

Supporting Information

Perovskite oxide interfaces tailored by cation ordering periodicities: experimentally resolved atomic structure and predicted magnetic coupling

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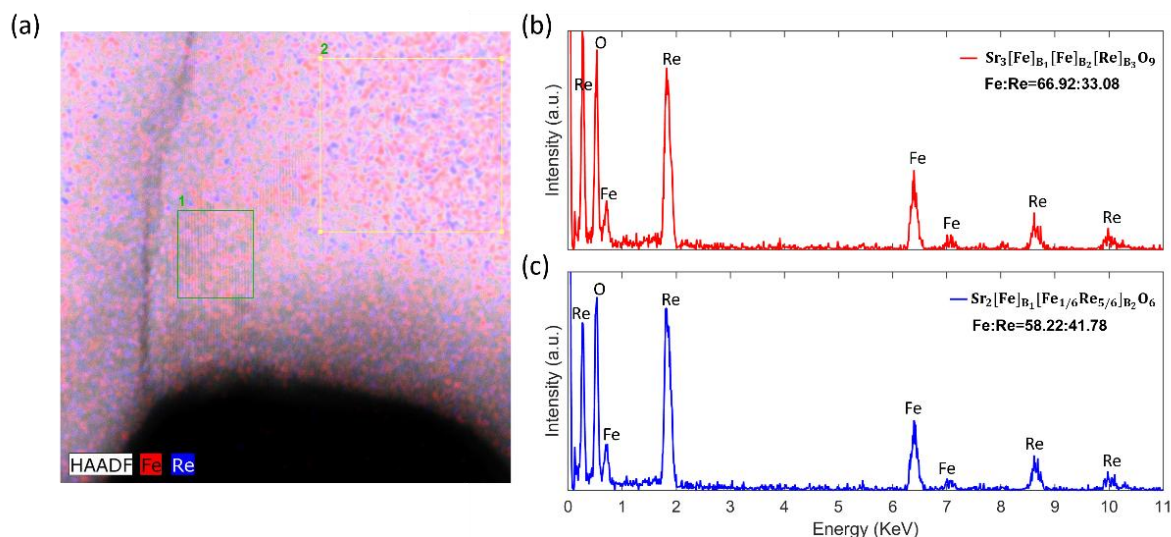


Figure S1. Quantitative statistical energy-dispersive X-ray spectroscopy (EDXS) analysis for perovskite oxide bulk (a) The off-axis STEM-EDXS mapping of the grain containing the interface between the double perovskites and triple perovskites. (b) The EDXS spectra of the triple perovskite $\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9$ area marked by the green rectangle in (a) and (c) The EDXS spectra of the double perovskite $\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Fe}_{1/6}\text{Re}_{5/6}]\text{B}_2\text{O}_6$ area marked by the yellow rectangle in (a). The intensity of the EDXS peak was normalised by Re M_α peak, which is approximately 1.84 keV.

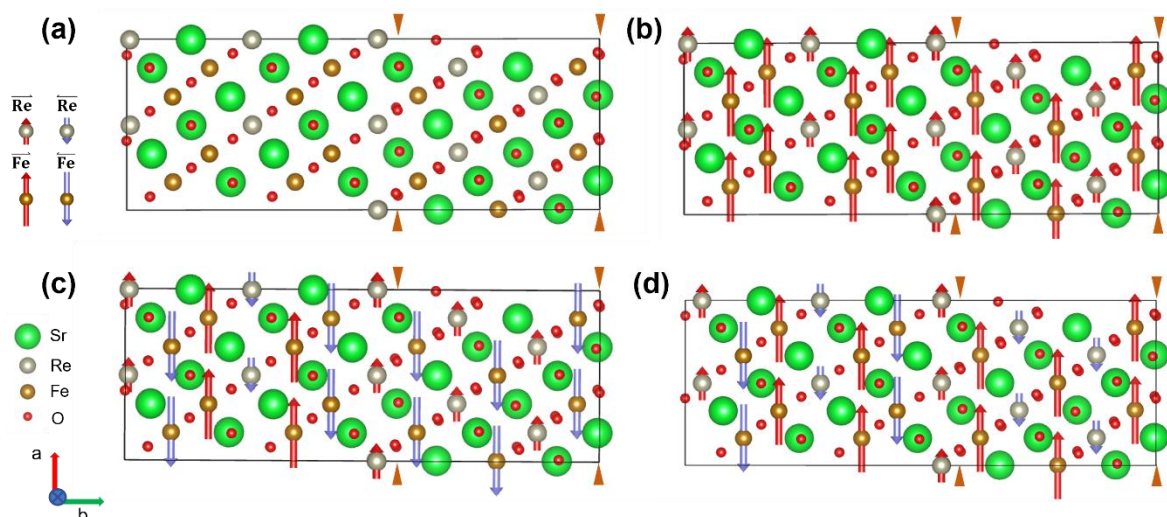


Figure S2. Schematic of (a) non-magnetic structure, (b) ferromagnetic (FM) structure, antiferromagnetic (AFM) structures with (c) AFM interface coupling and (d) FM interface coupling of the $\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9$ / $\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Re}]_{\text{B}_2}\text{O}_6$ interfaces based on the $\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9$ with the $P\bar{3}m1$ space group and $\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Re}]_{\text{B}_2}\text{O}_6$ with the $I4/m$ space group. The interface is indicated by a pair of orange triangles, and two such interfaces are present owing to the periodicity of the model. The atomic structures in panels (a-d) show Sr in green, Re in silver, Fe in gold, and O in red. Spin-down and spin-up magnetic moments are represented by violet and red arrows, respectively. The intrinsic spin moments of Re and Fe are approximately $1 \mu_{\text{B}}$ and $4 \mu_{\text{B}}$, respectively.

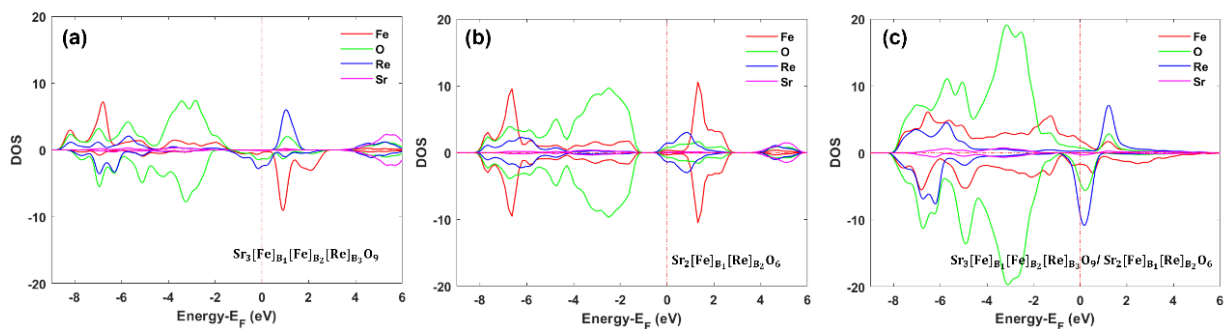


Figure S3. The density of states (DOS) of (a) $\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9$, its primitive cell having 30 atoms, (b) $\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Re}]_{\text{B}_2}\text{O}_6$, its primitive cell having 20 atoms (c) $\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9/\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Re}]_{\text{B}_2}\text{O}_6$ interface, its primitive cell with 120 atoms.

Quantitative EDXS for atomic-resolution elemental maps of interfaces. FEI Titan G2 80-200 CREWLEY equipped with FEI ChemiSTEM/Super-X EDXS detection technology is the platform used to collect the original EDXS data and to post-process the dataset independently from the exported Bruker Esprit maps. When users operate their commercial software to browse the raw data, the software automatically applies a map filter, typically involving averaging or Gaussian smoothing. Although this facilitates rapid visual inspection for users quickly reading their contrast, it might be involved artificial configuration issues in visualisation ^{1,2}. Therefore, we demonstrate a method to derive this quantitative elemental ratio. The raw dataset contains a 218×479 pixel spectrum image with 2048 energy channels. The spectrum image covered an area of approximately $5.81 \text{ nm} \times 2.64 \text{ nm}$, corresponding to a pixel size of approximately 0.0121 nm per pixel.

The Figure S4 data was regenerated directly from the raw spectrum image by integrating the relevant X-ray peaks after local side-band background subtraction: Fe K α , Re L α and Sr K α . No Bruker Esprit 2D filter, Gaussian, median filtering, or other spatial smoothing filter was applied to the maps used for analysis. To further ensure that the Fe:Re ratio is not an artefact of arbitrary spatial filtering, we repeated the analysis using the unit-cell intervals defined directly from raw dataset. In addition to the full unit-cell strip integration, we constructed a transition-metal-enriched ROI (Region of Interest) mask using the combined Fe + Re signal only as a locator ³. The Fe:Re ratios were then calculated from the unit cell, unfiltered, background-subtracted Fe K α and Re L α counts within these ROIs. This analysis produced the same trend: the first four rows of unit cells on the triple-perovskite side show Fe/Re ≈ 2 , whereas the ratio decreases sharply from roll 5 onwards. This confirms that the interfacial change in Fe:Re ratio is retained without relying on Bruker 2D-filtered elemental maps.

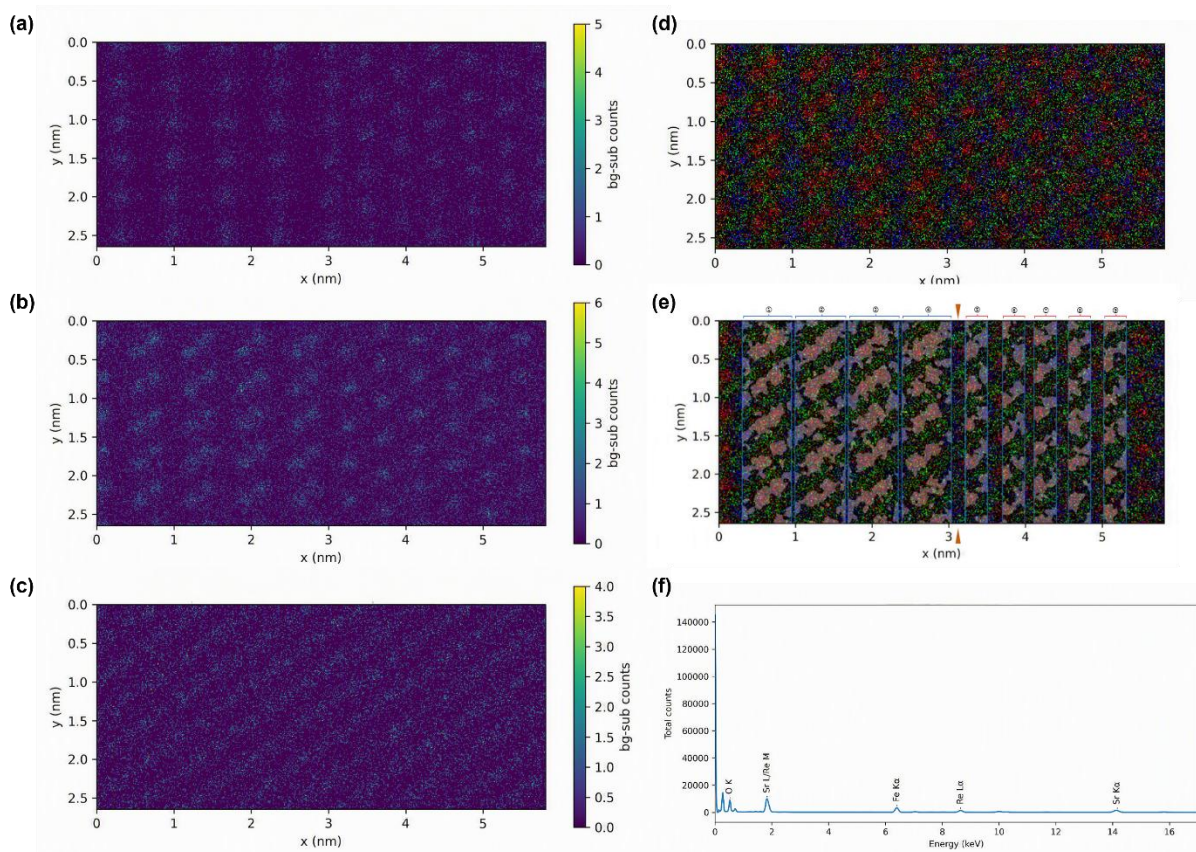


Figure S4. Background-subtracted elemental maps of non-filtered (a) Re L α , (b) Fe K α and (c) Sr K α (d) Raw-count Sr-Fe-Re RGB overlay. (e) Corrected unit cell intervals and transition metal enriched ROI mask used for Fe:Re extraction. (f) Summed EDXS spectrum from the analysed region.

We then compared several ways of extracting the Fe:Re ratio from the same raw EDXS data:

- (i) a non-mask unit-cell analysis;
- (ii) transition-metal-enriched masks using the top 30% of the σ^2 locator signal;
- (iii) transition-metal-enriched masks using the top 40% of the σ^2 locator signal;
- (iv) transition-metal-enriched masks using the top 50% of the σ^2 locator signal.

The locator map was defined as $L = I_{\text{Fe},K\alpha} + I_{\text{Re},L\alpha}$, using the background-subtracted Fe and Re maps only to identify transition-metal-rich regions. Thresholds corresponding to the top 30%, 40% and 50% of L were then used to construct different ROI masks.

The purpose of these analyses was not to redefine the bulk stoichiometry, but to test whether the observed Fe:Re ratio across the interface is sensitive to the specific ROI definition. The masks were overlaid on the elemental maps to verify that the selected regions correspond to the transition-metal-rich (B-site) columns, while the EDXS counts themselves were kept raw apart from the same background-subtraction procedure used for the original quantification. As shown in Figure S5, the resulting sensitivity analysis shows that the absolute local Fe:Re ratios vary slightly depending on the ROI definition and masking threshold, as expected for atomic-resolution zone-axis EDXS analysis. The error bars were estimated by propagating Poisson counting uncertainties of the background-subtracted Fe $K\alpha$ and Re $L\alpha$ intensities. However, the overall trend is robust. On the triple-perovskite side, unit cell 1 to 4 consistently show a Fe:Re ratio close to the expected 2:1 value after normalisation. Across the interface, located between unit cell 4 and 5, the Fe:Re ratio decreases abruptly. On the double-perovskite side, the local projected Fe:Re ratio is lower than that of the triple-perovskite side and gradually increases from approximately 1.3 to 1.4 near the interface to approximately 1.7 further away from the interface. This behaviour is reproduced by all ROI-mask methods tested.

This analysis shows that the value of ~ 1.7 in the original Figure 2f should not be interpreted as a statistically averaged bulk composition of the double-perovskite region. Rather, it is a local projected Fe:Re ratio obtained from a zone-axis, unit-cell-by-unit-cell EDXS analysis. Such local atomic-resolution EDXS quantification can be affected by projection, channelling, finite ROI width, local Fe:Re non-uniformity, and the choice of B-site column mask. In contrast, the

larger-area off-axis EDXS analysis in Figure S1 provides a more statistically representative composition, giving an average Fe:Re ratio of 1.39 ± 0.03 for the double-perovskite region, which is close to the expected value of 1.4 for $\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Fe}_{1/6}\text{Re}_{5/6}]_{\text{B}_2}\text{O}_6$.

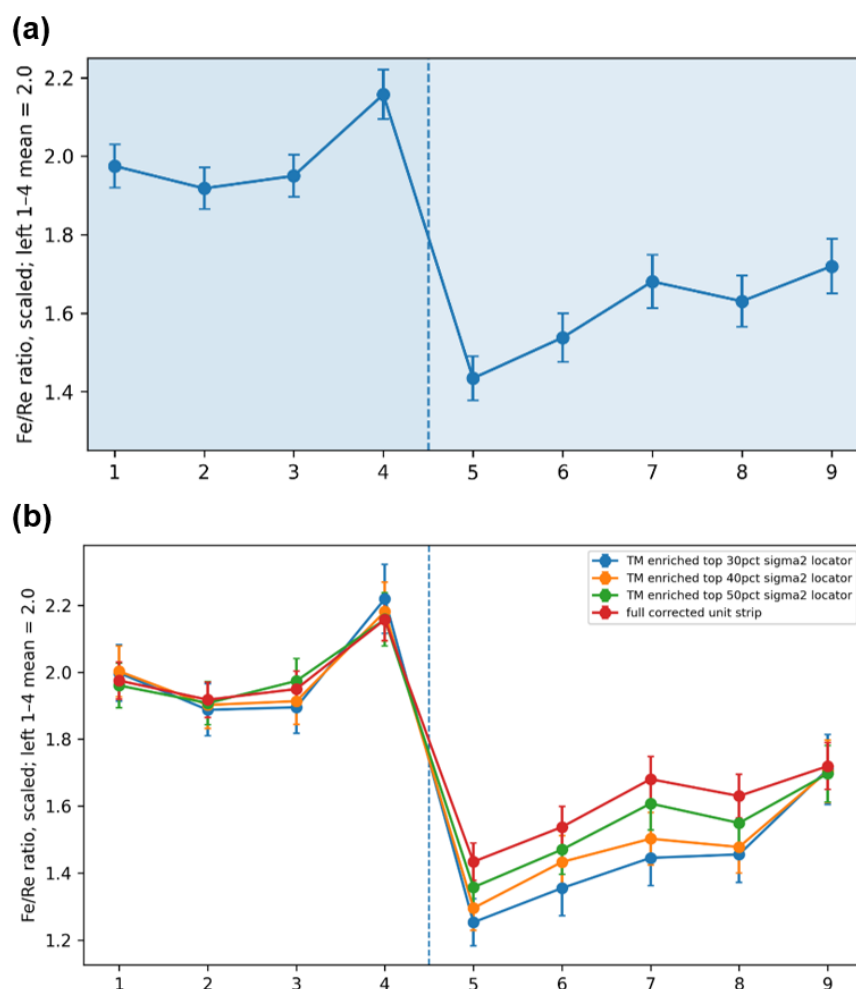


Figure S5. Unit-cell resolved Fe:Re ratios extracted from the raw background-subtracted EDXS spectrum image. (a) Fe:Re ratios obtained using unit-cell integration corresponding to Table S6. (b) Sensitivity comparison using transition metal enriched ROI masks defined by the top 30%, 40% and 50% of the combined Fe/Re locator signal.

Magnetic coupling of $\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9/\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Fe}_{1/6}\text{Re}_{5/6}]_{\text{B}_2}\text{O}_6$ interfaces. The preceding discussion primarily focuses on an idealised interface model constructed from a 1:2 B-site ordered triple perovskite $\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9$ and 1:1 B-site ordered double perovskite $\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Re}]_{\text{B}_2}\text{O}_6$. However, as previously noted, experimental observations reveal mixed Fe occupancy on the double perovskite side $\text{Sr}_2\text{Fe}_{1+x}\text{Re}_{1-x}\text{O}_6$ side, leading a deviation in elemental ratio. This deviation motivates a deeper investigation into the effects of Fe doping on the structural, electronic, and magnetic properties. of the triple perovskite $\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}/\text{Sr}_2\text{Fe}_{1+x}\text{Re}_{1-x}\text{O}_6$ interface. Doping introduces complex atomic site occupations, defects and alters magnetic coupling behaviour, making the study of such systems particularly challenging. In most cases, accurately capturing the influence of doping at perovskite interfaces necessitates large-scale supercell models, which pose significant computational demands for density functional theory (DFT) calculations. To address this, a simplified demonstration model within a limited primitive cell is presented in discussion of $\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9/\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Fe}_{1/6}\text{Re}_{5/6}]_{\text{B}_2}\text{O}_6$ interface of supporting information, aiming to provide initial insight into the potential impact of Fe substitution on the interfacial structure and magnetism.

With similar study strategy, the potential magnetic coupling configurations of the interfaces of $\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9/\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Fe}_{1/6}\text{Re}_{5/6}]_{\text{B}_2}\text{O}_6$ was displayed as Figure S6 and S7. we maintained the AFM coupling in each phase. Then we only change the magnetic coupling configurations of adjacent $\{\bar{1}1\bar{1}\}_{\text{pc}}$ planes at the very interface between two phases, which are an antiferromagnetically coupled interface and a ferromagnetically coupled interface, as depicted in Figure S7c and S7d, respectively along with the non-magnetic (NM) and ferromagnetic (FM) couplings settings in double and triple perovskite regions. The formation energy of different magnetic coupling settings in Table S3. indicates that the ferromagnetically

coupled interface exhibited is preferable setting, with an energy difference of 3.6 meV/atom compared to the antiferromagnetically coupled interface. This value is smaller than that of $\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9/\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Re}]_{\text{B}_2}\text{O}_6$ interface whose value is 5 meV/atom. This observation suggests that the Fe doping is prone to diminish the FM coupling between the interfaces.

Further, the four-state method was used to study the exchange coupling parameter of the transitional metals pairs, and the results were summarised in Table S4, corresponding to Figure S8. The results of the exchange coupling parameters further corroborate that the Fe-O-Re interface exhibits FM coupling for both pair ① and pair ②, with magnitudes of -0.0038 eV and -0.0089 eV, respectively. These findings align with the results obtained from the formation energy calculations. However, the exchange coupling value of FM in Fe-doped interface model is smaller than undoped interface model, since doping always leads to more complex impacts on both structure as well as electronic structure. It is theoretically demonstrated that the periodicity of B-site stacking ordering, rather than excess Fe atoms, plays a dominant role in FM coupling at the interface, after the doping effect of excess Fe in double perovskite as discussed in the supporting information.

Prior to assessing the interface model with mixed occupation, we constructed the corresponding bulk double perovskite $\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Fe}_{1/6}\text{Re}_{5/6}]_{\text{B}_2}\text{O}_6$ model with primitive cell containing 60 atoms. The corresponding formation energy results for different magnetic coupling configurations, as shown in Figure S6, average atomic formation energy for the AFM coupling setting is 3 meV lower than that of the FM coupling setting, suggesting that the AFM coupling remains energetically favorable. Notably, the Fe:Re ratio of 1.4:1 does not affect the intrinsic AFM coupling along the $(111)_{\text{pc}}$ plane of the interface model.

To learn the impacts on triple-/double- perovskites caused by Fe random doping, we build up and relax the bulk model of double perovskite $\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Fe}_{1/6}\text{Re}_{5/6}]_{\text{B}_2}\text{O}_6$ with 1.4:1 Fe:Re ratio, and its interface with triple perovskite $\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9$. Here the Fe:Re in double perovskite set as 1.4:1, because the limited substitution positions in double perovskite and well matched with the overall statistic results from EDXS in Figure S1. If one Re in Re layer was replaced by Fe, the Fe:Re ratio would be 1.4:1. If two Re in Re layers were replaced the Fe:Re ratio would be 2:1. It is challenging to represent the exact experimental substitution ratio within the limited supercell due to the limited primitive cell. Therefore, we set the $\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9/\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Fe}_{1/6}\text{Re}_{5/6}]_{\text{B}_2}\text{O}_6$ interface as a reference model for study of Fe doping.

As shown in Table 1, the formation of the interface induces notable structural distortions, characterised by deviations in both bond lengths and bond angles from those of an ideal transition metal–oxygen octahedron. In particular, the Fe–O–Re bond angle decreases from 180° to 166° , accompanied by a slight contraction of the Fe–O bond and an elongation of the Re–O bond. These modifications collectively weaken the super exchange interaction across the interface. In perovskite oxides, the emergence of ferrimagnetic coupling is generally associated with two primary mechanisms: orbital hybridisation and double exchange interactions^{4, 5}. Double exchange is a magnetic interaction mechanism that occurs in mixed-valence transition metal systems, where oxygen mediates electron hopping, thereby enhancing ferromagnetic (FM) coupling. In this context, an increase in the contribution of O 2p orbitals near the Fermi level would typically strengthen FM interactions. After structural and spin relaxation, the average atomic spin of Fe is $3.3 \mu_{\text{B}}$, whereas the average atomic spin of Re is $0.69 \mu_{\text{B}}$. The spin change occurs primarily in the Fe layer, whose valence remains relatively stable, as indicated

by the electron energy loss spectroscopy (EELS) in Figure 3a. Therefore, the contribution of double exchange due to mixed valence is minimal in driving the FM coupling transition.

Orbital hybridisation, in contrast, can induce a transition from antiferromagnetic (AFM) to ferromagnetic (FM) coupling by mixing transition metal orbitals, forming new hybridised states that redistribute electron density. The significant overlap in the density of states (DOS) between Fe 3*d* and Re 5*d* orbitals provides direct evidence for this hybridisation effect. At the interface, structural distortions modify orbital overlaps, resulting in hybridisation-dominated interactions⁶. In complex perovskite interface systems, super exchange and hybridisation coexist and collectively determine the final magnetic coupling. In the $\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9/\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Re}]_{\text{B}_2}\text{O}_6$ interface, hybridisation between Fe 3*d* and Re 5*d* orbitals plays a dominant role in driving the observed FM coupling. However, in the $\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9/\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Fe}_{1/6}\text{Re}_{5/6}]_{\text{B}_2}\text{O}_6$ interface, the effects of hybridisation are partially counteracted by an enhanced super exchange interaction, thus reducing the extent of FM coupling.

To further elucidate the mechanisms underlying the observed interfacial magnetic transition, we systematically investigated the lattice structure and local electronic configurations. Specifically, we analysed the local density of states (LDOS) distributions for a range of relevant phases: the ideal 1:1 B-site ordered double perovskite $\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Re}]_{\text{B}_2}\text{O}_6$, a partially Fe-substituted double perovskite $\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Fe}_{1/6}\text{Re}_{5/6}]_{\text{B}_2}\text{O}_6$, a triple perovskite $\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9$, and interface model of $\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9/\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Re}]_{\text{B}_2}\text{O}_6$ with a Fe:Re ratio of 1:1. Through the analysis of the coupling between transition metal *d* orbitals and oxygen 2*p* orbitals, we traced the evolution of super exchange interactions mediated by oxygen. As shown in Figure S9a-b, S9e-f, and S9i-j, in the three bulk materials, the Fe–O and Re–O hybridisations are primarily located

within the valence band below the Fermi level, signifying stable oxygen–transition metal bonding environments. In Figure S9d, S9h and S9l, the majority spin states of Fe and Re are distributed in opposite spin channels with minimal overlap, suggesting that adjacent Fe and Re layers adopt an antiferromagnetic alignment. This magnetic configuration is further supported by the linear Fe–O–Re bond angle of approximately 180° , as listed in Table 1, which is consistent with the conditions favouring strong antiferromagnetic super exchange according to the Goodenough-Kanamori-Anderson (GKA) rule ⁷⁻⁹.

The associated error and the electron-electron correlation factor. To further assess the magnetic ground state at the interface, we constructed an enlarged 240-atom supercell and explicitly compared antiferromagnetic (AFM) and ferromagnetic (FM) interfacial coupling configurations. The calculated total energies and average atomic formation energies consistently indicate that the FM-coupled interface is energetically favoured over the AFM configuration (Table S2). In particular, the FM interfacial state exhibits a lower total energy and a more negative average formation energy per atom, demonstrating enhanced thermodynamic stability. The persistence of this energy preference upon increasing the model size to 240 atoms (cf. Figure S10) confirms that the stabilisation of the FM interfacial coupling is not a finite-size artefact, but instead reflects the intrinsic magnetic ground state of the system.

Since the ferromagnetic interactions at the interface are significantly weaker than their antiferromagnetic counterparts in the bulk region, compared to the Fe doped double perovskite $\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Fe}_{1/6}\text{Re}_{5/6}]_{\text{B}_2}\text{O}_6$, the FM exchange parameter in double perovskite with an ideal 1:1 ratio (Table S4) is stronger. Here, the small values are attributed to Fe doping on the double perovskite side, indicating that the doping will induce more complicated situations. In this work, we would like to emphasise the existence of the novel interface with different B-site ordering

periodicity. We rearrange the model of the interface formed by $\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9$ and $\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Fe}_{1/6}\text{Re}_{5/6}]_{\text{B}_2}\text{O}_6$. Although the limited supercell size constrains the quantitative accuracy of the DFT model for predicting the magnetic behaviour of doping interface cases, they still provide important insights into the potential magnetic behaviour in this novel interface.

As for the small value of the FM exchange parameter in Table S5, we also examined tests of the Coulomb repulsion U value, a term to describe the electron-electron correlation. As mentioned in the manuscript, the U value was set according to the previous research about triple perovskite^{10, 11} with $U_{\text{eff}} = 3.2$ eV for Fe and $U_{\text{eff}} = 1$ eV for Re. We conducted further tests of U value from 3 eV, 3.5 eV, and 4 eV for Fe, and summarised the results as below. Although the electron-electron correlation factor will cause a variation in the exchange parameter value, it is hard to change the symbol for the orientation of the spin arrangement.

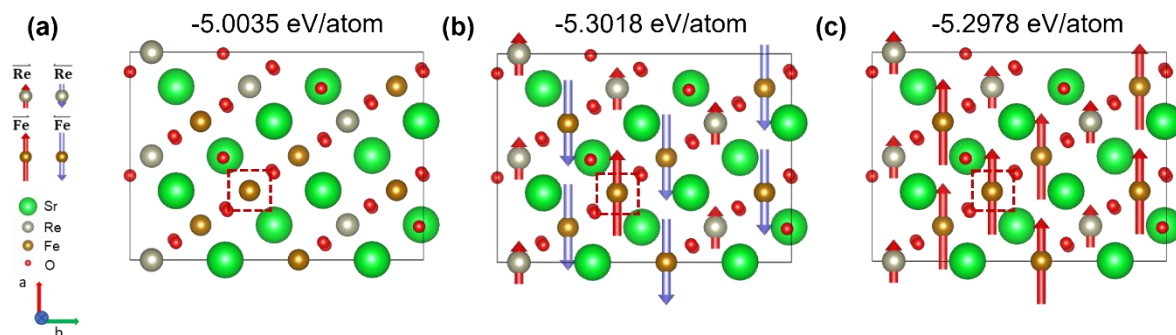


Figure S6. Structural models and calculated average formation energies per atom for the Fe-substituted double perovskite $\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Fe}_{1/6}\text{Re}_{5/6}]_{\text{B}_2}\text{O}_6$, corresponding to an Fe:Re ratio of 1.4:1, in the (a) non-magnetic (NM), (b) antiferromagnetic (AFM), and (c) ferromagnetic (FM) configurations. The substituted Fe atom occupying a nominal Re B_2 site is indicated by a red dashed rectangle. Sr, Re, Fe, and O atoms are shown in green, silver, gold, and red, respectively. Spin-down and spin-up magnetic moments are represented by violet and red arrows, respectively.

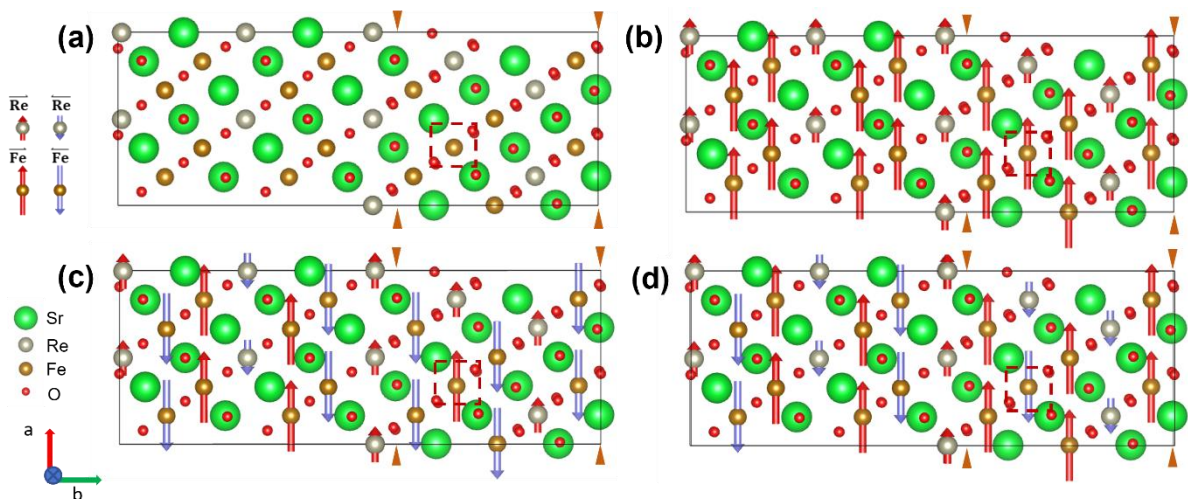


Figure S7. Magnetic configurations considered for the interface between the 1:2 B-site-ordered triple perovskite $\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9$ and the Fe-substituted 1:1 B-site-ordered double perovskite $\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Fe}_{1/6}\text{Re}_{5/6}]_{\text{B}_2}\text{O}_6$. (a) non-magnetic (NM), (b) ferromagnetic (FM) interface coupling based on the $P\bar{3}m1$ $\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9$ and $I4/m$ mixed atomic occupation $\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Fe}_{1/6}\text{Re}_{5/6}]_{\text{B}_2}\text{O}_6$, (c) antiferromagnetic bulk regions with antiferromagnetic interfacial coupling (AFM-int), and (d) antiferromagnetic bulk regions with ferromagnetic interfacial coupling (FM-int). The substituted Fe atom occupying a nominal Re B_2 site on the double-perovskite side is indicated by a red dashed rectangle. Each interface is marked by a pair of orange triangles; two interfaces are present in the periodic supercell. Sr, Re, Fe, and O atoms are shown in green, silver, gold, and red, respectively. Spin-down and spin-up magnetic moments are represented by violet and red arrows, respectively.

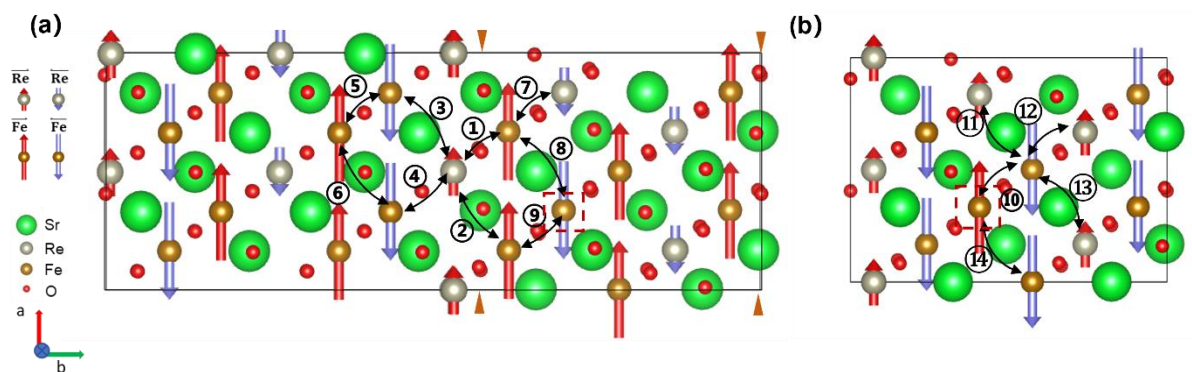


Figure S8. Structure models used to define the transition-metal pairs for the four-state exchange-coupling calculations reported in Table S4. (a) Fe-substituted $\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9/\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Fe}_{1/6}\text{Re}_{5/6}]_{\text{B}_2}\text{O}_6$ interface model, showing exchange pairs ① to ⑨ across the interface and within the adjacent double- and triple-perovskite regions. (b) Bulk Fe-substituted $\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Fe}_{1/6}\text{Re}_{5/6}]_{\text{B}_2}\text{O}_6$ model, showing exchange pairs ⑩ to ⑭. The interface is marked by a pair of orange triangles, and there are two interfaces in (a) due to the periodicity of the model. Atomic structure in (a-b) with Sr in green, Re in silver, Fe in golden and O in red, and spin down and spin up magnetic moments are noted as violet and red arrows, respectively.

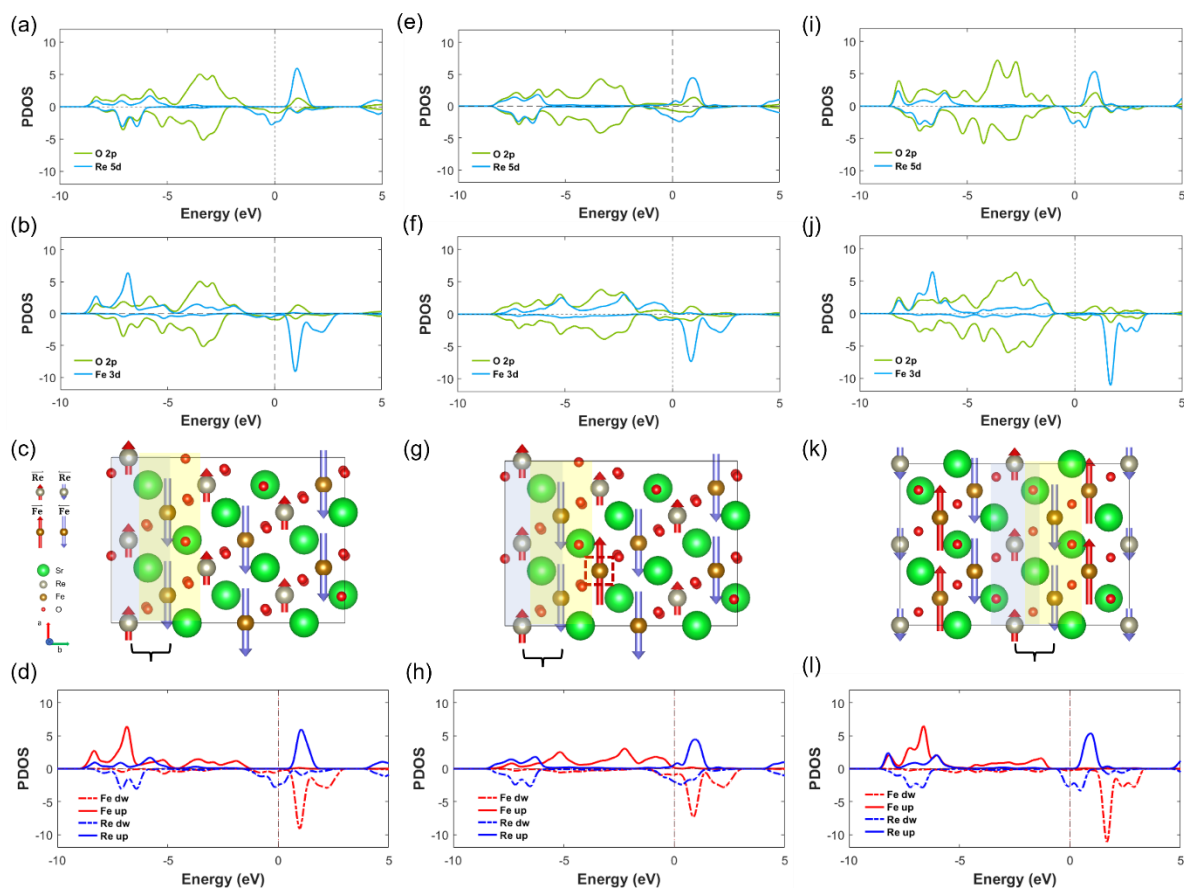


Figure S9. Projected density of states (PDOS) and corresponding atomic structures of the double and triple perovskites. (a) PDOS of the Re 5d and O 2p orbitals in the bulk double perovskite $\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Re}]_{\text{B}_2}\text{O}_6$ corresponding to the blue-shaded region in (c). (b) PDOS of the Fe 3d and O 2p orbitals in same structure, corresponding to the yellow-shaded region in (c). (c) Atomic model of bulk double perovskite $\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Re}]_{\text{B}_2}\text{O}_6$. (d) Comparison of the Re 5d and Fe 3d PDOS for the bulk double perovskite $\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Re}]_{\text{B}_2}\text{O}_6$ in (c), as indicated by the bracket. (e) PDOS of the Re 5d and O 2p orbitals in Fe-doped double perovskite $\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Fe}_{1/6}\text{Re}_{5/6}]_{\text{B}_2}\text{O}_6$, corresponding to the blue-shaded region in (g). (f) PDOS of the Fe 3d and O 2p orbitals in same Fe-doped structure of the double perovskite bulk, corresponding to the yellow-shaded region in (g). (g) Atomic model of the Fe-doped double perovskite $\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Fe}_{1/6}\text{Re}_{5/6}]_{\text{B}_2}\text{O}_6$, with the doped Fe atom highlighted by a dashed rectangle. (h) Comparison of Re 5d and Fe 3d PDOS for the Fe-doped double perovskite shown in (g), as

indicated by the bracket. (i) PDOS of Re $5d$ and O $2p$ orbitals in bulk triple perovskite $\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9$, corresponding to the blue-shaded region in (k). (j) PDOS of Fe $3d$ and O $2p$ orbitals in the same structure, corresponding to the yellow-shaded region in (k). (k) Atomic model of the bulk triple perovskite $\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9$, with the Fe site indicated by a dashed rectangle. (l) Comparison of Re $5d$ orbital and Fe $3d$ PDOS for the triple perovskite shown in (k), as indicated by the bracket. In panels (c), (g), and (k), Sr atoms are shown in green, Re in silver, Fe in gold, and O in red. Spin-down and spin-up magnetic moments are represented by violet and red arrows, respectively.

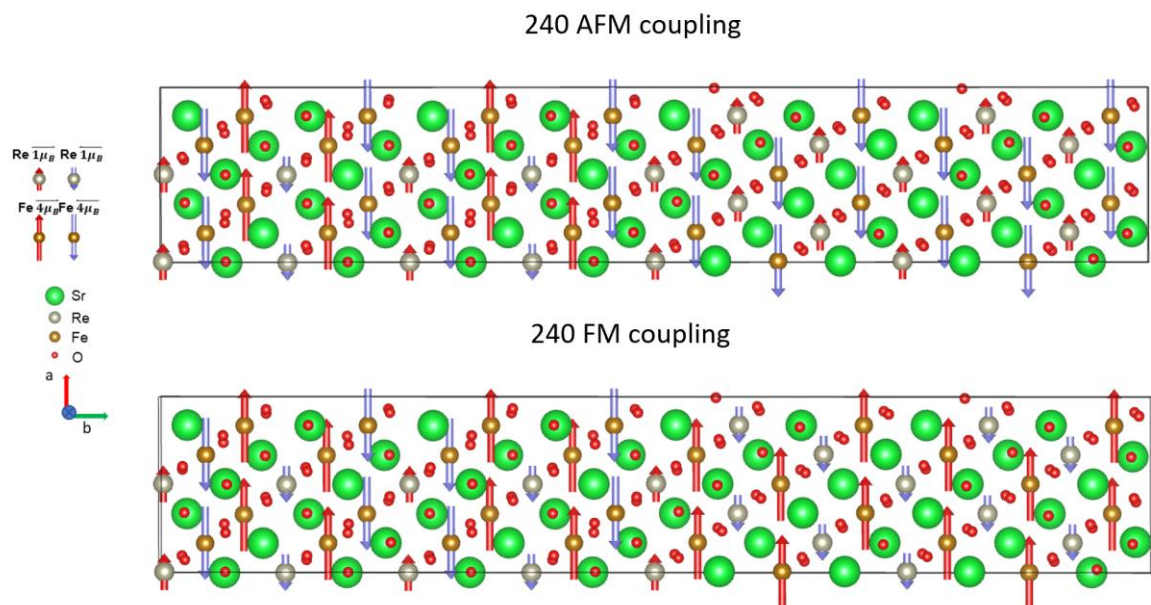


Figure S10. 240-atom supercell and explicitly compared antiferromagnetic and ferromagnetic interfacial coupling configurations of $\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9/\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Re}]_{\text{B}_2}\text{O}_6$ interface.

Table S1. Formation energy of $\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9/\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Re}]_{\text{B}_2}\text{O}_6$ interface with different magnetic coupling (eV/atom) in a 120 atoms mode case.

Type	PM	FM	AFM-int	FM-int
$\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9 (P\bar{3}m1)/$ $\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Re}]_{\text{B}_2}\text{O}_6 (I4/m)$	-4.9952	-5.2058	-5.2189	-5.2239

Table S2. Formation energy of $\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9/\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Re}]_{\text{B}_2}\text{O}_6$ interface with different magnetic coupling (eV/atom) in a 240 atoms mode case.

Type	PM	FM	AFM-int	FM-int
$\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9 (P\bar{3}m1)/$ $\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Re}]_{\text{B}_2}\text{O}_6 (I4/m)$	-4.9952	-5.2058	-5.9748	-5.9777

Table S3. Formation energy of $\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9/\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Fe}_{1/6}\text{Re}_{5/6}]_{\text{B}_2}\text{O}_6$ interface with different magnetic ordering. The unit is eV/atom.

Type	PM	FM	AFM-int	FM-int
$\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9(P\bar{3}m1)/$ $\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Fe}_{1/6}\text{Re}_{5/6}]_{\text{B}_2}\text{O}_6 (I4/m)$	-4.9482	-5.2891	-5.2907	-5.2942

Table S4. Exchange parameters (J) (in eV) for the $\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9$ / $\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Fe}_{1/6}\text{Re}_{5/6}]_{\text{B}_2}\text{O}_6$ interface and the corresponding ordered structure $\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Fe}_{1/6}\text{Re}_{5/6}]_{\text{B}_2}\text{O}_6$.

Structure	Angle	Pair	Atoms	J (eV)	Coupling type
$\text{Sr}_3[\text{Fe}]_{\text{B}_1}[\text{Fe}]_{\text{B}_2}[\text{Re}]_{\text{B}_3}\text{O}_9$ / $\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Fe}_{1/6}\text{Re}_{5/6}]_{\text{B}_2}\text{O}_6$ interface	172	1	Fe - Re	-0.0038	FM
	168	2	Fe - Re	-0.0089	FM
	169	3	Fe - Re	0.0237	AFM
	171	4	Fe - Re	0.0155	AFM
	172	5	Fe - Fe	0.0044	AFM
	167	6	Fe - Fe	0.0045	AFM
	166	7	Fe - Re	0.0112	AFM
	168	8	Fe - Fe	0.0123	AFM
	166	9	Fe - Fe	0.0280	AFM
$\text{Sr}_2[\text{Fe}]_{\text{B}_1}[\text{Fe}_{1/6}\text{Re}_{5/6}]_{\text{B}_2}\text{O}_6$	174	10	Fe - Re	0.0103	AFM
	172	11	Fe - Re	0.0330	AFM
	173	12	Fe - Re	0.0277	AFM
	172	13	Fe - Re	0.0427	AFM
	166	14	Fe - Fe	0.0281	AFM

Table S5. Coulomb repulsion U value test of magnetic exchange interactions for a four-states method.

Pair number	U=3	U=3.5	U=4
① Fe-Re	-0.00895	-0.00703	-0.00432
② Fe-Re	-0.01788	-0.00918	-0.00937
③ Fe-Re	0.02145	0.01343	0.01238
④ Fe-Re	0.01016	0.02064	0.01084

Table S6. EDXS elemental map corrected unit-cell Fe:Re ratio

Unit cell	Raw range / px	Width / px	Corrected Fe:Re ratio
1	25-78	53	1.98 ± 0.05
2	82-136	54	1.92 ± 0.05
3	139-193	54	1.95 ± 0.05
4	197-250	53	2.16 ± 0.06
5	265-289	24	1.43 ± 0.06
6	305-329	24	1.54 ± 0.06
7	339-363	24	1.68 ± 0.07
8	376-400	24	1.63 ± 0.07
9	414-438	24	1.72 ± 0.07

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