Strain-attenuated spin frustration in double perovskite $\text{Sr}_2\text{FeOsO}_6$

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Using density functional theory together with Monte Carlo simulations, we demonstrate that epitaxial strain, both compressive and tensile, attenuates the spin frustration of double perovskite $\text{Sr}_2\text{FeOsO}_6$ to significantly enhance the critical temperature to 310 K, enabling room-temperature applications. We discover under tensile strain a tetragonal ($I4/m$)-to-monoclinic ($P2_1/n$) structural transition concomitant with an antiferromagnetic-to-ferrimagnetic transition. Furthermore, an indirect-to-direct band gap transition is observed with the valence and conduction states localized on different transition metal sublattices, opening a route to efficient electron-hole separation upon photoexcitation.

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I. INTRODUCTION

Transition metal double perovskite oxides of the general formula $A_2BB'O_6$, with A being an alkali, alkaline earth, or rare earth atom and B/B' being a transition metal atom, continue to attract attention because of versatile magnetic properties such as high-temperature ferrimagnetism [1], half metallicity [2–4], insulating ferro- and ferrimagnetism [5–7], large magnetoresistance [8], and large coercivity and exchange bias [9]. Particularly, strongly localized $3d$ valence orbitals at the B site and more electron-itinerant $4d/5d$ valence orbitals at the B' site favor high-temperature magnetism as required for many spintronics applications.

Several $3d$ - $4d$ and $3d$ - $5d$ compounds with alkaline earth or rare earth atoms at the A site have been synthesized experimentally using various techniques [10–18]. Among the $3d$ - $5d$ compounds, $\text{Ca}_2\text{FeOsO}_6$ is monoclinic ($P2_1/n$) [17] and $\text{Sr}_2\text{FeOsO}_6$ tetragonal ($I4/m$) [15]. $\text{Sr}_2\text{CrOsO}_6$ (highest critical temperature of 725 K among all perovskite oxides) and $\text{Sr}_2\text{CoOsO}_6$ undergo structural phase transitions from rhombohedral ($R\bar{3}$; at 300 K) to cubic ($Fm\bar{3}m$; at 540 K) [16] and monoclinic ($I2/m$; below 108 K) to tetragonal ($I4/m$; above 108 K) [13], respectively. Magnetic susceptibility and specific heat measurements show that $\text{Ca}_2\text{FeOsO}_6$ is an insulating ferrimagnet with a high critical temperature of 320 K [17], while $\text{Sr}_2\text{FeOsO}_6$ undergoes an antiferromagnetic (AFM)-to-AFM transition at 67 K and has a critical temperature of 140 K [15]. According to neutron diffraction experiments, the two AFM phases of $\text{Sr}_2\text{FeOsO}_6$ differ from one another in the magnetic ordering along the c axis but not in the ab plane [19–21]. Along the c axis, there is AFM coupling between ferromagnetically coupled double layers in the low-temperature AFM phase and ferromagnetic (FM) coupling in the high-temperature AFM phase (C-AFM phase). In the C-AFM phase, FM out-of-plane superexchange arises from the 180° Fe-O-Os ($3d^5$ - $2p^6$ - $5d^3$) bond angle along the c axis

and AFM in-plane superexchange from the $\sim 165^\circ$ Fe-O-Os bond angle in the ab plane.

The low critical temperature (140 K) of $\text{Sr}_2\text{FeOsO}_6$ can be slightly enhanced by the substitution of smaller cations at the A site due to the generation of small structural distortions (magnetostructural coupling) [22]. For example, when half of the Sr atoms are replaced with Ca atoms the structure becomes monoclinic and the ordering ferrimagnetic (FiM) with a critical temperature of 210 K. On the other hand, an AFM-to-FiM transition driven by hydrostatic pressure has been reported and attributed to increasingly different cubic crystal field splittings at the Fe and Os sites, which precludes FM coupling of the e_g electrons along the c axis [23]. As a result, the AFM coupling of the t_{2g} electrons becomes dominant in both the in-plane and out-of-plane directions, leading to FiM ordering, however, only as long as the hydrostatic pressure is maintained.

A route to permanent FiM ordering and a significantly elevated critical temperature could be the application of epitaxial strain, because the observed low values recently have been attributed to spin frustration [24]. Generally, experimental progress in achieving high-quality thin films makes it possible to employ epitaxial strain for controlling the material properties. Specifically, experiments indicate that tensile strain (reduction of the c/a ratio) alters the 180° out-of-plane superexchange angle of $\text{Sr}_2\text{FeOsO}_6$ [23]. In this paper, we therefore use first-principles calculations to show that epitaxial strain is an effective tool to tune the magnetic properties of $3d$ - $5d$ compounds. Particularly, we consider $\text{Sr}_2\text{FeOsO}_6$, as this compound can be grown on various substrates [25] and the $3d$ (Fe) and $5d$ (Os) atoms form a checkerboard lattice in each layer. Monte Carlo simulations are used to show that epitaxial strain, both compressive and tensile, attenuates the spin frustration of $\text{Sr}_2\text{FeOsO}_6$ and, hence, significantly enhances the critical temperature of the FiM phase.

II. COMPUTATIONAL DETAILS

We employ spin-polarized density functional theory (DFT) and the generalized gradient approximation of Perdew-Burke-

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FIG. 1. Supercells with $a^-a^-c^+$ (left; $P2_1/n$) and $a^0a^0c^-$ (right; $I4/m$) tilt patterns of the oxygen octahedra.

Ernzerhof for the exchange correlation functional, using the QUANTUM ESPRESSO code [26]. We account for the electron correlation effects in the $3d$ and $5d$ transition metal orbitals by the DFT + U approach [27]. For the on-site interaction parameter we adopt the established literature values of 4 eV (Fe) and 2 eV (Os) [21]. Despite the presence of heavy elements, spin-orbit coupling turns out to have no impact on the electronic structure of $\text{Sr}_2\text{FeOsO}_6$ without strain (in agreement with Refs. [7,17,21]), except for a slight increase of the atomic magnetic moments without affecting the total magnetic moment, and therefore is neglected in calculations under strain to reduce the computational costs. Test calculations both without strain (C-AFM phase) and under 4% tensile strain (FiM phase) show that the spin-orbit coupling does not alter the crystal symmetry. A plane-wave cutoff of 90 Ry is used in the wave-function expansion and a 640 Ry cutoff for the augmentation charge. The Brillouin zone is integrated on a $8 \times 8 \times 6$ Monkhorst-Pack k mesh in the structure optimization and on a denser $14 \times 14 \times 12$ Monkhorst-Pack k mesh for calculating the density of states (DOS). All structures are optimized until the Hellmann-Feynman forces stay below $0.26 \text{ meV/\AA}$.

Starting from the cubic structure of $\text{Sr}_2\text{FeOsO}_6$, we construct 20-atom $\sqrt{2} \times \sqrt{2} \times 2$ tetragonal supercells to enable magnetic ordering. By rotating the oxygen octahedra we reduce the symmetry to achieve antipolar $I4/m$ and $P2_1/n$ space groups (see Fig. 1), which are compatible with cubic substrates [28,29]. Starting from the pseudocubic lattice parameter of $3.92 \text{ \AA}$ [30], we mimic epitaxial strain ϵ by varying the in-plane lattice constant as $a(\epsilon) = \sqrt{2}(1 + \epsilon) \times 3.92 \text{ \AA}$ (limited to values that realistically can be achieved by a substrate). The out-of-plane lattice vector then is optimized (length and direction) for each value of ϵ simultaneously with the atomic positions, corresponding to (001) epitaxial growth. This procedure is executed for the magnetic orderings shown in Fig. 2, both for the $I4/m$ and $P2_1/n$ symmetries to capture the lattice effect on the relative stabilities.

III. RESULTS AND DISCUSSION

The obtained energies are depicted in Fig. 3 with reference to the global minimum ($P2_1/n$ symmetry at 2% strain). We

FIG. 2. Considered magnetic orderings (left) and exchange paths connecting the Fe and Os atoms (right; arrows represent the magnetic moments in the C-AFM phase).

find that the magnetic ground state changes from C-AFM to FiM ordering at 0.8% tensile strain, which increases the total magnetic moment from 0 to $2\mu_B$ per formula unit. Simultaneously, the compound undergoes a structural transition from $I4/m$ to $P2_1/n$ symmetry. Constrained to $I4/m$ symmetry, we observe a transition from C-AFM to FiM ordering at 2.2% tensile strain during that the Fe-Os distance along the c axis shrinks to $3.97 \text{ \AA}$, in agreement with the experimental behavior under pressure along the c axis [23]. Although the Fe-O-Os bond angle remains 180° along the c axis (favoring FM double exchange), reduction of the c/a ratio by 5.8% enhances the difference between the crystal field splittings at the Fe and Os sites. This weakens the FM double exchange relative to the AFM superexchange. A transition to AFM coupling along the c axis, while the in-plane coupling remains AFM due to persistent Fe-O-Os buckling, leads to FiM ordering under the $I4/m$ symmetry constraint.

A similar mechanism applies to the magnetic transition accompanying the transition from $I4/m$ to $P2_1/n$ symmetry

FIG. 3. Relative energies of magnetic orderings as functions of epitaxial strain for the $I4/m$ (dashed lines) and $P2_1/n$ (solid lines) symmetries.

TABLE I. Fe and Os magnetic moments (μ_B) for different strains and magnetic orderings.

	E_1	E_2	E_3	E_4	E_5	E_6	E_7	E_8	E_9	E_{10}
-4%	3.93, 1.27	3.85, 1.21	3.85, 1.20	3.94, 1.25	3.85, 1.18	3.85, 1.23	3.85, 1.18	3.85, 1.25	3.85, 1.18	3.85, 1.25
-3%	3.96, 1.29	3.88, 1.23	3.89, 1.22	3.97, 1.38	3.89, 1.19	3.88, 1.26	3.88, 1.20	3.88, 1.27	3.88, 1.20	3.88, 1.27
-2%	3.98, 1.31	3.92, 1.24	3.92, 1.24	3.99, 1.39	3.92, 1.20	3.91, 1.27	3.90, 1.24	3.90, 1.27	3.90, 1.24	3.90, 1.27
-1%	3.99, 1.29	3.93, 1.24	3.95, 1.25	4.00, 1.39	3.95, 1.21	3.94, 1.30	3.93, 1.25	3.93, 1.28	3.93, 1.25	3.93, 1.28
0%	3.98, 1.29	3.94, 1.25	3.93, 1.24	4.00, 1.40	3.97, 1.22	3.96, 1.31	3.95, 1.21	3.95, 1.31	3.95, 1.21	3.95, 1.31
1%	4.00, 1.32	3.97, 1.27	3.96, 1.26	4.03, 1.41	4.00, 1.22	3.98, 1.32	3.96, 1.27	3.97, 1.32	3.96, 1.27	3.97, 1.32
2%	4.00, 1.32	3.97, 1.29	3.96, 1.27	4.03, 1.43	4.00, 1.22	3.98, 1.33	3.97, 1.28	3.99, 1.33	3.98, 1.28	3.99, 1.33
3%	3.99, 1.32	3.98, 1.30	3.96, 1.27	4.03, 1.44	3.99, 1.22	3.96, 1.33	3.96, 1.29	3.99, 1.33	3.96, 1.29	3.99, 1.33
4%	3.96, 1.33	3.97, 1.31	3.95, 1.28	4.02, 1.45	3.97, 1.22	3.94, 1.34	3.94, 1.28	3.97, 1.33	3.95, 1.29	3.97, 1.33
5%	3.93, 1.33	3.96, 1.32	3.92, 1.29	4.00, 1.45	3.95, 1.22	3.91, 1.34	3.91, 1.28	3.94, 1.34	3.91, 1.28	3.94, 1.33

under tensile strain. In the case of partial Ca substitution of Sr in $\text{Sr}_2\text{FeOsO}_6$ it has been argued that the structural transition from tetragonal to monoclinic symmetry is due to the fact that stronger/weaker lattice distortions support AFM/FM coupling [24]. Indeed, the induced chemical pressure drives a significant reduction of the c/a ratio due to rotations of the oxygen octahedra around the $[110]$ axis ($a^-a^-b^+$) [23]. Similarly, we find at 1% tensile strain that the reduction of the c/a ratio is larger for the $P2_1/n$ than the $I4/m$ symmetry by 1.2%. This fact causes rotations of the oxygen octahedra around the $[110]$ axis ($a^-a^-b^+$), i.e., bending of the out-of-plane Fe-O-Os bonds, and therefore out-of-plane AFM coupling. Together with the in-plane AFM coupling this results in FiM ordering.

To understand the evolution of the critical temperature under epitaxial strain, we next extract the magnetic coupling constants by mapping the energies obtained from density functional theory onto a Heisenberg model, $E = -\sum_{ij} J_{ij} \vec{S}_i \cdot \vec{S}_j$, where J_{ij} is the coupling constant between sites i and j , and $\vec{S}_i$ and $\vec{S}_j$ are the spin vectors. It is necessary to include the nearest-neighbor (NN) and next-nearest-neighbor (NNN) exchanges to obtain the critical temperature in agreement with experiment [15]. We consider the coupling constants defined in Fig. 2, i.e., the in-plane NN exchange (J_1), the out-of-plane NN exchange (J_2), the in-plane NNN exchanges along the a axis (J_3) and b axis (J_4), and the two out-of-plane NNN exchanges (J_5, J_6). When we assume that the spin vectors are collinear with magnitude 1 (as the real magnitude later will be taken into account in the Monte Carlo simulations), we can compute the magnetic coupling constants by solving the coupled equations

$$E_1 = E_0 + 8J_1 - 4J_2 + 4J_3 + 4J_4 - 8J_5 - 8J_6 \text{ (A-AFM)},$$

$$E_2 = E_0 - 8J_1 + 4J_2 + 4J_3 + 4J_4 - 8J_5 - 8J_6 \text{ (C-AFM)},$$

$$E_3 = E_0 - 8J_1 - 4J_2 + 4J_3 + 4J_4 + 8J_5 + 8J_6 \text{ (FiM)},$$

$$E_4 = E_0 + 8J_1 + 4J_2 + 4J_3 + 4J_4 + 8J_5 + 8J_6 \text{ (FM)},$$

$$E_5 = E_0 + 4J_3 + 4J_4 + 8J_5 - 8J_6,$$

$$E_6 = E_0 + 4J_3 + 4J_4 - 8J_5 + 8J_6,$$

$$E_7 = E_0 - 4J_2 - 4J_3 + 4J_4,$$

$$E_8 = E_0 + 4J_2 - 4J_3 + 4J_4,$$

$$E_9 = E_0 - 4J_2 + 4J_3 - 4J_4,$$

$$E_{10} = E_0 + 4J_2 + 4J_3 - 4J_4,$$

where E_0 is the lattice energy and E_1 - E_{10} are the energies of the magnetic orderings obtained from density functional theory. The corresponding Fe and Os magnetic moments are summarized in Table I.

According to the results in Fig. 4 and in agreement with Ref. [24], we find without strain that the NN exchange is AFM and approximately four times stronger in the in-plane (J_1) than in the out-of-plane (J_2) direction. J_1 decreases/increases and J_2 increases/decreases under tensile/compressive strain due to the decreasing/increasing c/a ratio and superexchange angle. Despite the AFM NN exchanges, the compound realizes below 0.8% tensile strain C-AFM ordering due to the growing dominance of J_5 and J_6 combined over J_2 . On the other hand, above 0.8% tensile strain ($P2_1/n$ symmetry) J_1 and J_2 exceed all other coupling constants due to favorable superexchange angles. This dominance of J_1 and J_2 reduces the spin frustration and leads to FiM ordering (resembling $\text{Ca}_2\text{FeOsO}_6$ [17]). Strain thus turns out to be an efficient tool for controlling the spin frustration.

To compute the critical temperature of the magnetic ordering for the different strain values we employ classical Monte Carlo simulations [31] for Ising spins in a $12 \times 12 \times 12$ supercell, using 80 000 sweeps for thermalization and 70 000 additional sweeps in the equilibrium. The obtained susceptibilities are shown in Fig. 5 and the resulting phase diagram

FIG. 4. Variation of the magnetic coupling constants under epitaxial strain.

FIG. 5. Susceptibilities of the $I4/m$ (top) and $P2_1/n$ (bottom) phases as functions of the temperature at various epitaxial strains. The peaks indicate the critical temperatures.

is given in Fig. 6. Without strain we find a low T_N close to the experimental value of 140 K, which has been attributed to competing magnetic interactions in Ref. [24]. Under compressive strain J_1 dominates more and more over the other

FIG. 6. Strain-temperature phase diagram obtained from Monte Carlo simulations.

FIG. 7. DOS obtained for the C-AFM phase without strain (top) and the FiM phase at 4% tensile strain (bottom). Dotted vertical lines indicate the valence band maximum.

coupling constants (Fig. 4), which reduces the spin frustration. Thus, T_N increases to 310 K at -4% compressive strain. On the other hand, the Curie temperature (T_C) of the FiM ordering increases to 270 K at 5% tensile strain. This behavior also can be attributed to a reduction of the spin frustration, as under tensile strain J_2 dominates more and more over the other coupling constants (Fig. 4).

According to Fig. 7, the up- and down-spin channels are equal without strain due to the C-AFM ordering. As mentioned earlier, effects of spin-orbit coupling can be neglected (Fig. 8). In the FiM phase the magnetic moments of NN Fe and Os atoms are aligned antiparallel in the in-plane and out-of-plane directions. Therefore, the up- and down-spin channels are not equal and we obtain a net magnetic moment of $2\mu_B$ per formula unit. Throughout the considered range of epitaxial strain the Fe and Os atoms maintain $3+(t_{2g}^3 e_g^2)$ and $5+(t_{2g}^3 e_g^0)$ oxidation states, respectively, with high spin configurations. Due to these oxidation states and the 158° in-plane superexchange angle, we have always AFM ordering in the in-plane directions. Below 0.8% tensile strain we have FM ordering in the out-of-plane direction due to the 180° out-of-plane superexchange angle [32–34], which gives rise to an overall C-AFM ordering. Above 0.8% tensile strain the out-of-plane Fe-O-Os bonds bend

FIG. 8. DOS obtained for the C-AFM phase without strain, taking into account spin-orbit coupling.

significantly, leading to a $\sim 160^\circ$ out-of-plane superexchange angle and, therefore, AFM ordering in the out-of-plane direction, which gives rise to overall FiM ordering with a net magnetic moment of $2\mu_B$ per formula unit. We find that the spin coherence length $\lambda_c = \pi/|k_F^\uparrow - k_F^\downarrow|$ of the FiM phase under 4% tensile strain (2.96 nm) clearly exceeds that of the leading 3d-5d room-temperature spintronics material $\text{Sr}_2\text{FeReO}_6$ (2.16 nm).

As shown in Fig. 9, we obtain a small band gap that further decreases both under compressive and tensile strain. The small band gap and the fact that the transition from $I4/m$ to $P2_1/n$ symmetry is accompanied by an indirect-to-direct band gap transition (Fig. 10) enables efficient absorption of sunlight. Figure 7 shows for the C-AFM phase that the valence band edge is dominated by hybridized Os 5d and O 2p states, whereas the conduction band edge additionally involves Fe d states. For the FiM phase the up-spin channel is characterized by a wide band gap of 2.2 eV and the down-spin channel by a narrow band gap of 0.8 eV. In the down-spin channel (which forms the direct band gap) the valence band edge is dominated by hybridized Os 5d

FIG. 9. Variation of the electronic band gap under epitaxial strain.

FIG. 10. Electronic band structure of the C-AFM phase without strain (top), FiM phase at 1% tensile strain (middle), and FiM phase at 4% tensile strain (bottom). Black/red lines represent the spin-up/spin-down channel.

and O 2p states, whereas the conduction band edge is almost entirely due to Fe 3d states. As a consequence, photoexcitation will lead to a spatial electron-hole separation between the Fe (conduction band minimum) and Os (valence band maximum) sublattices, similar to $\text{Bi}_2\text{FeCrO}_6$ [35], implying that the electron-hole transition matrix element and thus the electron-hole recombination rate are small, which is desirable for photovoltaics. Based on the frequency-dependent complex dielectric function, we obtain for $\text{Sr}_2\text{FeOsO}_6$ an outstanding spectroscopic limited maximum efficiency [36] of 32%,

outperforming even the prototypical perovskite solar cell material MAPbI₃ (MA = methylammonium; 31%).

IV. CONCLUSION

In conclusion, Sr₂FeOsO₆ is found to undergo under epitaxial strain a phase transition from *I4/m* to *P2₁/n* symmetry and from C-AFM to FiM ordering. Magnetic coupling constants extracted from a Heisenberg model indicate decreasing spin frustration under both tensile and compressive strain, and Monte Carlo simulations accordingly demonstrate enhancement of the critical temperature. Specifically, T_N of the C-AFM phase increases to ~ 310 K at -4% compressive strain and T_C of the FiM phase increases to ~ 270 K at 5% tensile strain due to the decreasing spin frustration. Therefore, the competition between magnetic interactions, the prime reason behind the low T_N of the C-AFM phase without strain, can be

controlled by heteroepitaxy. The complex interplay of tensile strain with the spin and orbital degrees of freedom establishes a FiM phase in Sr₂FeOsO₆ and makes the compound a high- T_C *3d-5d* insulator with a large magnetic moment of $2\mu_B$ per formula unit (as Ca₂FeOsO₆), which opens application potentials in spintronics [37–39] and magnetic storage devices [40–42]. The observation of an indirect-to-direct band gap transition under epitaxial strain and electron-hole separation between the Fe and Os sublattices is interesting for photovoltaics.

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