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Unlocking Exceptional Negative Valency and Spin Reconstruction in Non-Collinear Anti-Ferromagnetic Antiperovskite Mn₃NiN Film

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Antiperovskite manganese nitrides have intriguing magnetic and electronic properties that are not well understood. Just as their perovskite oxide counterparts, they are expected to display properties tunable through epitaxial strain engineering, which has barely been explored yet. Here, three notable contributions are made to the understanding and tuning of these fascinating materials, focusing on Mn₃NiN. First, combining X-ray spectroscopy measurements and first-principles calculations, an unusually large negative oxidation state of Ni³⁻is reported. Second, a substantial shift of the antiferromagnetic ordering temperature by 116 K, from 266 to 150 K, is reported by growing Mn₃NiN films on different substrates. This shift is due to the mixed contributions of ferrimagnetic and antiferromagnetic phases. Third, a plasmonic signature with a high optical extinction coefficient in the infrared to visible range is exhibited, tunable by different substrates. The findings suggest that Mn₃NiN has significant potential in antiferromagnetic spintronics, and plasmonics, expanding the scope of new materials for electromagnetic field-controlled plasmonics, piezo spintronics, and multicaloric applications.

1. Introduction

Antiferromagnetic spintronics is a promising innovative field due to the immunity of antiferromagnets to external magnetic fields and for potential applications in memory, terahertz, and low-power devices.^[1] The field of antiferromagnetic spintronics is beginning to focus more on non-collinear antiferromagnetic materials because of the peculiar functionalities induced by their inherent Berry curvature.^[2] Among such materials, antiferromagnets with antiperovskite crystal structure show various emergent phenomena. For instance, manganese-based antiperovskite nitride (Mn₃AN; where A=Ga, Sn, Pt, Ni, Ge) materials, with the inverse occupation of their anionic and cationic positions forming the reversed NMn₆ octahedra as compared to their perovskite counterparts,

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have drawn special attention. This is due to their non-collinear spin structures and unusual physical properties such as the large magneto-volume effect (MVE),^[3] near-zero temperature coefficient of resistivity (NZ-TCR),^[4,5] magnetocaloric effect,^[6] giant magnetoresistance,^[7] superconductivity,^[8] magnetostriction,^[9] spin-glass (SG) states ^[10] piezomagnetic effects,^[11] as well as negative thermal expansion (NTE).^[12]

Being strong spin-lattice coupling systems,^[13] antiperovskite compounds exhibit physical properties closely tied to their magnetic structure. Here, Mn-based antiperovskite compounds with a triangular magnetic lattice display a variety of magnetic structures, including collinear, noncollinear, and even noncoplanar.^[14] Theoretical studies have revealed that the noncollinear $\Gamma_{5\sigma}$ antiferromagnetic (AFM) structure was a key factor for the large MVE in antiperovskite compounds.^[13] So far, efforts have been made on antiperovskite Mn₃XN (X=Cu, Zn, etc.) compounds for tuning the properties of the $\Gamma_{5\,g}$ AFM phase, $^{[15]}$ especially the NZ-TCR caused by strong spin-lattice coupling of the $\Gamma_{5\sigma}$ AFM phase.^[16,13] Also, a non-collinear antiferromagnetic structure has been proposed from neutron scattering studies both for strained and unstrained Mn₃NiN within the temperature range 180 K < T < 266 K, where the magnetic moments rotate in the (111) plane.^[17] Moreover, transition metals predominantly exhibit positive oxidation states due to their inherent tendency to donate electrons. However, the realization of negative oxidation states in antiperovskite systems presents a paradigm shift, offering novel insights into the electronic structure and chemical behavior of transition metals within these unique lattice frameworks. Additionally, the negative oxidation states observed in metals in other systems, shown in materials such as CsAu,^[18] Na-Au,^[19] Ba-Pt,^[20] Zn₂M₄,^[21] and SrSnO₃,^[22] have garnered significant interest because of the potential to reveal novel physics. Recently, E. Triana-Ramírez et. al theoretically proposed for the first time an anionic valence state of nickel metal in Mn₃NiN.^[23] The comprehensive experimental realization as well as theoretical validation of the anionic valence state of metal (Ni), straininterface effects on magnetization, especially spin reversal, near zero optical dielectric constant, and tunable optical conductivity within the framework of spin-orbital manipulation in strained antiperovskite Mn₃NiN are still lacking and need to be probed. The detailed element-specific microscopic magnetization study around Mn and Ni, incorporating XMCD, may reveal the local magnetic (spin) correlations with distinct strains. Furthermore, theoretical calculations may further validate the experimental results, confirming the spin-charge-orbital-lattice intimacy in antiperovskites.

In this article, we investigate the manipulation of non-collinear antiferromagnetic structure, the significant shift of the Néel temperature (T_N), and the existence of an unusual negative anionic state of transition metal (Ni). We also examine the optical intraband transitions, tunable optical conductivity, and high extinction coefficient in Mn₃NiN films. XMCD measurements confirm the non-collinear spin reconstruction at different Mn lattice sites, correlating with noncollinear $\Gamma_{5\,g}$ and $\Gamma_{4\,g}$ magnetic interactions. The first principles theory confirms the claim of having a negative valency of Ni-based on Bader charges and illustrates the intimacy of structure and magnetic parameters. Our observations on structural, magnetic, optical, and transport functionalities confirm the possible magnetic-electronic-structural-optical

coupling due to geometrically frustrated spin orientation with the lattice as well as exchange interactions and the emergence of $\Gamma_{5\,g}$ and $\Gamma_{4\,g}$ phases. This study presents a unique pathway to correlate the magnetic, electronic, structural, and optical coupling through distinct substrate-induced strain in Mn₃NiN single-layer thin films.

2. Results and Discussion

2.1. Growth, Composition, and Structure

For this study, 35, and 45 nm thick $Mn_3 NiN$ (a = 3.880 Å) singlelayer thin films were grown on single crystalline LaAlO₂ (001) $(a = 3.790 \text{ Å}), (La_{0.3}Sr_{0.7})(Al_{0.65}Ta_{0.35})O_3 (LSAT) (001) (a = 3.868)$ Å), SrTiO₃ (001) (a = 3.905 Å), and MgO (001) (a = 4.212 Å) substratesby using a DC sputtering system (PLASSYS-France) (details in Experimental Section). Unstrained Mn₃NiN generally shows a cubic structure with space group, *pm-3 m*, a = b = c =3.880 Å, $\alpha = \beta = \gamma = 90^{\circ}$ and coordinates of Mn (0, 0.5, 0.5), Ni (0, 0, 0), and N (0.5, 0.5, 0.5).^[24] Here, Figure S1 (Supporting Information) depicts a schematic of a typical crystal structure of Mn₃NiN under strain and representing atomic positions in a unit cell. In this structure, N is positioned at the center, forming NMn₆ octahedra (similar to BO₆ octahedra for ABO₃ perovskites) with six neighboring Mn atoms, while Ni atoms are placed at the corner of the unit cell. This inverse pattern (with respect to perovskites) of NMn₆ octahedra changes the atomic position and occupancy, which produces the corner-sharing triangular geometrical frustration.^[15] To obtain a comprehensive picture of the crystal structure of the films, X-ray diffraction (XRD) is performed on Mn₃NiN films (details in Experimental Section). The X-ray reflectivity (Figure S2a,b, Supporting Information) exhibits the Kiessig fringes, indicating smooth layer structure and welldefined interfaces between the $\rm Mn_3NiN$ layer and substrates. The thickness of the sample was \approx 30–35 nm. The XRD 2 θ -w scans around (002)-reflections of the Mn₃NiN films grown on various substrates show the film peak around the Bragg peaks of the substrate, revealing the epitaxial quality of all Mn₃NiN films (Figure 1a). The out-of-plane lattice parameter (c) of the Mn₃NiN film grown on the LAO substrate is enhanced (c = 3.890 Å) compared to the bulk Mn_3NiN (*c* = 3.880 Å, represented by dashed line in Figure 1a), indicates that the in-plane lattice parameter of the film is compressed. In contrast, the *c* lattice parameter of the films on the STO (c = 3.866 Å) and the MgO (c = 3.854 Å) substrate was reduced relative to the bulk value, suggesting inthe plane expansion of the lattice parameter of the film. Moreover, the peak positions for Mn₂NiN on the LSAT substrate overlapped almost perfectly, indicating the same *c* lattice parameter of Mn₃NiN with the substrate (Figure 1b). The representative atomic force microscopy (AFM) (details in Experimental Section) image unveils a smooth particulate-free surface morphology with low roughness (R $_{\rm rms}$ \approx 300 pm), confirming the high quality of the films (Inset Figure 1b; Figure S2e-g, Supporting Information). Additionally, X-ray rocking curve analysis was conducted around the 002-diffraction peak for both Mn₃NiN and the respective substrates (Figure 1c). The full-width-at-half-maximum (FWHM) values for the Mn₂NiN films grown on STO, and MgO substrates are comparable, indicating similar levels of crystallinity among these samples. In contrast, the Mn₃NiN film grown on the LAO

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Figure 1. Structural characterization of 35 nm Mn_3NiN thin film on different substrates. a) $2\theta \cdot \omega$ scan diffraction around the (002)-reflection, demonstrating the single-phase crystallinity of Mn_3NiN films. b) Variation of the out-of-plane lattice parameter *c* calculated from (a) of the films in accordance with the substrate in-plane lattice parameter. The systematic *c* lattice parameter of the Mn_3NiN films enhance on LAO, and LSAT to the reduced on STO and MgO. The atomic force microscopy image on LSAT substrates confirms no secondary phases and exhibits a smooth surface morphology with roughness $\approx 600 \text{ pm}$. c) Rocking curves about the 002-diffraction conditions of the Mn3NiN on films and LAO, STO, and MgO substrate. d) The XRD in-plane φ scans of Mn_3NiN films grown on LAO (top), STO (middle), and MgO (bottom) around the (103) reflection indicate that all Mn_3NiN films are epitaxially grown on the substrates. e) The RBS spectrum (black line) of Mn_3NiN film grown on a MgO Substrate. The backscattered ion yield is plotted as a function of energy. The simulated fit (red line) indicates that the film composition matches the expected Mn:3, Ni:1, N:1, and stoichiometry.

substrate exhibits a slightly larger FWHM, suggesting a reduction in crystallinity, likely due to a large lattice mismatch between the film and the substrate. Further, the in-plane XRD φ scan confirms that all Mn₂NiN films are epitaxially grown on the substrates (Figure 1d). The scan reveals four peaks evenly separated by 90° intervals, indicating a distinct four-fold symmetry. This result suggests an in-plane "cube-on-cube" epitaxial relationship between the film and the substrate. In addition to confirming the epitaxial growth of the films, the observation of sharp and intense peaks signifies the good crystallinity of the synthesized Mn₃NiN films on the substrates. The stoichiometry of the Mn₃NiN film was determined using Rutherford Backscattering Spectroscopy (RBS) (Figure 1e; Figure S3 and Notes S1-S2, Supporting Information, details in Method), where peak positions along the energy axis correspond to different elements based on their atomic numbers. Higher energy peaks indicate heavier elements like Mn and Ni, while lower energy peaks are associated with lighter elements such as nitrogen (N). The areas under these peaks are proportional to the atomic concentrations of each element. A comparison of the relative peak areas of Mn, Ni, and N, aligned with

a best-fit model ($R^2 = 0.999$), confirms the expected stoichiometry, approximately matching the Mn:Ni:N ratio of 3:1:1. After confirming the composition and structure of Mn₃NiN, our focus shifts to investigating the anionic state of the transition metal Ni.

2.2. Anionic State of Transition Metal Ni in Mn₃NiN Films

The high-resolution X-ray photoemission spectroscopy (XPS) core level spectra of Mn 2*p*, Ni 2*p*, and N 1*s* levels of Mn₃NiN films, where the solid curve on the experimental data shows a satisfactory fit with a pseudo-Voigt background (**Figure 2**; Figure S4, Supporting Information; details in Experimental Section). Using the Gaussian-Lorentzian function, the peaks are fitted well for each level. The deconvolution of peaks reveals that each of the spin-split levels ($2p_{1/2}$ and $2p_{3/2}$) exhibits only a single peak, which indicates the presence of a single valence state of Mn (Mn⁺²)^[25] and distinct valency of the Ni (Figure 2a,b; Figure S5, Supporting Information). Therefore, in the antiperovskite structure, Ni $2p_{3/2}$ undergoes a particular negative valence state, which is in

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Figure 2. Elemental composition analysis and anionic nickel vacancy in $Mn_3 NiN$ film on different substrates. Utilizing high-resolution XPS, the following insights were obtained: a) Mn-2p spectra confirm the Mn^{+2} oxidation state of the film. b) Ni-2p spectra confirm the unusual negative valency, i.e., to depict the charge neutrality of the $Mn_3 NiN$ compound the Ni has Ni^{-3} oxidation state of the film (shoulder peak close to the main peak indicated by blue wide arrow). c) N-1s spectra clarify the strong Mn-N hybridization and presence of minor amounts of oxygen in the film.

sharp contrast to the (Ni⁺³),^[26] (Ni⁺²),^[27] (Ni),^[28] in perovskite oxides (Figure S5, Supporting Information). This finding is in close agreement with what was reported for other anti-perovskites such as SrSnO₃ and Sr₃SnO.^[15,29] Additionally, oxygen (O) was detected as a minor contaminant in the sample surface, in addition to Mn, Ni, and N (discussed later). Although it is rare for transition metals to exhibit negative and positive valence states in the Ni and Mn sites, respectively, the charge neutrality of the compound Mn₃NiN depicts it as a Mn₃⁺²Ni⁻³N⁻³ compound, i.e., with Ni in a -3-oxidation state; further confirmed by density functional theory, to be discussed later. The peaks are observed close to 642 eV for Mn- $2p_{3/2}$ and a systematic shift of Mn- $2p_{1/2}$ peak depending on substrate is depicted (Figure 2a). However, a residual peak (\approx 645 eV) is seen close to Mn $2p_{3/2}$ at higher binding energies, which is consistent with the reported results.^[30] Similarly, Ni-2p also shows characteristic Ni- $2p_{3/2}$ peak and Ni- $2p_{1/2}$ peak close to 852 and 870 eV, respectively. Satellite peaks are observed at 855 and 875 eV but an additional peak is observed at 847 eV which suggests the significant shifting toward a lower binding energy relative to Ni metal (852.6 eV), indicating again a negative valence state of Ni (denoted by the wide blue arrow in Figure 2b; Figure S5, Supporting Information). The Ni and N core-levels exhibit minor shifts, which are relatively less pronounced compared to the significant shifts observed in the Mn peaks. These shifts in the Mn XPS spectra directly result from substrate-induced strain, leading to alterations in the local crystal field and bonding environment surrounding Mn atoms. In contrast, the shifts in the Ni and N spectra are more subtle, reflecting their distinct bonding environments within the Mn₃NiN structure and the lesser influence of the substrate-induced strain on these elements. Additionally, the width and asymmetry of the N-1s peak (Figure 2c) can be fitted with two peaks. The peak at 397 eV is attributed to the covalent nature of Ni (Mn) 2p-N 1s hybridization and the shoulder peak at 400 eV is from the residual contaminants like minor oxygen on the surface.^[28] To further confirm the electronic configuration of element in Mn₃NiN films, element-specific X-ray absorption spectroscopy (XAS) performed at the Mn L_{3,2}-edge, Ni L_{3,2}-edge and O K-edge of Mn₃NiN films (Figure 3; Figure S6, Supporting Information and details in Experimental Section). Notably, a shoulder peak at ≈642 eV (marked by an arrow; ≈ 2 eV apart from the main peak) is observed and is attributed to the hybridization between the orbitals of N 2p and Mn 3d and confirming the single valence state (Mn²⁺). The Ni $L_{3,2}$ -edge XAS spectra of Mn₃NiN film do not show such shoulder peak (Figure 3b), as observed in other compounds like Ni_xFe_{4-x}N, indicating that the Ni atom occupies a corner position.^[31] The details of the electronic configuration of the Ni in Mn₃NiN are shown in Note S3 (Supporting Information), which further supports the Ni in a negative valency state to ensure the charge neutrality in the Mn₃NiN film. Furthermore, O K-edge XAS of Mn₃NiN thin films on different substrates, measured alongside the bare STO substrate for comparison, shows featureless spectra in this energy range. A closer view (Inset in Figure S6, Supporting Information) reveals tiny features at the onset energy, corresponding to the transition metal 3d-oxygen 2p hybridization, suggesting minimal surface oxidation. The XAS





Figure 3. Electronic structure of the Mn₃NiN films on different substrates. a) XAS measurement at the Mn $L_{3,2}$ edges shows strong peaks at \approx 640.28 and \approx 652 eV, confirming Mn⁺² valency state of Mn. The shoulder peak close to the main peak (indicated by an arrow) within 2 eV, resolves from N 2p and Mn 3d hybridized orbital state. XAS spectra confirm Mn valency irrespective of substrates. The spectra from different samples have been offset for clarity. Reference data for Mn²⁺ ions in MnO bulk and Mn³⁺ ions in Mn₂O₃ are included for comparison. b) XAS spectra at the Ni $L_{3,2}$ edge exhibit a sharp peak at L_3 edge (\approx 632 eV), suggesting the possibility of an anionic nickel valence state as discussed in the main text. The spectra from different samples have been offset for clarity. Reference data in NiO is included for comparison.

signal, measured via total electron yield (TEY), probes a depth of 5–7 nm, while XPS, being more surface-sensitive, probes \approx 1–1.5 nm. This indicates that the adsorbed oxygen is limited to the topmost surface layer, appearing in XPS but not significantly in XAS.

2.3. Magnetic Analysis and Spin Reconstruction of the $\mathsf{Mn}_3\mathsf{NiN}$ Film

Next, we turn our attention to a peculiar magnetic property of the Mn₃NiN films on various substrates; we have performed SQUID (superconducting quantum interference device) magnetometry and employed synchrotron-based X-ray magnetic circular dichroism (XMCD) techniques (Figure 4 and details in Experimental Section). The temperature-dependent magnetization measured in the film plane along [100] direction and the data reveal a high-temperature paramagnetic to low-temperature antiferromagnetic transition (T_N ; the peak in the M–T curve) and a shift of T_N is observed for the Mn₃NiN film (Figure 4a; Figure S7, Supporting Information). Broadly, the magnetic structure of Mn₃NiN is a combination of two reducible symmetries, antiferromagnetic $\Gamma_{5~g}$ and ferrimagnetic $\Gamma_{4~g}$, depending on the rotation of Mn moments below the T_N.^[32] In Mn₃NiN/STO, Mn₃NiN/LSAT, and Mn₃NiN/LAO films, the magnetization curve suggests that the Mn₃NiN also exhibits predominantly antiferromagnetic behavior due to Mn atom's antiferromagnetic orientation ($\Gamma_{5 g}$) compared to the ferrimagnetic orientation ($\Gamma_{4 g}$) close to T_N , confirmed by our theoretical simulation (discussed later), similar to the earlier report.^[26,33] A distinct behavior is observed in Mn₃NiN/MgO, which shows a well-defined antiferromagnetic transition ≈ 150 K, marked as T_N. Upon further cooling, the magnetic moment begins to increase below 120 K, as highlighted in the figure by T_{com}

(stands for compensation temperature), where an arrangement of Mn spins with unequal moments and opposite orientations leads to partial cancellation of the magnetic moments, resulting in a transition to a ferrimagnetic state with a Γ_4 _g configuration below 120 K. The resultant T_N is well align with Yuantuan et al.^[34] Moreover, the reduced T_N was observed in comparison to bulk Mn_3NiN ($T_N = 266$ K) (Figure S7, Supporting Information) as well as the findings of Boldrin, David, et al.^[24] may arise from several factors, including finite-size effects, substrate-induced strain or strain relaxation, interface quality between the film and substrate, and variations in growth conditions relative to those reported in other studies.^[35–37] Notably, the Mn₂NiN/LSAT film exhibits an unusually broadened magnetization profile with temperature, despite being unstrained (Figure 4a). This distinct magnetization behavior observed in Mn₃NiN films on LSAT, as compared to films on other substrates, may stem from finite-size effects and interface quality. Further investigation is required to fully understand the underlying mechanisms contributing to this unique magnetization profile.^[26,38,39] Furthermore, magnetization as a function of the magnetic field (M-H curve) has been recorded at 10 K in the film plane along a [100] direction (Figure 4b; Figure S8, Supporting Information, details in Experimental Section). The M-H curve reveals a two-step switching process under an applied magnetic field. Initially, some Mn spins align along the field direction, while others remain misaligned. This switching sequence is subtle due to the strong antiferromagnetic interlayer coupling between Mn spins, which may lead to varying switching behaviors depending on the Mn spin structure. Although the samples are antiferromagnetic below the T_N, they all exhibit hysteresis in the M-H curves at 10 K, with no saturation magnetization observed even up to high magnetic fields (≈ 4 T). In particular, the M–H curve for Mn₃NiN/MgO indicates a reduction in the two-step

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Figure 4. Magnetic structure and spin reorientation of the Mn_3 NiN films on different substrates. a) M-T curves measured during warm up the samples at 0.05T along in-plane directions of the samples after zero field cooled the sample. The curve is shown after subtracting the diamagnetic contribution from the substrates closely depicts the antiferromagnetic nature below T_N , indicated by arrow. b) M—H loops are recorded at 10 K along in-plane directions of the samples after zero field cooled the sample. Even though the samples exhibit antiferromagnetic behavior below T_N , they all display hysteresis at 10 K, indicating the potential presence of a non-collinear spin structure with both ferrimagnetic (FM) and antiferromagnetic contributions coexisting. c) Top panel: Experimental XMCD spectra at the Mn L_{3,2} edge at 130 K, measured at ±0.6T, indicate a non-collinear spin arrangement between Mn (I) (α_1), Mn (II) (α_2) and Mn (III) (α_3). Bottom panel: Simulated XMCD spectra between Mn (I) (α_1), Mn (II) (α_2), and Mn (III) (α_3) for the Mn₃NiN on LSAT. d) The XMCD spectra at Ni L_{3,2}-edges at 130 K, measured at ±0.6T, observed the finite signal of XMCD, indicating that Ni possesses very small spin and orbital magnetic nature is preserved. e) Temperature-dependent resistivity of Mn₃NiN films on various substrates, measured form 40 K to 320 K, highlighting the near-zero temperature coefficient of resistivity (TCR) effect. f) Magnified views of (e) reveal distinct resistivity changes around the Néel temperature T_N , consistent with the T_N observed in (a). These changes mark the onset of antiferromagnetic ordering, corresponding to shifts in spin scattering and the evolution of magnetic ordering within the material's structure.

switching process, suggesting an emerging ferrimagnetic-like behavior. To gain further insight into the non-collinear spin interaction and spin rearrangement, synchrotron-based XMCD measurements were performed at 130 K (below T_N) at the Mn $L_{3,2}$ edge. The spectra exhibit a pattern of negative (α_1), positive (α_2) , and subsequently negative (α_3) signs as the photon energy increases from low to high, mostly observed around the L_3 -edge for LAO, MgO and STO substrate (Figure 4c; Figures 59 and S10, Supporting Information; details in Experimental Section). The deconvolution of XMCD spectra or the superposition of spectra with different signs using multiplet simulations with CTM4XAS suggests the presence of specific Mn magnetic spin moments, such as α_1 for Mn(I), α_2 for Mn(II) and α_3 for Mn(III) within an NMn₆ octahedra. The same sign of α_1 and α_3 indicates the same spin direction of Mn(I) and Mn(III), while the opposite sign of α_2 denotes the Mn(II) spin being antiparallel to both

that of Mn(I) and Mn(III), confirming the overall non-collinear antiferromagnetic nature. This is further confirmed by theoretical simulation, which shows the coexistence of Γ_4 , and $\Gamma_{5 \text{ g}}$ structures in the system (Figure 6). Simultaneously, for Mn₃NiN on LSAT, the signs of α_1 , α_2 , and α_3 show exactly the opposite with respect to other substrates due to microscopic magnetization reversal among Mn(I), Mn(II), and Mn(III) within NMn₆ octahedra, although antiferromagnetism is preserved (Figure 4c). Furthermore, in the case of MgO, the Mn(II) peak (α_2) is significantly reduced, and a tendency to approach the same direction as Mn(I) (α_1) and Mn(III) (α_3) is observed. Here, the charge transfer multiplet simulations are also performed (Figure 4c bottom panel for Mn₃NiN on LSAT, Figure S11a-c, Supporting Information; details in Experimental Section) to get a clear view of the separate contributions from individual Mn lattice sites by varying the respective parameters such as

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Figure 5. Plasmonic and intra-band characteristics of Mn_3 NiN thin films on different substrates. a) The frequency-dependent real part of the optical dielectric permittivity under different substrates shows positivity in the very low-frequency range, transitioning to the negative region across the entire IR to UV range. This behavior is indicative of a metallic (plasmonic) response. b) The imaginary part of the dielectric permittivity, approaching zero with frequency, indicates high optical loss in the IR region with a decreasing trend toward the UV region. c) The variation of reflectivity versus incident photon energy shows maximum intra-band transition at IR range for all the Mn_3 NiN films. Frequency-dependent d) Refractive index e) Optical conductivity displays the systematic substrate in-plane lattice constant blue shifts (shift toward lower wavelength, i.e., higher photon energy). f) Bulk carrier concentration and mobility versus in-plane substrate lattice constant. g) Comparative analysis of optical conductivity for different substrates shows increased optical conductivity ranging from lower substrate in-plane lattice constant to higher substrate in-plane lattice constant. higher substrate in-plane lattice constant (k) at lower energy, denoting were substrate in-plane lattice constant. b) Extinction coefficient (n) versus photon energy curve show a higher n value which signifies lower density of states and higher extinction coefficient (k) at lower energy, denoting (eV). Data include ZnS ref.),^[38] TiO₂ (ref.),^[39] WO_xN_y (ref.),^[40] InN (ref.),^[41] AlN (ref.),^[41] Cu₃N (ref.),^[42] Mg₃AsN (ref.),^[43] Ni₃SnN (ref.),^[44] and Mn_3 NiN (this work) shows a high value of extension coefficient at near IR region in Mn_3 NiN film which is very important in optical devices.

crystal-field splitting energy (10*Dq*), charge-transfer energy (Δ), *d*-*d* coulomb repulsion energy (U_{*dd*}), core hole potential (U_{*pd*} \approx 1.2 U_{*dd*}), and O 2*p*-Mn 3*d* hybridization strength ($\sqrt{3pd\sigma}$) (Table S1, Supporting Information). This observation may suggest an antiferromagnetic to ferrimagnetic transition even close to 130 K, supporting the macroscopic SQUID magnetometry data (Figure 4a,b). In parallel, XMCD spectra at Ni L_{3,2} edges at 130K clarify that the finite signal of XMCD due to possible [Ar]3d⁸4s²4p³ electronic configuration), which is opposite to the Mn $L_{3,2}$ edges and is correlated to the opposite direction of the Ni magnetic moments with respect to Mn. Thus, the net magnetization depends on the orientation of Mn and Ni magnetic lattices, and close to T_N , antiferromagnetic nature is preserved. To gain insight into the effect of T_N on the electrical transport properties of Mn₃NiN grown on various substrates, we performed four-probe resistivity measurements (Figure 4e, details in Experimental Section) to measure the electrical transport of the Mn₃NiN films. The temperature-dependent resistivity curves for Mn₃NiN on various substrates

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Figure 6. Band structures of Mn_3NiN under biaxial strain. a) The band structures of chiral antiferromagnetic noncollinear $\Gamma_{4~g}$ (blue) and $\Gamma_{5~g}$ (red) phases of Mn_3NiN under strain -3%, 0%, and 3%. The band structures are calculated using DFT+U with SOC. Biaxial strain changes the band structure, and the change is more pronounced along the X-M path. The band structures exhibit a nuanced change in the Γ_4 and $\Gamma_{5~g}$ phases. The difference is more pronounced under compressive strain compared to tensile strain. b) Radial plots representing the magnetic moment of Mn atoms in Mn_3NiN under different strains (-3%, 0%, and 3%) for $\Gamma_{4~g}$ (top) and $\Gamma_{5~g}$ (bottom) (right) phases. Each vertex corresponds to a distinct Mn atomic site, showing how the magnetic alignment varies with strain and between the two phases. The colors represent different strain levels, with blue indicating -3%, orange indicating 0%, and green indicating 3% strain. Here, M_x , M_y , and M_z denotes the magnetization along x, y, and z-direction, respectively. c) Schematic of spin orientation of non-collinear AFM Γ_4 and $\Gamma_5~g$ under different substrates calculated from theoretical simulation, where Ni atoms (blue), Mn (I) atom (red), Mn (III) atom (yellow) and N atoms (green) are shown. Film on LSAT shows spin reconstruction within Mn sublattices unlike other substrates (LAO, STO, and MgO).

exhibit no significant change in resistivity (Figure 4e). The absence of notable resistivity variations with increasing temperature suggests a near-zero temperature coefficient of resistivity (TCR), a characteristic emergent property of antiperovskite $\rm Mn_3NiN$ (Note S4, Supporting Information).^[40] A magnified view of Figure 4e, shown in Figure 4f, reveals a distinct resistivity anomaly near $\rm T_N$, indicating a strong magneto-structural coupling.

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2.4. Optical Properties: Plasmonic and Intra-Band Characteristics of Mn_3NiN Films

To gain an insight into the optical properties of the Mn₃NiN films, spectroscopic ellipsometry is employed to unveil the optical dielectric permittivity by fitting the experimentally obtained psi (ψ) and delta (Δ) spectra with a combination of Drude-Lorentz oscillator model (Figure 5, details in Experimental Section).^[41] Generally, the dielectric behavior of a material holds a dominant consequence, accompanied by other distinct optical properties such as refractive index (n), extinction coefficient (k), and reflectivity (R). Here, the positive to negative crossover in the real part of the dielectric permittivity $\varepsilon'(\omega)$, characteristic of an epsilon-near -zero (ENZ) signature in the near-infrared region, indicates the metallic (plasmonic) character of the films (Figure 5a-dashed line). Specifically, for Mn₃NiN/LAO, Mn₃NiN/LSAT, Mn₃NiN/STO, and Mn₃NiN/MgO, the ENZ energies are 0.7, 1.0, 1.55, and 1.8 eV respectively, revealing their unique ENZ signatures, where blue shift (shift toward lower wavelength, i.e., higher energy) in MgO corresponds to a higher free electron concentration of the film compared to its counterparts (Mn₃NiN on LAO, LSAT, and STO). Here, the low energy dielectric spectra (infrared region) shifts occur due to the electronic inter-band transitions correlating to the effect of strain and a Drude-like behavior is consistent with the van-der-pauw method resistivity data (Figure S12, Supporting Information, details in Experimental Section) similar to Ti₃TlN and Ni₃SnN.^[42] The imaginary part, $\varepsilon''(\omega)$, (Figure 5b), corresponding to optical loss, approaches a low value with increasing frequency, further indicating the consistent metallic nature of the films. The reflectivity maxima near the IR region (Figure 5c) for all Mn₃NiN films corresponds to the intra-band transitions and collective oscillations of free electrons. The refractive index (n) (Figure 5d; Figure S12, Supporting Information; details in Experimental Section) undergoes almost similar trends for the Mn₃NiN on various substrates, which shows a decreasing trend in the refractive index values with an increment of energy correlated to effective internal reflections. A higher "n" value is significant, as it is linked to the velocity or deceleration of photons due to successive interactions with electrons, while a lower "n" can be ascribed to the lower density of states. Optical conductivity, a key parameter for the conduction of electrons under an applied electromagnetic field, is computed from the dielectric permittivity by using the relation, $\sigma_1(\omega) = \omega \varepsilon_0 \varepsilon''(\omega)$ (Figure 5g, details in Experimental Section). A comparative plot of the maximum optical conductivity of Mn₃NiN film reveals that the peak value increases for the Mn₃NiN on STO and MgO, which confirms the tunability of the optical conductivity of Mn₃NiN with substrateinduced strain. Now, the high optical conductivity (metallicity) corroborates with the higher carrier concentration and mobility in Mn₃NiN/MgO (Figure 5f), supporting a higher value of the plasma frequency compared to the other films. Furthermore, to understand the light absorption properties of our films, we calculated the extinction coefficient (k) (Figure 5h, details in Experimental Section), which is directly linked to the light absorption (α). A higher extinction coefficient (k) at lower energy (higher wavelength) indicates the high absorption nature of Mn₃NiN films (Figure 5h). The detailed comparison of the extinction coefficient of Mn₃NiN films with other materials like ZnS,^[43] TiO₂,^[44] WO_xN_y,^[45] InN,^[46] AlN,^[39] Cu₃N,^[47] Mg₃AsN,^[48] and Ni₃SnN^[49]

(Figure 5i) clarifies a higher value near the IR region in our work. This indicates a strong absorption of infrared light, and this property can be harnessed for specific purposes more specifically infrared absorbers, IR shielding, IR filters, windows, etc. Therefore, the tunable nature of the plasmonic characteristics and high extinction coefficient through the lens of strain promises an easy and effective pathway to harness energy-selective switching optical devices.

2.5. Theoretical Analysis

To theoretically validate our experimental observations, we conducted density functional theory (DFT) computations on Mn₃NiN (Figure 6, details in Experimental Section). Our investigation encompassed the Mn₃NiN films on different substrates, i.e., under different strains. Through systematic exploration of Mn₃NiN under biaxial strains and incorporating the first principles of DFT calculations, we gained insights into the variations of the structural, electronic, and magnetic attributes of Mn₃NiN on distinct substrates. Our findings reveal that, in the absence of external strain, the compound exhibits a distinct octahedral arrangement of Mn atoms, maintaining a consistent 60° interatomic angle. However, the application of strain disrupts this equilibrium, leading to deformations in the octahedral geometry and alterations in the Mn-Mn bond lengths (Table S2, Supporting Information). This phenomenon of octahedral deformations in Mn₃NiN persists as the material undergoes varying strains on distinct substrates. To further substantiate the negative valency of nickel (Ni) within Mn₃NiN, we employed Bader charge calculations, as proposed by Bader.^[50] The electron charge density, derived from first-principles calculations utilizing the PBEsol+U approach, served as the basis for the Bader charge analysis of Mn₃NiN. The results of the Bader charge analysis (Table S3, Supporting Information) indicate that Mn atoms exhibit cationic behavior, whereas Ni and nitrogen (N) atoms exhibit anionic behavior. The observed negative oxidation state of Ni situated at the corner site of the antiperovskite is consistent with our experimental findings (Figures 2 and 6) and corroborates previous studies.^[31,51] It is noteworthy that the overall structure maintains charge neutrality, and nuanced changes in the Bader charge of atoms are evident with variations in the magnetic phase and applied strain. Furthermore, magnetic moments predominantly emanate from the magnetically active Mn sites. Considering the unstrained state, the Mn(I)-Mn(II)-Mn(III) angle exhibits a 120° angle, resulting in a net zero magnetic moment for both the Γ_{4g} and Γ_{5g} phases. It is crucial to emphasize that the magnetic orientation of Mn atoms at each magnetic site varies in these two configurations (Figure 6b; Table S4, Supporting Information), with the total magnetic moment being zero in all directions in pristine Mn₃NiN at room temperature. The magnetic contribution from Ni is marginally compared to Mn in pristine Mn₂NiN, similar to experimental observation, i.e., a significantly lesser amount of strain-mediated magnetic contribution of Ni compared to Mn is observed (Table S5, Supporting Information; Figure 6). Nevertheless, the application of substrate induced strain introduces magnetic moment components in each direction (Figure 6b; Table S6, Supporting Information) and the stability of Mn₃NiN is evaluated by computing the energy difference between two phases,

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denoted as $\Delta E = E(\Gamma_{4 g})-E(\Gamma_{5 g})$ (Figure S13a and Table S7, Supporting Information). This shows that pristine Mn₃NiN demonstrates higher stability of the $\Gamma_{\!\!4\ g}$ phase at low temperatures compared to the $\Gamma_{5 g}$ phase, and this trend persists under various substrate induced strains with a clear electronic structural illustration (Figure 6; Figure S13b, Supporting Information).^[14] The unusual magnetic behavior observed in Mn₃ NiN/LSAT, such as the finite magnetic moment persisting even at room temperature in the M-T measurements (Figure 4a), remains an intriguing phenomenon that is not yet fully understood and warrants further investigation. We correlated experimental results with density functional theory (DFT) calculations under various substrates, mapping the magnetic structures of the Γ_4 and Γ_5 a states across various substrates using DFT-derived magnetic moment data. The magnetic structures were visualized using VESTA software, with the magnetic orientation vectors fixed according to values obtained from the DFT magnetic structure calculations. A theoretical representation of mixed ratios of ferrimagnetic symmetry Γ_{4g} and antiferromagnetic symmetry $\Gamma_{5,\sigma}$ in Mn₃NiN under different strain is shown in Figure 6c. The strain application leads to notable adjustments in the band structure, particularly along the Γ -X-M path. Additionally, the gap between two electron pockets near the Fermi level undergoes a subtle change with strain, approaching proximity at 3%, with a disparity of ≈ 0.5 eV at -3% strain. However, in the unstrained case, no electronic states are observed at the high symmetric point M near the Fermi level, while in the strained scenario, states have been seen to emerge at M. The band structure and total density of states clarify the increase in the total number of states near the Fermi level. Consequently, a systematic change in the electronic structure of the $\Gamma_{4\sigma}$ and $\Gamma_{5 g}$ phases also emerged. Notably, the difference in the band structure of the two phases is more pronounced under compressive strain than the tensile strain. These alterations in the electronic structure below the Fermi level are particularly noteworthy, spanning from -1 to -2 eV, supporting our experimental observations.

3. Conclusion

In summary, our investigation reveals that Mn₃NiN films exhibit noncollinear antiferromagnetic behavior with contributions from both $\Gamma_{4\,\mathrm{g}}$ and $\Gamma_{5\,\mathrm{g}}$ phases and a significant shift in the Néel temperature (T_N) up to 116 K. Additionally, the films demonstrate a rare negative oxidation state of the transition metal and exhibit metallic behavior, along with positive to negative dielectric permittivity with tunable optical conductivity, very high extinction coefficient, and intra-band transitions. Our study highlights the intricate interplay of magnetic moments, emphasizing the need for future investigations to manipulate spin-based metallic devices. Moreover, The zero TCR effect holds substantial significance for technological applications. Materials exhibiting stable resistivity across a broad temperature range are highly desirable for precision electronic components, including resistors, sensors, and other devices requiring temperature-invariant performance. Furthermore, achieving zero TCR through strain engineering in epitaxial films offers a promising avenue for tailoring the transport properties of anti-perovskites, thereby enhancing their potential for advanced electronic and functional device applications. Overall, our findings unravel intricate magneto-structural correlations influenced by substrate interactions in Mn_3NiN films. Importantly, it also demonstrates a pathway for controlling the magnetization of this material, which could pave the way for designing antiperovskite materials for room-temperature antiferromagnetic systems, providing valuable insights for potential applications in spintronic devices and magneto-optical systems.

4. Experimental Section

Sample Fabrication: The antiperovskite thin films were grown by DC reactive sputtering using a Mn₃Ni stoichiometric target (99.9% purity) in an Ar atmosphere with [30 standard cubic centimeters per minute (sccm)]/N₂ (3.2 sccm) atmosphere of 9 mTorr. The deposition temperature was 500 °C and the input power was 20W. The sample-to-target distance was fixed at 6 cm. Before deposition, the base pressure of the chamber was 10^{-7} torr and waited for 1 h in that pressure. After the film growth, the samples were cooled down at a rate of 5 °C min⁻¹ to room temperature at the growth pressure.

Structural Characterization: Structural characterizations were carried out using a Bruker D8 discover X-ray Diffraction (XRD) diffractometer with Cu Ka radiation ($\lambda = 1.54056$ Å). X-ray reflectivity scan done at the range of 0.4–4.5°, reveals Kessing oscillation of the films. The XRD 20-w scans around (002)-reflections done from 35 to 60° show a single crystalline phase of the films. The rocking curve was performed within –2.5–+2.5° and phi scan from 0 to 310°.

Rutherford Backscattering Spectrum: RBS was utilized to determine the stoichiometry, thickness, and composition of the Mn₃NiN films. The measurements were performed using a 2 MeV helium ion beam at normal incidence, with a backscattering angle of 168.2° to enhance mass resolution at the Inter-University Accelerator Centre (IUAC), Delhi. The helium ion beam was directed onto the surface of Mn3NiN films grown on MgO substrates. However, for films grown on other substrates, such as those containing La and Sr, RBS could not provide reliable data due to the higher atomic masses of these elements compared to those in the film. A silicon surface barrier detector was used to detect the scattered ions from the film surface. The RBS spectra were analyzed using the SIMNRA, and XRUMP software, a standard tool for simulating ion beam analysis spectra. SIM-NRA was used to fit the experimental spectra and extract the depth profiles and elemental composition of the films. The fitting process involved iteratively adjusting parameters until a best-fit curve with a high coefficient of determination ($R^2 \approx 0.999$) was obtained by SIMNRA and the figure was made by XRUMP, indicating strong agreement between the experimental and simulated spectra.

Atomic Force Microscopy: Atomic Force Microscopy (AFM) (Asylum Research MFP 3D origin plus) was used to characterize the roughness and morphology of the sample. After acquiring the AFM images, them using Gwyddion software were analyzed to calculate the roughness parameters.

X-Ray Photoemission Spectroscopy (XPS): X-ray photoemission spectroscopy (XPS) was performed using Theromofisher Scientific. The instrument was equipped with a monochromatic Mg K α X-ray source. Prior to XPS measurements, the samples were appropriately cleaned and mounted. Special care was taken to ensure the surface's integrity and remove any contaminants that might interfere with the measurement. XPS spectra were acquired by positioning the samples in the analysis chamber under ultra-high vacuum conditions. Survey spectra were collected over a wide energy range to identify the elemental composition of the sample surface. The acquired data were analyzed using XPSPEAK41. Peak fitting and deconvolution were performed to determine the contributions of different chemical states for each element detected. However, near to the Ni peak in the XPS spectra, a small shoulder peak was also observed which is due to the N–O bonding present in the surface of the Mn₃NiN films. However, the intensity of the peak significantly reduced when the films were cleaned using isopropanol, this depicts that the oxygen is present on the surface only.

XAS, and XMCD Measurements: Element-sensitive XAS and XMCD measurements were performed at P04 Beamline, PETRA III, DESY, Germany on Mn and Ni L-edge in the surface-sensitive total electron yield (TEY) modes both at 130 K. The process was carried out under a background vacuum of 8 \times 10⁻⁷ Torr. The normalization of spectra was performed so that the L₃ pre-edge spectral region was set to zero, in addition to the peak at the L₃ edge being set to one. Circularly polarized X-rays with $\approx 100\%$ polarization was used in normal incidence with respect to the sample plane and parallel to the applied magnetic field. The XMCD was obtained by taking the difference of the XAS spectra, i.e., $\sigma^+ - \sigma^-$, by flipping the magnetic field of ± 0.6 Tesla at a fixed x-ray helicity and vice versa in out-of-plane geometry. For the theoretical formulation of the XMCD spectra, the charge transfer multiplet for X-ray absorption spectroscopy (CTM4XAS) program^[52] was used under the ligand field and the charge transfer multiplet approach. The simulation was done by varying the crystal-field splitting energy 10Dq, charge-transfer energy Δ , d-d coulomb repulsion energy U_{dd} , core hole potential U_{pd} (\approx 1.2 times of U_{dd}), and O 2*p*-Mn 3*d* hybridization strength $\sqrt{3}(pd\sigma)$. The hopping integral between the Mn-3d and O-2p orbitals was calculated for the various Mn-O bond lengths according to Harrison's descriptions.^[53] The values of 10Dq were tuned to match the experimental spectra.

Magnetic Measurements: A commercially available Superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS) was used for magnetic characterization of the Mn_3NiN films as a function temperature and applied field. M—T is done at 0.05 T during warming from 10–350 K after zero field cool (ZFC). The M—H was performed at 10 K after zero-field cooling of the sample. The field was applied along the in-plane direction.

Ellipsometry Measurements: A variable-angle spectroscopic ellipsometer (VASE J.A. Woollam Co.) was used to measure the optical properties of the films in reflection mode at three different incident angles (55, 65, 75°). The experimental Psi (ψ) and Delta (Δ) spectrums of Mn₃NiN films were fitted using general oscillator models (Drude and Lorentz oscillator) in Complete EASE software. The optical properties of Mn₃NiN thin films were determined using the frequency-dependent dielectric function, $\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$. The plasma frequency (ω_p), which depends on the carrier concentration (N) and the effective mass (m^{*}), is given by the Equation (1):

$$\omega_p = \sqrt{\frac{Ne^2}{\epsilon_0 m^*}} \tag{1}$$

where *e* represents the electron charge, and ε_0 denotes the vacuum permittivity. Now, the optical conductivity is calculated by incorporating the Equation (2),

$$\sigma (\omega) = -i\frac{\omega}{4\pi} \left| \epsilon'(\omega) - 1 \right|$$
⁽²⁾

The refractive index is deduced from the Equation (3),

$$n(\omega) = \left[\frac{\varepsilon r(\omega)}{2} + \sqrt{\frac{\varepsilon'(\omega) \varepsilon''^{2}(\omega)}{2}}\right]^{1/2}$$
(3)

The extinction coefficient (k), which is directly linked to the light absorption (α), is calculated as $k = \frac{\alpha \lambda}{4\pi}$. The reflectivity (R) is calculated following the Equation (4),

$$R(\omega) = \left[\frac{\sqrt{\varepsilon'(\omega) + i\varepsilon''(\omega)} - 1}{\sqrt{\varepsilon'(\omega) + i\varepsilon''(\omega)} + 1}\right]^2$$
(4)

Transport Measurements: Electrical transport measurements of Mn_3NiN films were performed by the Cryogenics system with the help of the Lakeshore 331 temperature controller. The temperature was

controlled, and using a Standford lock-in-amplifier, the resistivity of the film was measured, which was based on the four-probe method; bulk concentration and Mobility of the film with respect to Strain were measured via Ecopia HMS-5000, which was based on the van der pau method. To get an excellent ohmic contact, platinum contact is grown using PLD. In hall measurement (Schematic Figure 1a), we pass the current I_a from 1 to 2 and measure the voltage (let's say V_a), then changing the direction of the current, pass the current I_b and measure the voltage (let's say V_b). Similarly, measure voltage from all four corners and calculate the resistance R_{1234} , R_{2341} , R_{3421} , and R_{4123} . From Ohm's law, resistivity ρ of the sample

$$V_{a} - - V_{b} / I_{a} - - I_{b} = R_{1234}$$
(5)

$$V_{c} - - V_{d} / I_{c} - - I_{d} = R_{2341}$$
 (6)

$$V_{e} - -V_{f}/I_{e} - -I_{f} = R_{3412}$$
(7)

$$V_g - - V_h / I_g - - I_h = R_{4123}$$
 (8)

$$\rho_1 = \frac{\pi ft \left(R_{1234} + R_{2341} \right)}{\ln 2 2} \rho_2 = \frac{\pi ft \left(R_{3412} + R_{4123} \right)}{\ln 2 2} \rho = \frac{\rho_1 + \rho_2}{2} \tag{9}$$

Here f is the factor constant of the instrument, t is the thickness of the sample.

Theoretical Calculations: The DFT calculations were performed by using the Quantum Espresso software package.^[54] Atomistic simulations were performed using an ultrasoft pseudopotential and the PBEsol functional within the generalized gradient approximation. The kinetic energy cut-off for the wave function is taken as 75 Ry. Variable-cell relaxation calculations were performed with a k-grid of $6 \times 6 \times 6$ to determine the equilibrium lattice parameters of Mn₃NiN. For the electronic structure calculations, a denser $13 \times 13 \times 13$ k-grid was employed. The convergence threshold for the self-consistent field was taken as 10^{-9} Ry atom⁻¹. The exchange-correlation for the d-electrons was corrected through the DFT+U approximation using the linear response approach.[55] This has been fine-tuned to accurately replicate the experimentally observed lattice parameters. During geometric optimization, values of $\dot{U} = 1.5$ eV for the Mn-d orbitals and U = 2 eV for the Ni-d orbitals were used to match lattice parameters with those of the experimentally observed values. Spinorbit coupling (SOC) was included in the calculation to account for noncollinear magnetic configurations in the $\Gamma_{4\ g}$ and $\Gamma_{5\ g}$ phases of the system. Bader charges were evaluated using the algorithm developed by G. Henkelman et al. The atomic structure figures were visualized with the VESTA code.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

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The authors declare no conflict of interest.

Author Contributions

A.K, P.D., and N.D. contributed equally to this work. S.D. and M.B. designed the experiments. A.K. and S.D. carried out the synthesis. A.K., P.D., J.K.D, B.S., S.D performed the characterization of the samples. M.H., F.A., and S.C conducted the synchrotron experiment. A.K, N.D., P.D., J.K.D., B.R., B.S. M.B., and S.D. analyzed the data and co-wrote the manuscript. M.B. and S.D. supervised the research. All authors contributed to the discussions and manuscript preparation.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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- T. Jungwirth, X. Marti, P. Wadley, J. Wunderlich, Nat. Nanotechnol. 2016, 11, 231.
- [2] F. Johnson, D. Boldrin, J. Zemen, D. Pesquera, J. Kim, X. Moya, H. Zhang, H. K. Singh, I. Samathrakis, L. F. Cohen, *Appl. Phys. Lett.* 2021, 119, 22.
- [3] K. Takenaka, Sci. Technol. Adv. Mater. 2012, 13, 013001.
- [4] E. O. Chi, W. S. Kim, N. H. Hur, Solid State Commun. 2001, 120, 307.
- [5] K. Takenaka, A. Ozawa, T. Shibayama, N.-h. Kaneko, T. Oe, C. Urano, *Appl. Phys. Lett.* **2011**, *98*, 022103.
- [6] J. Yan, Y. Sun, H. Wu, Q. Z. Huang, C. Wang, Z. X. Shi, S. H. Deng, K. W. Shi, H. Q. Lu, L. H. Chu, *Acta Mater.* 2014, *74*, 58.
- [7] K. Kamishima, T. Goto, H. Nakagawa, N. Miura, M. Ohashi, N. Mori, T. Sasaki, T. Kanomata, *Phys. Rev. B* 2000, *63*, 024426.
- [8] T. He, Q. Huang, A. P. Ramirez, Y. Wang, K. A. Regan, N. Rogado, M. A. Hayward, M. K. Haas, J. S. Slusky, K. Inumara, H. W. Zandbergen, N. P. Ong, R. J. Cava, *Nature* 2001, 411, 54.
- [9] K. Asano, K. Koyama, K. Takenaka, Appl. Phys. Lett. 2008, 92, 161909.
- [10] L. Zu, S. Lin, J. C. Lin, B. Yuan, X. C. Kan, P. Tong, W. H. Song, Y. P. Sun, Inorg. Chem. 2016, 55, 9346.
- [11] P. Lukashev, R. F. Sabirianov, K. Belashchenko, Phys. Rev. B 2008, 78, 184414.
- [12] K. Takenaka, H. Takagi, Appl. Phys. Lett. 2005, 87, 261902.
- [13] C. Wang, L. H. Chu, Q. R. Yao, Y. Sun, M. M. Wu, L. Ding, J. Yan, Y. Y. Na, W. H. Tang, G. N. Li, Q. Z. Huang, J. W. Lynn, *Phys. Rev. B* 2012, 85, 220103.
- [14] D. Fruchart, E. F. Bertaut, J. Phys. Soc. Jpn 1978, 44, 781.

- [15] K. Takenaka, M. Ichigo, T. Hamada, A. Ozawa, T. Shibayama, T. Inagaki, K. Asano, *Sci. Technol. Adv. Mater.* 2014, *15*, 015009.
- [16] X. Y. Song, Z. H. Sun, Q. Z. Huang, M. Rettenmayr, X. M. Liu, M. Seyring, G. N. Li, G. H. Rao, F. X. Yin, *Adv. Mater.* **2011**, *23*, 4690.
- [17] D. Boldrin, F. Johnson, R. Thompson, A. P. Mihai, B. Zou, J. Zemen, J. Griffiths, P. Gubeljak, K. L. Ormandy, P. Manuel, D. D. Khalyavin, B. Ouladdiaf, N. Qureshi, P. Petrov, W. Branford, L. F. Cohen, *Adv. Funct. Mater.* **2019**, *29*, 1902502.
- [18] M. Jansen, Chem. Soc. Rev. 2008, 37, 1826.
- [19] K. Takemura, H. Fujihisa, Phys. Rev. B: Condens. Matter Mater. Phys. 2011, 84, 014117.
 [20] A. Karpov, J. Nuss, U. Wedig, M. Jansen, J. Am. Chem. Soc. 2004, 126,
- 14123. [21] X. Liu, M. Zhang, S. Wu, R. Zhong, Y. Liu, A. M. Arif, Y. Geng, Z. Su,
- Chem. Phys. Chem 2020, 21, 459. [22] A. Ikeda, S. Koibuchi, S. Kitao, M. Oudah, S. Yonezawa, M. Seto, Y.
- Maeno, Phys. Rev. B 2019, 100, 245145. [23] E. Triana-Ramírez, et al., Phys. Chem. Chem. Phys. 2023, 25, 14992.
- [24] D. Boldrin, I. Samathrakis, J. Zemen, A. Mihai, B. Zou, F. Johnson, B. D. Esser, D. W. McComb, P. K. Petrov, H. Zhang, L. F. Cohen, *Phys. Rev. Mater.* 2019, *3*, 094409.
- [25] V. Di Castro, G. Polzonetti, J. Electron Spectrosc. Relat. Phenom. 1989, 48, 117.
- [26] Z. Fu, J. Hu, W. Hu, S. Yang, Y. Luo, Appl. Surf. Sci. 2018, 441, 1048.
- [27] A. R. González-Elipe, R. Alvarez, J. P. Holgado, J. P. Espinos, G. Munuera, J. M. Sanz, Appl. Surf. Sci. 1991, 51, 19.
- [28] A. P. Grosvenor, M. C. Biesinger, R. S.t.C. Smart, N. S. McIntyre, Surf. Sci. 2006, 600, 1771.
- [29] D. Huang, H. Nakamura, K. Küster, A. Yaresko, D. Samal, N. B. M. Schröter, V. N. Strocov, U. Starke, H. Takagi, *Phys. Rev. Mater.* 2019, 3, 124203.
- [30] V. Di Castro, G. Polzonetti, J. Electron Spectrosc. Relat. Phenom. 1989, 48, 117.
- [31] F. Takata, K. Ito, Y. Takeda, Y. Saitoh, K. Takanashi, A. Kimura, T. Suemasu, Phys. Rev. Mater. 2018, 2, 024407.
- [32] S. Deng, Y. Sun, H. Wu, Q. Huang, J. Yan, K. Shi, M. I. Malik, H. Lu, L. Wang, R. Huang, L. Li, C. Wang, *Chem. Mater.* **2015**, *27*, 2495.
- [33] K. Kodama, S. Iikubo, K. Takenaka, M. Takigawa, H. Takagi, S. Shamoto, *Phys. Rev. B* 2010, *81*, 224419.
- [34] Y. Na, C. Wang, L. Chu, L. Ding, J. Yan, Y. Xue, W. Xie, X. Chen, Mater. Lett. 2011, 65, 3447.
- [35] L. He, C. Chen, N. Wang, W. Zhou, L. Guo, J. Appl. Phys. 2007, 102, 103911.
- [36] J. H. Lee, L. Marcano, R. Aeschlimann, M.-A. Mawass, C. Luo, A. Gloter, J. Varignon, F. Radu, S. Valencia, M. Bibes, *APL Mater.* 2022, 10, 081101.
- [37] W. Zhang, Z. Zhou, Y. Zhong, T. Zhang, Y. Huang, C. Sun, AIP Adv. 2015, 5, 117228.
- [38] G. Gurung, D.-F.u Shao, T. R. Paudel, E. Y. Tsymbal, *Phys. Rev. Mater.* 2019, 3, 044409.
- [39] I. Samathrakis, H. Zhang, Phys. Rev. B 2020, 10, 1214423.
- [40] C. X. Quintela, N. Campbell, D. F. Shao, J. Irwin, D. T. Harris, L. Xie, T. J. Anderson, N. Reiser, X. Q. Pan, E. Y. Tsymbal, M. S. Rzchowski, C. B. Eom, *APL Mater.* **2017**, *5*, 096103.
- [41] A. B. Chaib, M. Zouini, A. Tahiri, Opt. Mater. 2022, 133, 112895.
- [42] K. Das, M. A. Ali, M. M. Hossain, S. H. Naqib, A. K. M. A. Islam, M. M. Uddin, AIP Adv. 2020, 10, 095226.
- [43] M. Y. Nadeem, W. Ahmed, Turkish J. Phy. 2000, 24, 6.
- [44] S. Y. Kim, Appl. Opt. 1996, 35, 6703.
- [45] S. H. Mohamed, E. R. Shaaban, Mater. Chem. Phys. 2010, 121, 249.
- [46] J. M. Khoshman, M. E. Kordesch, Phys. Stat. Sol. 2005, 2, 2821.
- [47] S. Okrasa, M. Wilczopolska, G. Strzelecki, K. Nowakowska-Langier, R. Chodun, R. Minikayev, K. Król, L. Skowronski, K. Namyslak, B. Wicher, A. Wiraszka, K. Zdunek, *Thin Solid Films* **2021**, *735*, 138889.

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www.advancedsciencenews.com



- [48] X. Li, Y. Zhang, W. Kang, Z. Yan, Y. Shen, J. Huo, Comput. Mater. Sci. 2023, 225, 112188.
- [49] K. Das, M. A. Ali, M. M. Hossain, S. H. Naqib, A. K. M. A. Islam, M. M. Uddin, AIP Adv. 2020, 10, 9.
- [50] G. Henkelman, A. Arnaldsson, H. Jónsson, Comput. Mater. Sci. 2006, 36, 354.
- [51] J. Batool, S. Muhammad Alay-e-Abbas, N. Amin, J. Appl. Phys. 2018, 123, 16.
- [52] E. Stavitski, F. M. F. D.e Groot, *Micron* 2010, 417, 687.

- [53] W. A. Harrison, W. H. Freeman, S. F. Co, *JMoSt* 1981, 71, 355.
- [54] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, et al., *J. Phys.: Condens. Matter* **2009**, *21*, 395502.
- [55] C. Matteo, S. De Gironcoli, Phys. Rev. B 2005, 71, 035105.