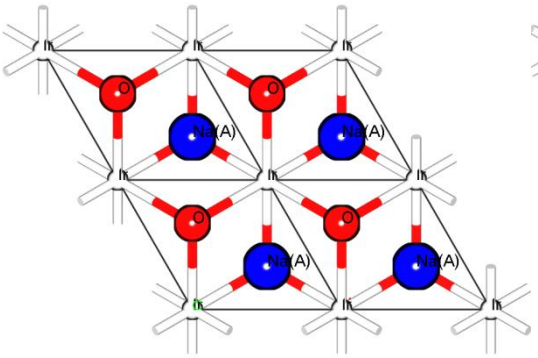
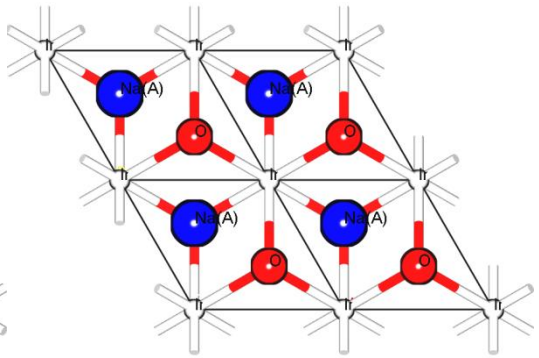
(a) NaA

First layer



Second Layer



(b) NaB

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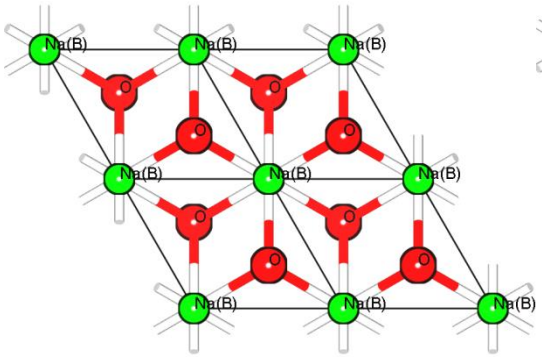

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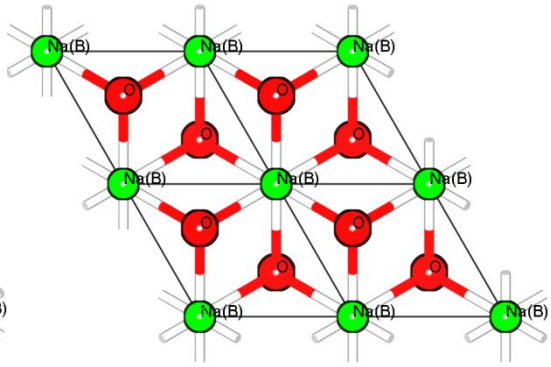

(c) NaANaB

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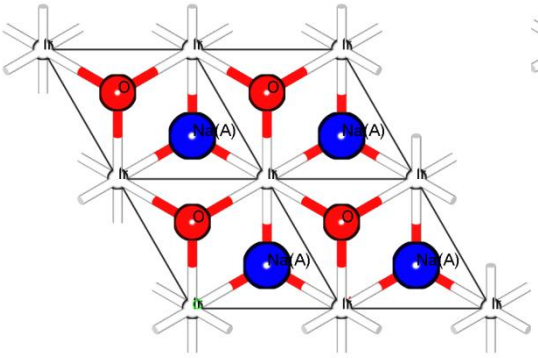

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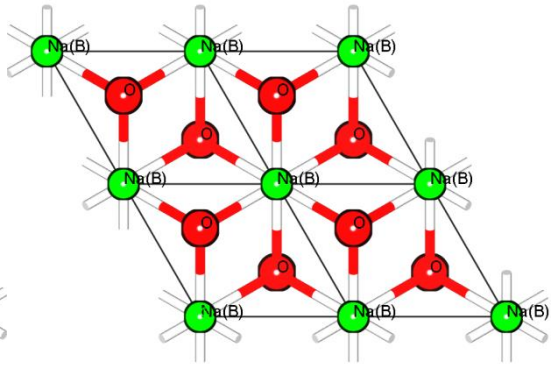
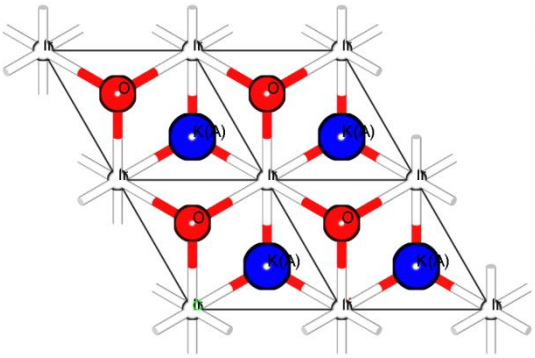


(d) KA

First layer



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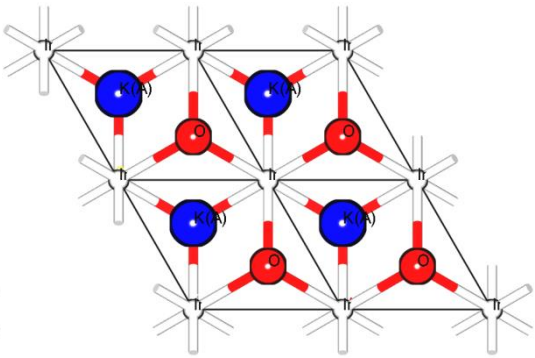
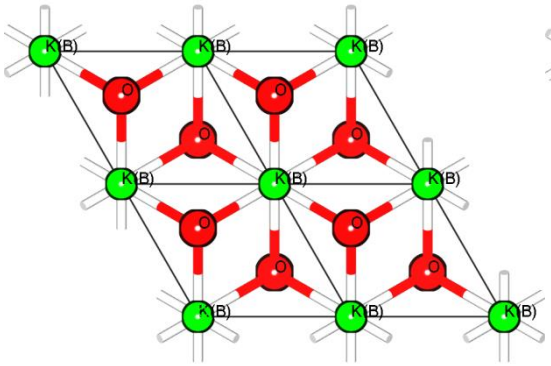


(e) KB

First layer



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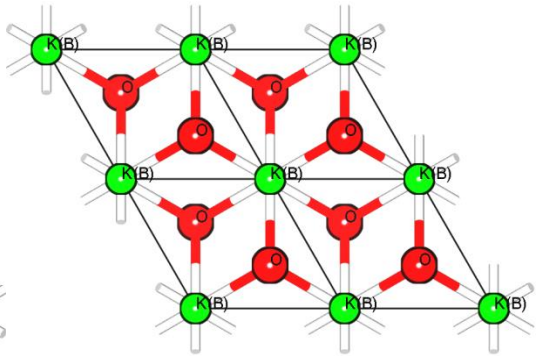
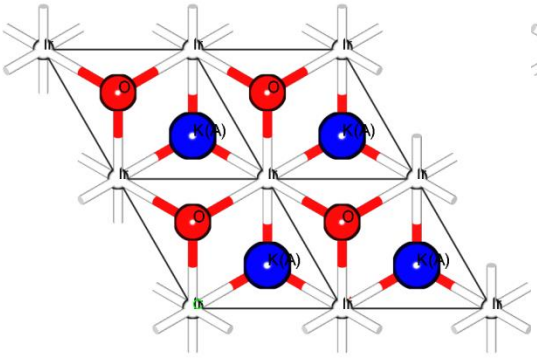


(f) KAKB

First layer



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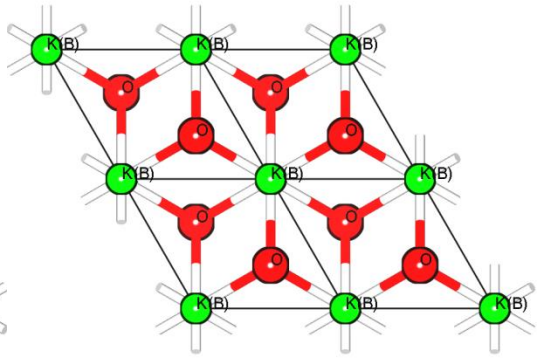

(g) KANaB

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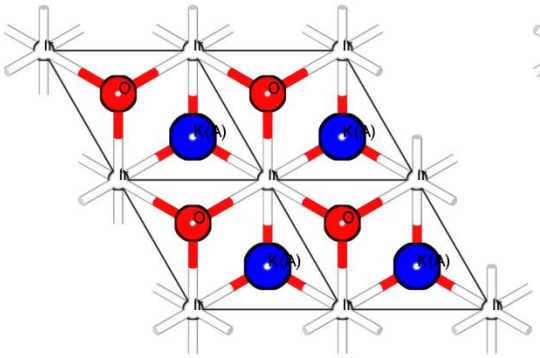

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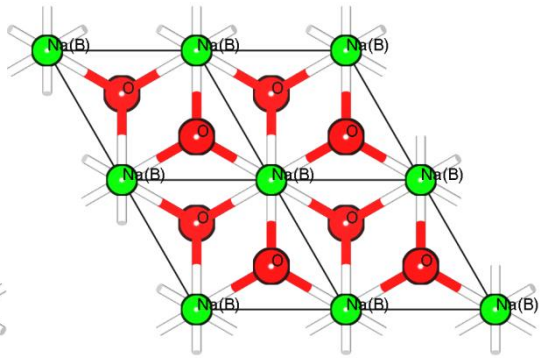
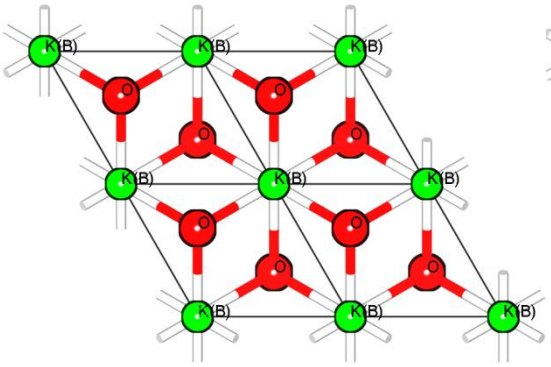
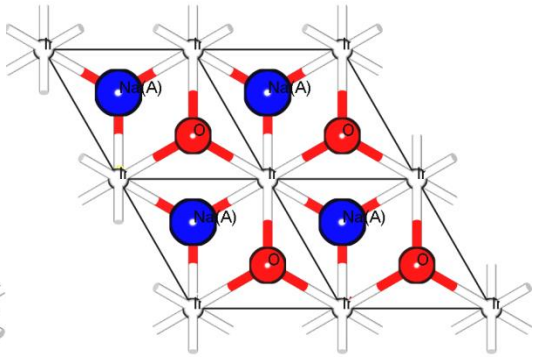


(h) KBNaA

First layer

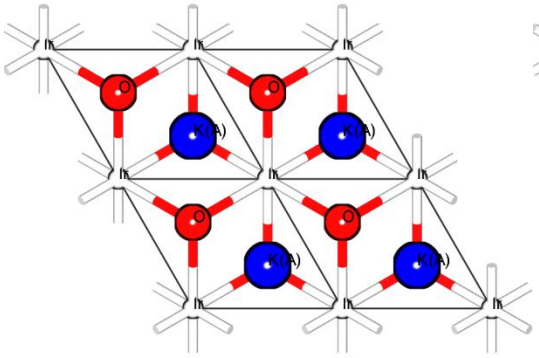


Second Layer

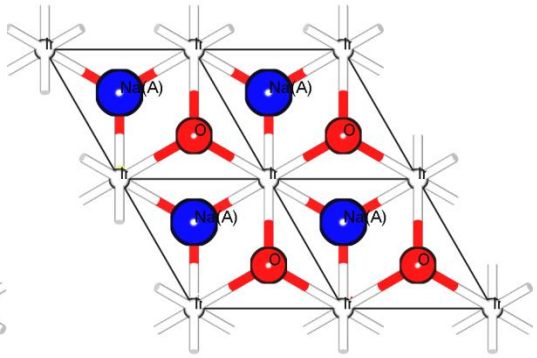


(i) KANaA

First layer



Second Layer



(j) KBNaB

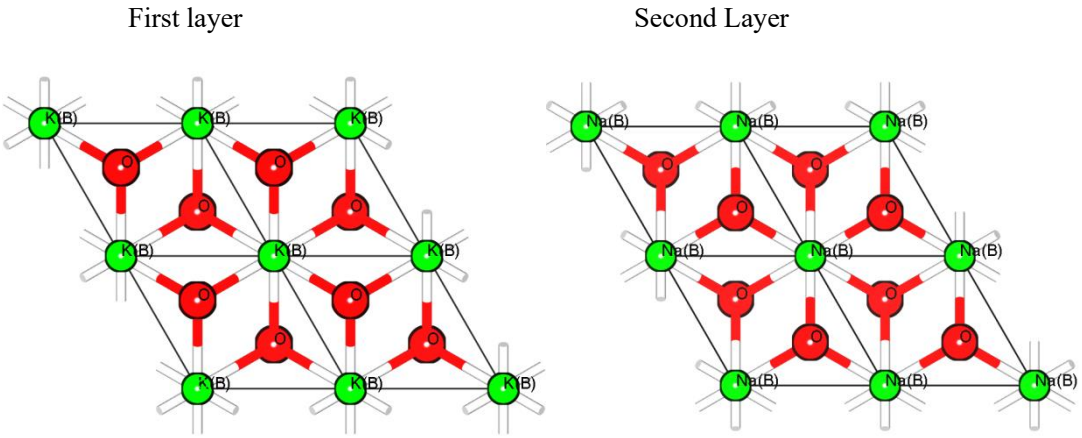


Figure S1 Schematic ten types of interlayer alkali ions occupancy in the crystallographic unit cell (solid line) of iridate $K_{0.75}Na_{0.25}IrO_2$: (a) NaA (Na ions only occupy the interlayer positions A, and there are no K ions), (b) NaB (Na ions only occupy the interlayer positions B, and there are no K ions), (c) NaANaB (Na ions occupy the positions A in one interlayer space, and occupy positions B in another interlayer space, and there are no K ions), (d) KA (K ions only occupy the interlayer positions A, and there are no Na ions), (e) KB (K ions only occupy the interlayer positions B, and there are no Na ions), (f) KAKB (K ions occupy the positions A in one interlayer space, and occupy the positions B in another interlayer space, and there are no Na ions), (g) KANaB (K ions occupy the positions A in one interlayer space, and Na ions occupy the positions B in another interlayer space), (h) KBNaA (K ions occupy the positions B in one interlayer space, and Na ions occupy the positions A in another interlayer space), (i) KANaA (K ions occupy the positions A in one interlayer space, and Na ions occupy the positions A in another interlayer space), and (j) KBNaB (K ions occupy the positions B in one interlayer space, and Na ions occupy the positions B in another interlayer space). The schematic structural figures are plotted with 2×2×1 cell, where the letters in the parentheses after the alkali element symbol indicate the interlayer A/B positions and denoted by big/small balls. Due to the limitation of the unit cell, real compositions of the model are $NaIrO_2$ ((a), (b) and (c)), $KIrO_2$ ((d), (e) and (f)) or $K_{0.5}Na_{0.5}IrO_2$ ((g), (h), (i) and (j)) in these ten configurations.

Table S1 Optimized lattice constants with different exchange-correlation functional with or without van der Waals (vdW) corrections.

	Method	NaA	NaB	NaANaB	KA	KB	KAKB	KANaB	KBNaA
a	PBE	3.263	3.213	3.237	3.323	3.277	3.300	3.273	3.270
	PBEsol	3.231	3.178	3.206	3.286	3.236	3.260	3.236	3.233
	PBE + DFT-D3 method of Grimme	3.251	3.195	3.222	3.312	3.265	3.287	3.259	3.256
	PBE +DFT-D2 method of Grimme	3.271	3.169	3.222	3.325	3.259	3.291	3.257	3.263
	PBE +DFT-D3 method with Becke-Jonson damping	3.241	3.181	3.210	3.302	3.252	3.276	3.248	3.244
	PBE +optB86b-vdW	3.246	3.185	3.215	3.305	3.250	3.276	3.250	3.246
	PBE +optPBE-vdW	3.269	3.211	3.239	3.332	3.279	3.305	3.276	3.271
	PBE +optB88-vdW	3.276	3.217	3.246	3.342	3.287	3.314	3.285	3.280
	Method	NaA	NaB	NaANaB	KA	KB	KAKB	KANaB	KBNaA
c	PBE	10.168	11.011	10.600	11.342	12.092	11.730	11.207	11.129
	PBEsol	9.999	10.886	10.459	11.126	11.904	11.528	11.032	10.952
	PBE + DFT-D3 method of Grimme	9.953	10.913	10.450	11.196	12.035	11.635	11.088	10.998
	PBE +DFT-D2 method of Grimme	9.730	11.031	10.401	11.177	12.037	11.629	11.119	10.896
	PBE +DFT-D3 method with Becke-Jonson damping	9.976	10.892	10.453	11.186	11.971	11.599	11.071	10.979
	PBE +optB86b-vdW	10.013	10.930	10.494	11.165	11.980	11.596	11.086	11.006
	PBE +optPBE-vdW	10.126	11.009	10.584	11.304	12.107	11.720	11.197	11.120
	PBE +optB88-vdW	10.115	11.002	10.577	11.315	12.123	11.735	11.200	11.120

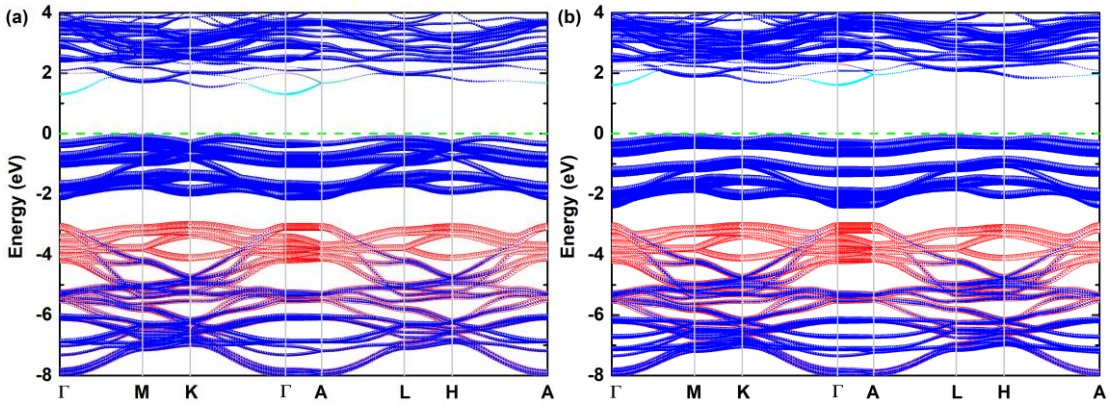


Figure S2 Projected band structures calculated within optPBE-vdW + *U* without SOC (a) or including SOC (b) for the case of Figure 2(a) in main text. The bands are projected onto K 4*s*, Na 3*s*, O 2*p* and Ir 5*d* states, denoted by cyan diamond, black circle, red hollow balls and blue solid balls. The size of the symbols is proportional to the contribution from the corresponding elements.

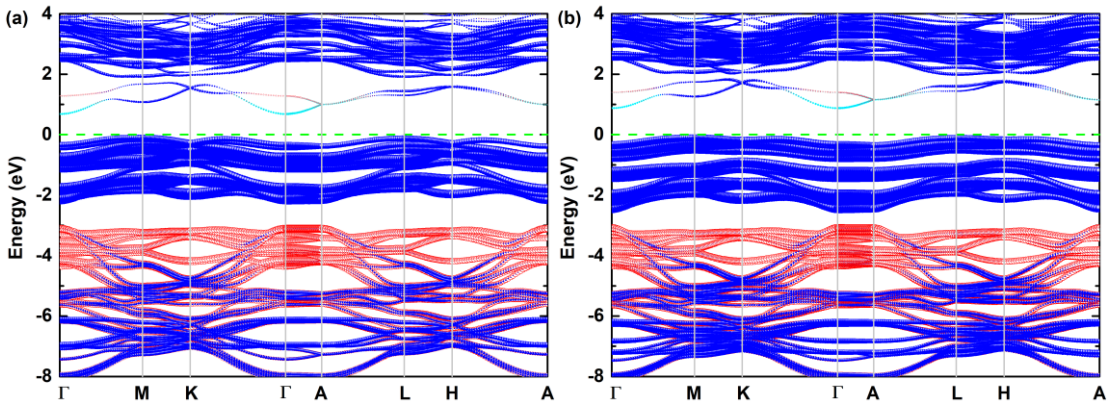


Figure S3 Projected band structures calculated within optPBE-vdW + *U* without SOC (a) or including SOC (b) for the case of Figure 2(c) in main text. The bands are projected onto K 4*s*, Na 3*s*, O 2*p* and Ir 5*d* states, denoted by cyan diamond, black circle, red hollow balls and blue solid balls. The size of the symbols is proportional to the contribution from the corresponding elements.

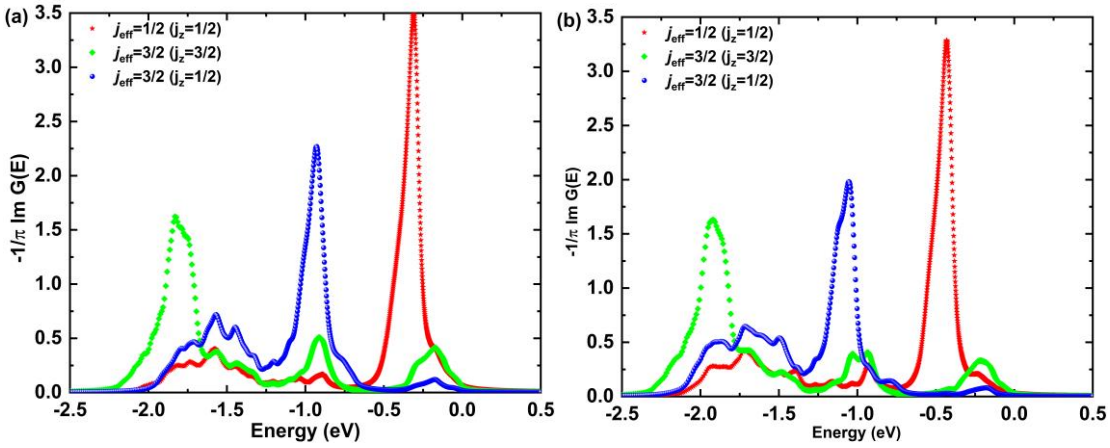


Figure S4 The projection of the t_{2g} states onto the j_{eff} states for $K_{0.75}Na_{0.25}IrO_2$ iridates with the mixed occupancy configurations of alkali metal ions as shown in **Figs. 2(a)** and **(c)** in the main text. (a) and (b) correspond to the mixed occupancy configurations of **Figs. 2(a)** and **(c)**, respectively.

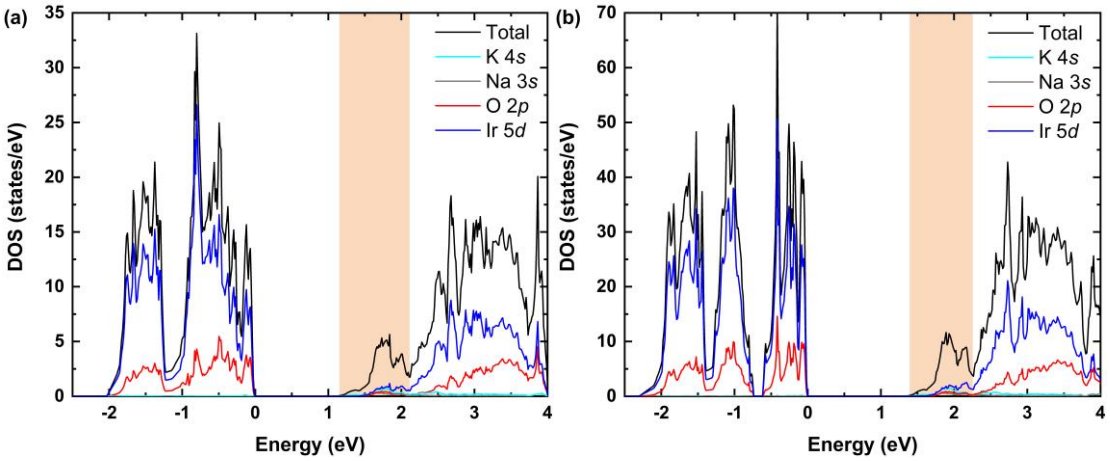


Figure S5 Density of states (DOS) of $K_{0.75}Na_{0.25}IrO_2$ with the mixed occupancy configurations of alkali metal ions as shown in **Fig. 2**(b) in main text. (a) and (b) are total and projected DOS calculated within optPBE-vdW + *U* without SOC and including SOC, respectively. The in-gap states are highlighted with the shadow region.

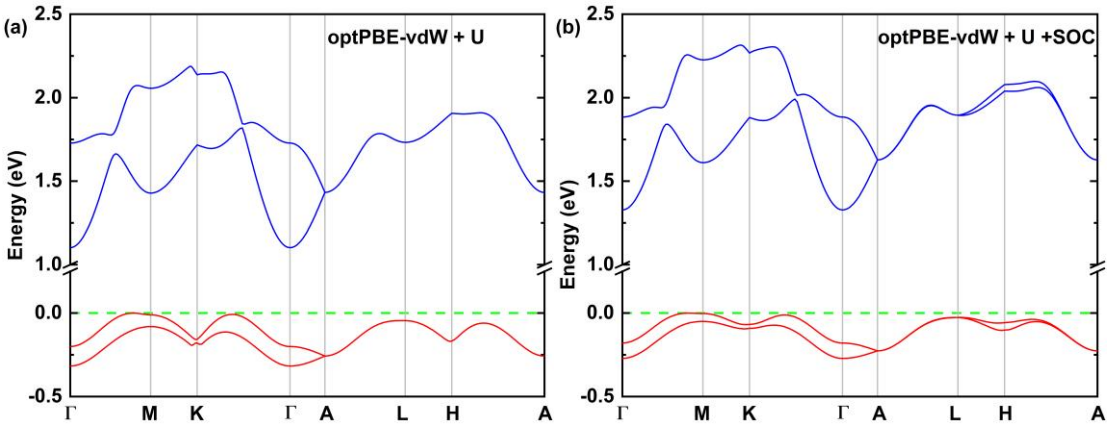


Figure S6 The zoom-in view of the band structure around Fermi level calculated within optPBE-vdW + *U* without SOC (a) or including SOC (b) for $K_{0.75}Na_{0.25}IrO_2$ iridate as shown in **Fig. 2(b)** in main text.

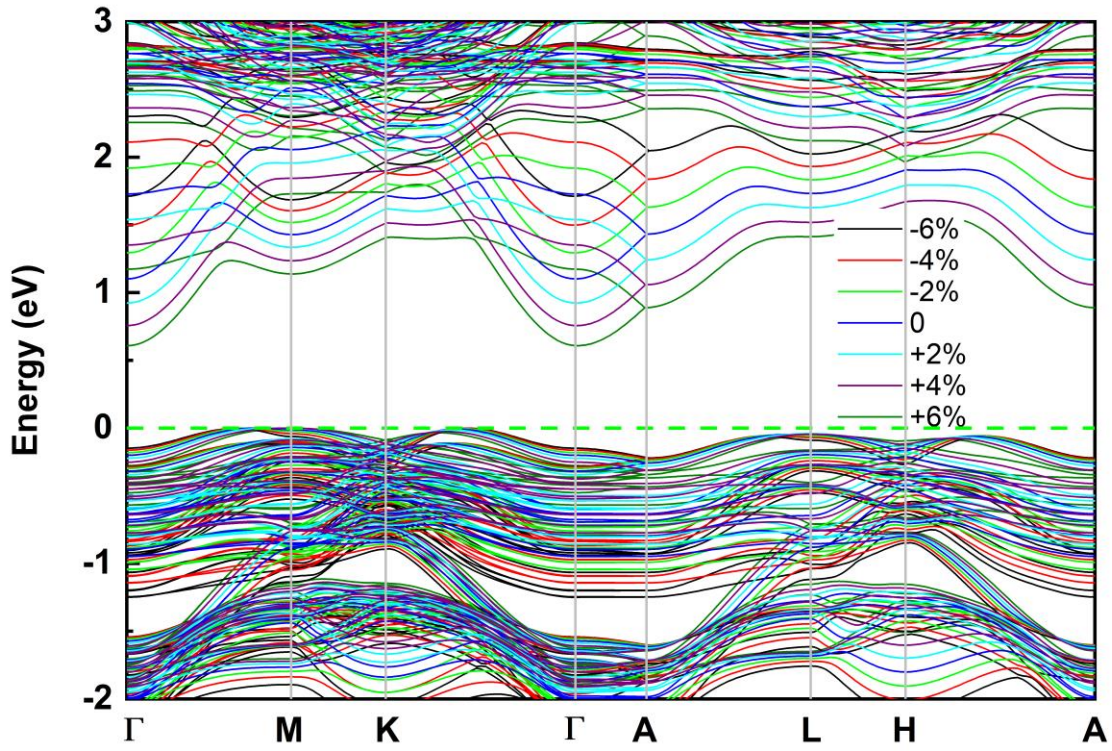
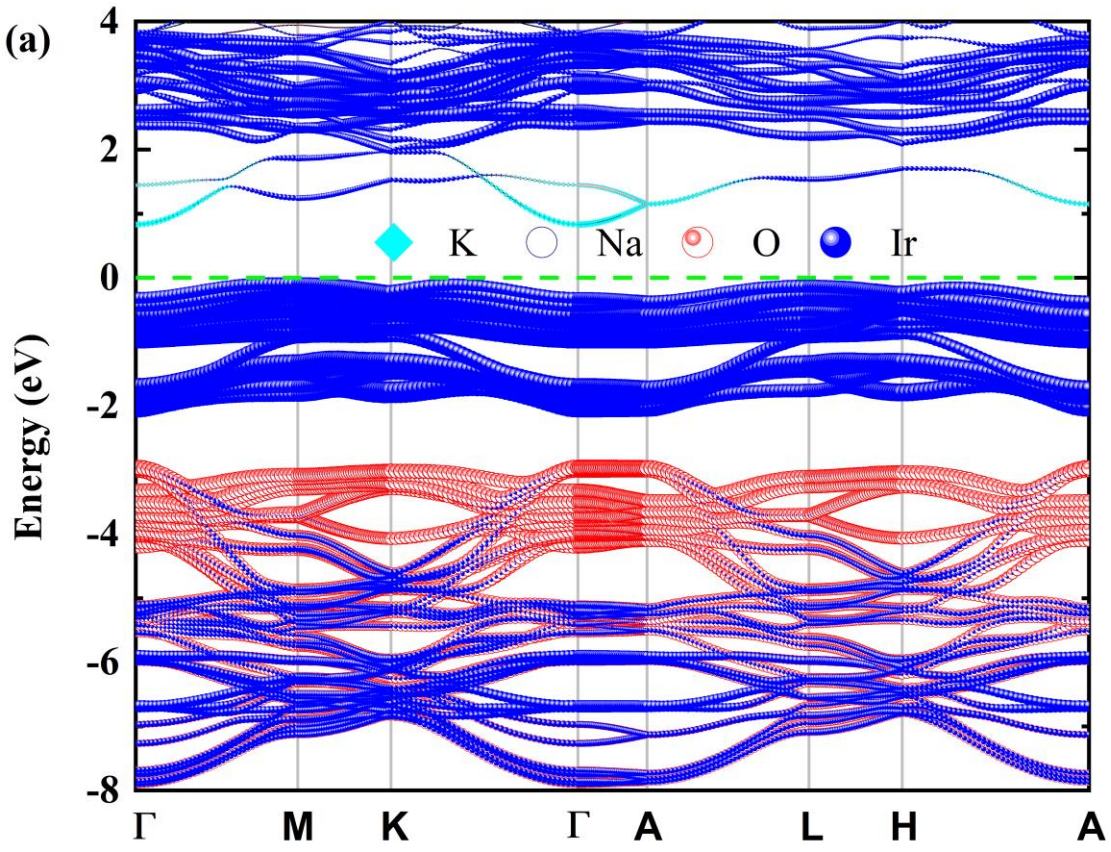
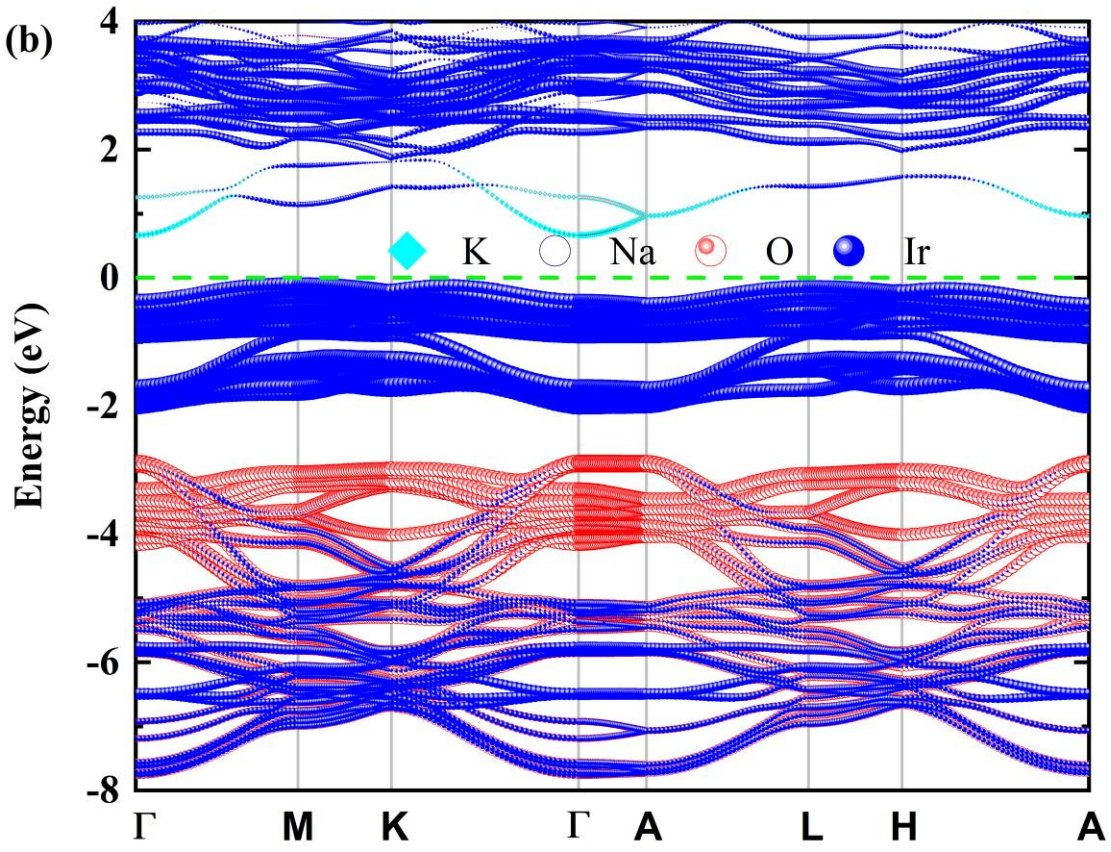


Figure S7 The evolutions of the band structure of $K_{0.75}Na_{0.25}IrO_2$ as shown in **Fig. 2(b)** along with the applied strain calculated with optPBE-vdW + *U*.


(a)
Energy (eV)
4
2
0
-2
-4
-6
-8
K
Na
O
Ir
Γ
M
K
Γ
A
L
H
A


(b)
Energy (eV)
4
2
0
-2
-4
-6
-8
K
Na
O
Ir
Γ
M
K
Γ
A
L
H
A

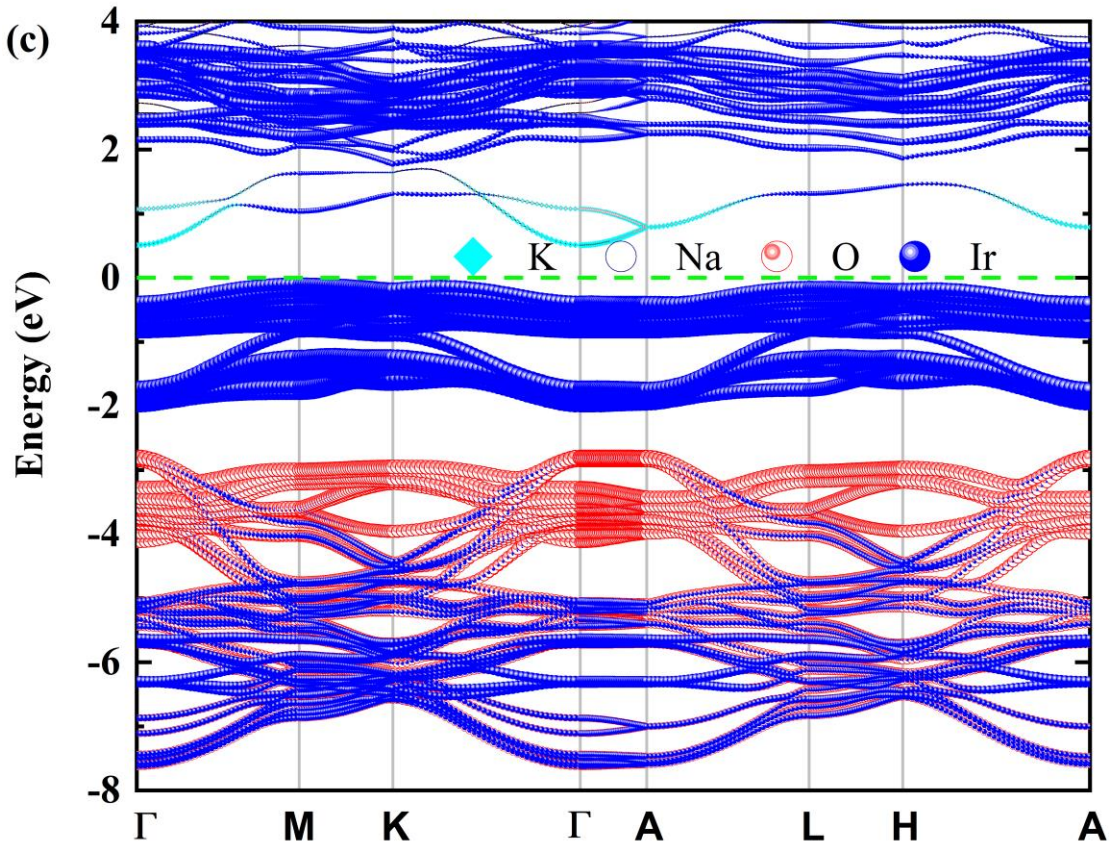
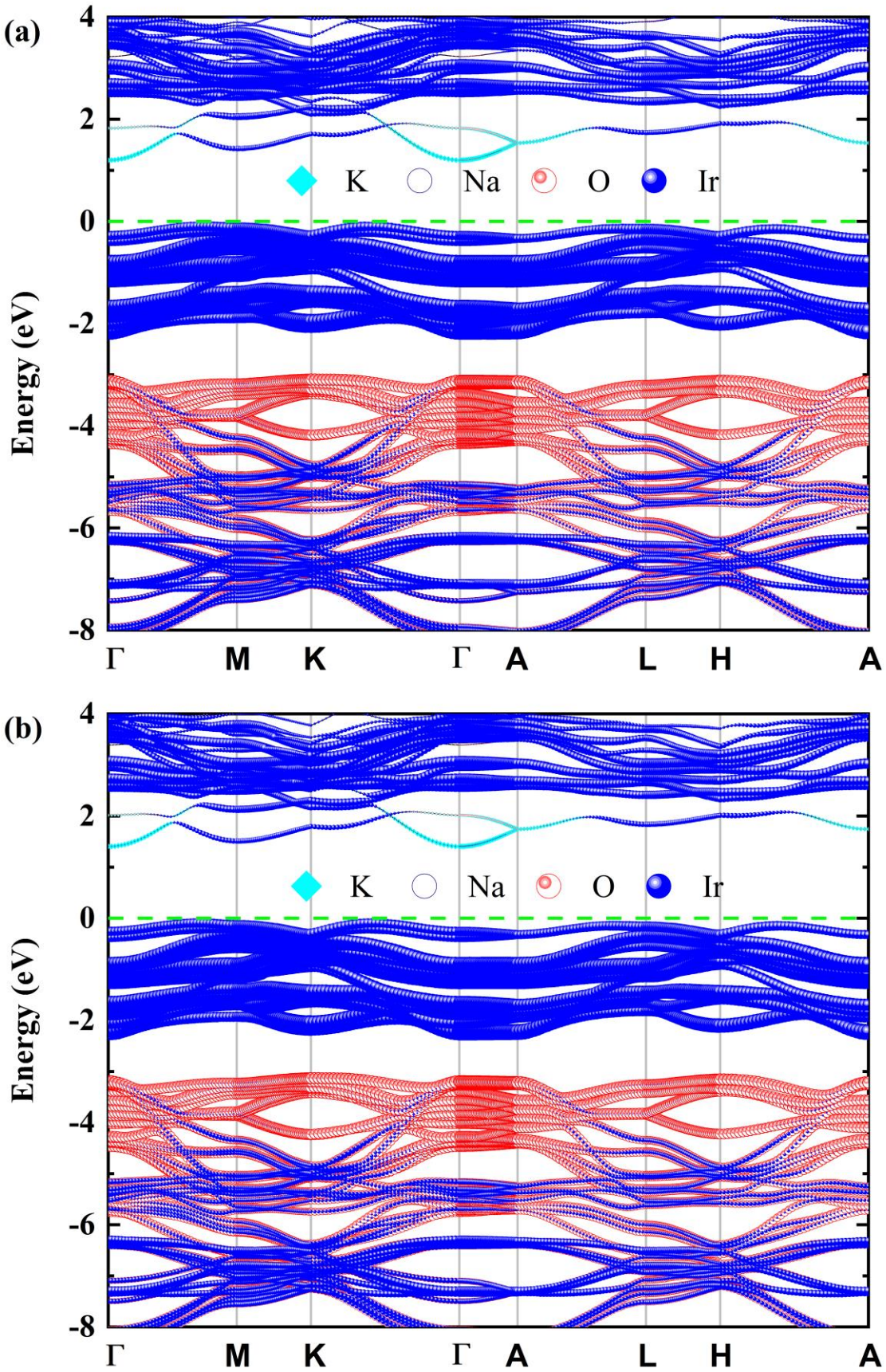


Figure S8 The evolutions of projected band structure under tensile strains ($\varepsilon > 0$) calculated within optPBE-vdW + *U*: (a) 2%, (b) 4%, (c) 6%. The bands are projected onto K 4*s*, Na 3*s*, O 2*p* and Ir 5*d* states, denoted by cyan diamond, black circle, red hollow balls and blue solid balls. The size of the symbols is proportional to the contribution from the corresponding elements.


(a)
4
2
0
-2
-4
-6
-8
Energy (eV)
K
Na
O
Ir
Γ
M
K
Γ
A
L
H
A
(b)
4
2
0
-2
-4
-6
-8
Energy (eV)
K
Na
O
Ir
Γ
M
K
Γ
A
L
H
A

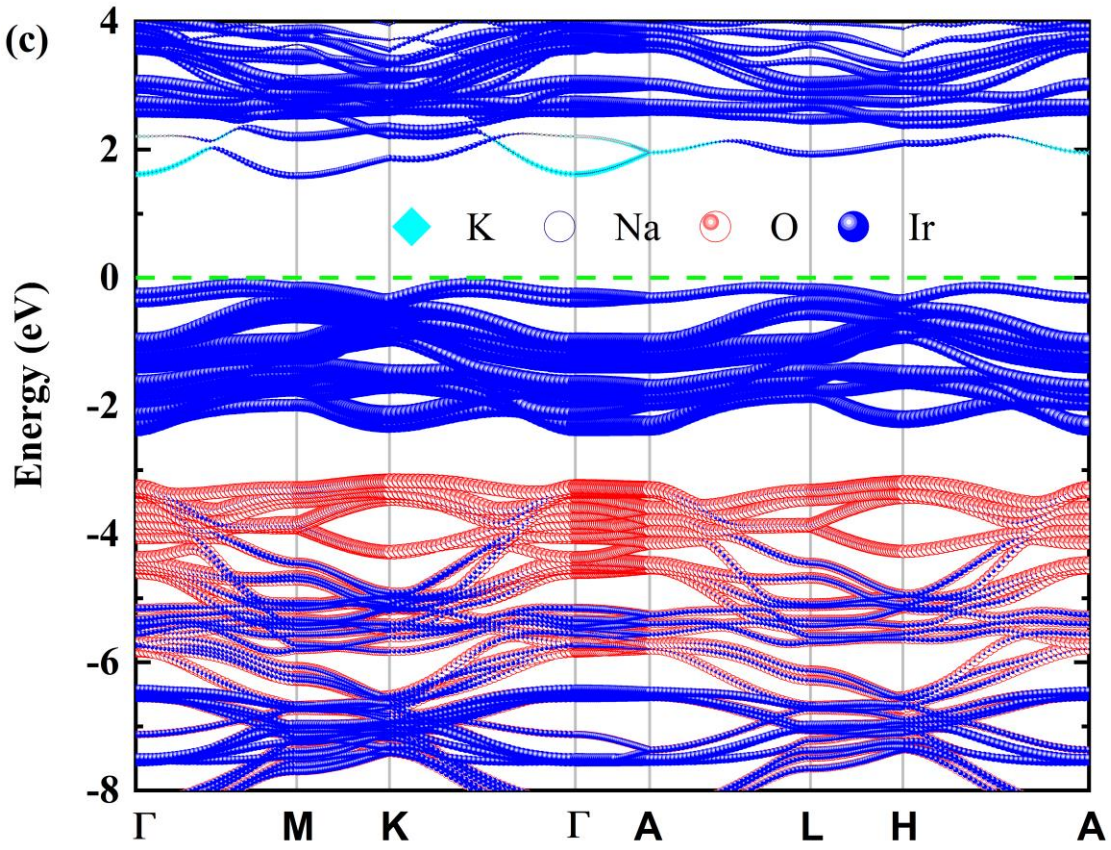


Figure S9 The evolutions of projected band structure under compressive strains ($\varepsilon < 0$) calculated within optPBE-vdW + *U*: (a) -2%, (b) -4%, (c) -6%. The bands are projected onto K 4*s*, Na 3*s*, O 2*p* and Ir 5*d* states, denoted by cyan diamond, black circle, red hollow balls and blue solid balls. The size of the symbols is proportional to the contribution from the corresponding elements.