Interfacial charge-transfer Mott state in iridate–nickelate superlattices

Xiaoran Liu, Michele Kotiuga, Heung-Sik Kim, Alpha T. N’Diaye, Yongseong Choi, Qinghua Zhang, Yanwei Cao, Mikhail Kareev, Fangdi Wen, Banabir Pal, John W. Freeland, Lin Gu, Daniel Haskell, Padraic Shafer, Elke Arenholz, Kristjan Haule, David Vanderbilt, Karin M. Rabe, and Jak Chakhalian

*Department of Physics and Astronomy, Rutgers University, Piscataway, NJ 08854; Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720; Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439; Beijing National Laboratory for Condensed-Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China; and Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang 315201, China

Contributed by Karin M. Rabe, August 16, 2019 (sent for review May 6, 2019; reviewed by Ivan Bozovic and Claude Ederer)

We investigate SrIrO$_3$/LaNiO$_3$ superlattices in which we observe a full electron transfer at the interface from Ir to Ni, triggering a massive structural and electronic reconstruction. Through experimental characterization and first-principles calculations, we determine that a large crystal field splitting from the distorted interfacial IrO$_6$ octahedra surprisingly dominates over the spin-orbit coupling and together with the Hund’s coupling results in the high-spin ($S = 1$) configurations on both the Ir and Ni sites. This demonstrates the power of interfacial charge transfer in coupling lattice, charge, orbital, and spin degrees of freedom, opening fresh avenues of investigation of quantum states in oxide superlattices.

---

**Significance**

Heterojunctions between dissimilar materials provide an opportunity to generate emergent properties not present in their individual components. These properties are often linked to interfacial charge transfer, an important mechanism allowing one to access and control novel quantum states. Here, we have grown unit-cell scale superlattices composed of 5$d$ SrIrO$_3$ and 3$d$ LaNiO$_3$. We have discovered a massive interfacial charge transfer from Ir to Ni, triggering dramatic electronic and magnetic reconstructions at the interface that suppress strong spin-orbit coupling effects normally present in the iridates. These findings call for careful evaluation and reinterpretation of experiments on spin-orbit-driven physics in thin films and heterostructures based on prototypical 5$d$ transition metal oxides.

---


Reviewers: I.B., Brookhaven National Laboratory (US Department of Energy); and C.E., ETH Zurich.

The authors declare no conflict of interest.

Published under the PNAS license.

1 To whom correspondence may be addressed. Email: xiaoran.liu@rutgers.edu or kmrabe@physics.rutgers.edu

2 Present address: Cornell High Energy Synchrotron Source, Cornell University, Ithaca, NY 14853.

This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1907043116/-/DCSupplemental.

First published September 16, 2019.
We begin our experimental characterization of the ICT using element-specific XAS measurements (Fig. 2A and B). For each superlattice, the Ni L2 edge shows a mixture of both Ni$^{2+}$ and Ni$^{3+}$ features and the peak position of the Ir L3 edge shifts toward higher energy with respect to the reference peak of Ir$^{4+}$, indicating the Ir oxidation state increases (39). These combined results clearly demonstrate that electrons are intrinsically transferred from Ir to Ni sites, giving rise to hole-electron-doped SrIrO$_3$ (LaNiO$_3$) layers, respectively. We estimate the average oxidation state of Ir by calculating the relative peak shift with respect to the positions of nominal Ir$^{4+}$ and Ir$^{5+}$ reference materials (39) and of Ni by spectral deconvolution of Ni L$_2$ XAS (SI Appendix, Fig. S4). For the 1I/nN series (Fig. 2C), we observe that the average Ir oxidation state remains almost constant at Ir$^{5+}$, indicating that the single-unit-cell SrIrO$_3$ layer is hole doped at about 1 hole per Ir. The Ni oxidation state at $n=1$ is significantly reduced from the nominal Ni$^{3+}$ to Ni$^{2+}$, indicating that the single-unit-cell LaNiO$_3$ layer is electron doped at about 1 electron per Ni. As $n$ increases, the average Ni oxidation state approaches the nominal valence, consistent with a net transfer of 1 electron from the single-unit-cell SrIrO$_3$ layer, independent of $n$. For the mI/3N series (Fig. 2D), the average Ir oxidation state increases from Ir$^{4+}$ ($m=4$) to Ir$^{3+}$ ($m=1$) with decreasing $m$, whereas the average Ni oxidation state remains almost constant at Ir$^{5+}$.

Results and Discussion

first-principles calculations and X-ray linear dichroism (XLD) measurements. X-ray magnetic circular dichroism (XMCD) measurements and first-principles results demonstrate that these electronic and structural changes drive SrIrO$_3$ from the strong SOC state to a Mott state stabilized by the crystal field splitting with $S=1$ high-spin configurations on both the Ni and Ir sites. These findings demonstrate how, by virtue of interface engineering, the interplay between ICT, electron correlation, SOC, and lattice degrees of freedom gives rise to unusual quantum states.

A series of $(\text{SrIrO}_3)_m/(\text{LaNiO}_3)_n | N$ superlattices (“$| mN/ nN | N$”: Here $m$ and $n$ refer to the number of SrIrO$_3$ and LaNiO$_3$ pseudocubic unit cells, respectively) are epitaxially grown on (001) SrTiO$_3$ substrates by pulsed laser deposition (PLD), starting with LaNiO$_3$ and terminated by SrIrO$_3$ layers. We grew and experimentally characterized the 1I/1N, 1I/3N, 2I/3N, 4I/3N, and 1I/10N superlattices. While the interfaces are polar, the layers in our systems are too thin for a polarization catastrophe to occur, except for the 1I/10N superlattice, in which the LaNiO$_3$ layer is metallic (35). As the SrTiO$_3$ substrates are not chemically treated, we did not specifically control the termination of each layer, and the interface termination in PLD growth is likely a mixture of both IrO$_2$, SrO-NiO$_2$, LaO, and SrO-IrO$_2$, LaO-NiO$_2$ cases. The periodicity $N$ is selected to keep the total thickness of each superlattice between 15 and 20 nm. Complementary atomic-scale information about atomic arrangement and electronic states at the interface is obtained from first-principles density-functional theory (DFT) calculations for the 1I/1N superlattice to focus on the interfacial effects.
oxidation state remains constant at approximately Ni$^{2+\cdot 6+}$. Using a simple model assuming a net transfer of 1 electron per lateral unit cell from the $m$-unit-cell SrIrO$_3$ layer to the $n$-unit-cell LaNiO$_3$ layer, we find good agreement with the experimental results (dashed lines in Fig. 2 C and D). In this model, the average oxidation state of Ni is given by $3-1/n$ and the average oxidation state of Ir is given by $4+1/m$. If the transferred electron and hole are taken to selectively localize on a single ion, which in general will involve symmetry breaking, this results in integer values in an unusual configuration: Ir$^{4+}/$Ni$^{3+} \rightarrow$ Ir$^{5+}$/Ni$^{2+}$.

To quantify the effect of such a massive ICT on the orbital splitting and spin states, we probe the occupation of Ni $e_g$ orbitals by XLD. As sketched in Fig. 3A, this approach uses X-rays with different linear polarizations (i.e., in-plane $E \parallel ab$ vs. out-of-plane $E \parallel c$), which can selectively probe the valence holes on orbitals with different orientations, in our case $d_{3z^2-r^2}$ vs. $d_{x^2-y^2}$. The difference of these 2 spectra gives rise to the XLD vs. out-of-plane local moments (4.22 eV vs. 3.76 eV), all samples exhibit a negative signal at the Ir $L_3$ edge that is modest compared to bulk Sr$_2$IrO$_4$ (44) and a markedly smaller signal with no clear meaning of the Ir moments in the superlattices may be either paramagnetic or canted antiferromagnetic.

With this information, we can determine which density-of-states scenario (Fig. 1 E or F) is realized in these superlattices. As the XMCD results clearly demonstrate the existence of a local moment on Ir, the system cannot be in the strong SOC limit, as would one then expect a nonmagnetic $J_{eff} = 0$ ground state (Fig. 1E). Furthermore, as our XLD results suggest elongated octahedral distortions which can induce a noncubic CF splitting with elongated NiO$_6$ octahedra (Fig. 1F) and in-plane $g$-axes (Fig. 1D). Furthermore, the integrated value of the 1I/1N XLD signal near the Ir $L_3$ edge is reported to be close to 0 (37) or to have the opposite sign (42, 43). Furthermore, the integrated value of the 1I/1N XLD intensity is close to 0, indicating that both orbitals are almost equally occupied (42), consistent with a transferred electron yielding high-spin ($S = 1$) Ni$^{3+}$, favored by Hund’s coupling. We therefore attribute the observed splitting to the deformation of Ir$^{4+}$O$_6$ and Ni$^{3+}$O$_6$ octahedra caused by the ICT, leading to a significant noncubic CF splitting with elongated NiO$_6$ octahedra (Fig. 1F). This is further supported by the result shown in Fig. 3C that the XLD signal diminishes in intensity, indicating a smaller splitting, as $n$ increases and the proportion of Ni$^{2+}$/O$_6$ octahedra decreases.

To investigate the magnetism of iridium, we measure the XAS near the Ir $L_{2,3}$ edges using both left- and right- polarized X-rays. The spectral difference, known as the XMCD, is sensitive to the net magnetic moments of the ions. Specifically, a nonmagnetic system would have no XMCD signal, a ferromagnetic system would exhibit a large signal, and an antiferromagnetic or paramagnetic system would exhibit a small signal in an applied magnetic field. As displayed in Fig. 3D, all samples exhibit a negative signal at the Ir $L_3$ edge that is modest compared to bulk Sr$_2$IrO$_4$ (44) and a markedly smaller signal with no clear meaning of the Ir moments in the superlattices may be either paramagnetic or canted antiferromagnetic.

With this information, we can determine which density-of-states scenario (Fig. 1 E or F) is realized in these superlattices. As the XMCD results clearly demonstrate the existence of a local moment on Ir, the system cannot be in the strong SOC limit, as would one then expect a nonmagnetic $J_{eff} = 0$ ground state (Fig. 1E). Furthermore, as our XLD results suggest elongated octahedra, we expect the adjacent Ir$_2$O$_6$ octahedra to be compressed, removing the $t_{2g}$ degeneracy by lowering the $d_{xy}$ orbital. In fact, it has been recently shown that the validity of the strong SOC limit critically depends on the degree of Ir$_6$ octahedral distortions which can induce a noncubic CF splitting of comparable strength (33, 34), causing strong mixing of the $J_{eff} = 1/2$ and $J_{eff} = 3/2$ states. As a result, the SOC no longer dominates the level structure of the Ir $t_{2g}$ orbitals and, instead, the CF energy scale dominates the electronic structure (Fig. 1F). This scenario is consistent with all our experimental observations.

To further elucidate the microscopic details of the SrIrO$_3$/LaNiO$_3$ interface and the associated electronic reconstruction, we carried out first-principles calculations. As the films are coherently strained to SrTiO$_3$, we constrain the in-plane lattice constants ($a$ and $b$) while allowing the $c$ axis to relax for a variety of starting tilt patterns. The lowest-energy structure found has $Pc$ symmetry and $c = 8.13$ Å, with a tilt pattern derived from $a\rightarrow a\rightarrow c\rightarrow c\rightarrow a\rightarrow c$, where the tilt angles around the $c$ axis are different in the Ni and Ir layers, consistent with our experimental observation (SI Appendix, Fig. S2). The computed $c$ axis of the LaNiO$_3$ layer ($4.22$ Å) is elongated relative to LaNiO$_3$ under tensile strain on SrTiO$_3$ ($3.76$ Å) and the $c$ axis of the
SrIrO$_3$ layer (3.91 Å) is compressed relative to SrIrO$_3$ under compressive strain on SrTiO$_3$ (4.05 Å). The NiO$_6$ octahedra are elongated along one axis and have a volume of 11.4 Å$^3$, about 13% larger than in LaNiO$_3$ on SrTiO$_3$, similar to electron-doped SmNiO$_3$ (47, 48). The IrO$_6$ octahedra have a volume of 10.9 Å$^3$, about 4% smaller than SrIrO$_3$ on SrTiO$_3$, and are compressed along one axis of the octahedra. It is the electron transfer that leads to the substantial difference from the strained bulk values and leads to a net overall volume increase of the system relative to the average of the constituent compound volumes. We conjecture that such a deformation of octahedra at the interface is due to the cooperative effects of the NiO$_6$ octahedra expansion within the epitaxial constraint and the Madelung energy response to the charge modulation. The latter is described by a simple ionic model (49) in which the charge transfer leads to the formation of Ni$^{2+}$O$_6$ and Ir$^{3+}$O$_6$ planes, with net charge $-$2 and +1, respectively. The apical O$^{2-}$ ions tend to shift away from the negatively charged NiO$_2$ planes and toward the positively charged IrO$_2$ planes. As a consequence, the NiO$_6$ octahedra are elongated while the adjacent IrO$_6$ octahedra are compressed.

We find the relative energies of the Ir and Ni orbitals, consistent with Fig. 1F, to be intimately linked with the octahedral compression and elongation, respectively, and the associated crystal-field splitting. Ni has a local magnetic moment of 1.6 $\mu_B$ indicating a high-spin ($S = 1$) Ni$^{2+}$ state and Ir has a magnetic moment of 0.8 $\mu_B$ indicating an orbital splitting dictated by the crystal-field splitting, noting that SOC alone would result in a nonmagnetic $J_B = 0$ state. The magnetic ordering in the Ni layers is checkerboard-type antiferromagnetic (AFM), with moments directed along the c axis. In the Ir layers, the moments lie in the ab plane with a checkerboard ordering where the moments have an $\approx 150^\circ$ angle to one another, resulting in an in-plane ferrimagnetic ordering. Doubling the supercell along the c axis, we find that the magnetic orderings within the Ni and Ir layers remain the same and various relative alignments from layer to layer result in the same energy to within 0.3 meV per magnetic ion. This negligible interplane coupling implies that the system is not ferromagnetic and suggests the smallness of the XMCD signal arises from an AFM interlayer ordering of the Ir layers or a paramagnetic ordering (see SI Appendix, Table S3 for moment components).

The results for the band structure and the Ir and Ni d-orbital projected density of states (displayed in Fig. 4) show a semimetallic state with a very small overlap between the Ni-dominated valence band (purple) and the Ir-dominated conduction band (green). This overlap can be attributed to the approximate treatment of correlation effects in DFT, which often underestimates the band gap. The top of the valence band, with Ni $d_{3z^2-r^2}$ character, is composed of the states into which the electron has been transferred. The remaining occupied Ni states ($t_{2g}$ and $d_{3x^2-r^2}$ orbitals) are lower in energy, consistent with the crystal-field splitting of an octahedron elongated along the $z$ axis. The unoccupied Ni $e_g$ orbitals are well above the conduction band minimum (SI Appendix, Fig. S7). The conduction band minimum is associated with the hole left from the transferred electron and is composed of the Ir $d_{x^2-y^2}$ orbitals, while the remaining Ir $t_{2g}$ orbitals are occupied and are positioned well below the valence band, with the unoccupied Ir $e_g$ orbitals above the conduction band minimum. We comment that first-principles calculation for FM ordering within the Ni layers shows dispersive $d_{x^2-y^2}$ bands which lead to metallic character (SI Appendix, Fig. S8).

Overall we find that the transferred electron localizes on Ni, leading to an $S = 1$ state due to its large Hund’s coupling. The NiO$_6$ octahedra elongate along the $c$ axis as a result of electron doping and the in-plane constraint, compressing the IrO$_6$ octahedra. This stabilizes an $S = 1$ Ir state, where the large low-symmetry crystal-field splitting dominates the spin–orbit coupling.

Going forward, first-principles calculations of the electronic structure for longer-period superlattices ($m$ and/or $n > 1$) could address a number of interesting open questions. With 1 electron per lateral unit cell transferred from the SrIrO$_3$ layer to the LaNiO$_3$ layer, as indicated by the XAS results, charge-ordered layers are expected in the longer-period superlattices, which could couple to local structural distortions and electronic states at the interface. Investigation of the transport properties for thicker layers, including charge ordering, could explain the underlying mechanism of the insulating nature of the short-period superlattices experimentally characterized and suggest additional experimental characterization.

### Conclusions

In summary, we have experimentally realized a series of high-quality iridate–niclakate superlattices. We observe up to a full electron transfer at the SrIrO$_3$/LaNiO$_3$ interface from the Ir to the Ni site, triggering a dramatic electronic and magnetic reconstruction. Unlike the vast majority of iridates where the strong SOC dominates and thus defines the ground state, here the interface-driven octahedral distortions induce a large crystal-field splitting leading to the breakdown of the SOC picture. An unusual $S = 1$ magnetic state emerges for the Ir$^{3+}$ ions in the superlattices. The experimental findings are well supported by the first-principles calculations, which reveal the Mott...
character of the band gap, determined collectively by Ir and Ni Hubbard subbands. Our findings push past the idea of “band bending” (50) for ICT systems to a regime of “band reorganization” and highlight the need for careful evaluation and possible reinterpretation of the spin–orbit-driven physics in ultrathin films and heterostructures based on 5d transition metal oxides.

Materials and Methods

Superlattice Growth. All superlattices were deposited on a (001) SrTiO₃ substrate. Sintered SrIrO₃ and LaNiO₃ targets were alternately ablated by a KrF excimer laser (λ = 248 nm, fluence ~ 1 J cm⁻²) at 2 Hz and 10 Hz, respectively (38, 51). A substrate temperature of 650 °C and an oxygen partial pressure of 50 mTorr were maintained during deposition. After growth the samples were cooled down to room temperature in 1 atm of pure oxygen. Combined in situ reflection high-energy electron diffraction, X-ray diffraction, scanning transmission electron microscopy, and reciprocal space mapping confirm the high crystallinity of the coherently strained samples with abrupt interfaces, as well as the expected thickness and periodicity (SI Appendix, Fig. S1).

Polarized X-Ray Absorption Spectra. Resonant XAS and XLD measurements near Ni L₂,3 edges were taken in the luminescence yield detection mode at beamlines 6.3.1 and 4.0.2 of the Advanced Light Source (ALS), Lawrence Berkeley National Laboratory. The X-rays were incident at an angle of 20° relative to the film surface. Resonant XMCD spectra near Ir L₂,3 edges were taken in the fluorescence yield mode at beamline 4IDD of the Advanced Photon Source (APS), Argonne National Laboratory. The X-rays were incident at an angle of 3° relative to the film surface. Data were taken in both +4 T and −4 T magnetic fields to eliminate experimental artifacts.

First-Principles Calculations. First-principles DFT calculations were carried out on the 11/11 superlattice using VASP (52), using the Perdew–Burke–Ernzerhof (PBE) exchange-correlation potential (53, 54) along with projector augmented wave (PAW) potentials (55, 56). A Hubbard U (within the rotationally invariant method of Liechtenstein et al. (57)) was included using $U_{eff} = 4.6, U_0 = 2.6, J_H = 0.6$. We use a 2 × 2 × 2 supercell, relative to the 5 atom perovskite primitive cell, with 4 B sites in each layer. To satisfy the epitaxial constraint, the in-plane lattice parameter is fixed to that of SrIrO₃ with $a = 3.94$ Å, the calculated lattice parameter of SrIrO₃ with DFT-PBE. This follows standard practice for first-principles calculations of the effects of epitaxial strain, which is based on the assumption that the relative lattice parameters for the compounds of interest are correct despite the known discrepancies of the absolute numbers from the experimental values. The out-of-plane lattice parameter is relaxed along with the internal coordinates to a tolerance of 0.005 eV/Å. The density-of-states calculations used the tetrahedral method with Bloch corrections (58) and included spin–orbit coupling.

ACKNOWLEDGMENTS. We gratefully acknowledge experimental assistance from X. Li, J.-S. Zhou, and E. Karapetrova. X.L. and J.C. were supported by the Department of Defense High Performance Computing Modernization Program for computational resources. H.-S.K. and K.H. were supported by NSF Grant DMR-1629509. D.V. acknowledges support from Office of Naval Research Grant N00014-16-1-2951. This research used resources of the Advanced Light Source, which is a DOE Office of Science User Facility under contract DE-AC02-05CH11231. This research used resources of the Advanced Photon Source, a U.S. DOE Office of Science User Facility operated by Argonne National Laboratory under contract DE-AC02-06CH11357.