Inducing n- and p-type thermoelectricity in oxide superlattices by strain tuning of orbital-selective transport resonances

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By combining first-principles simulations including an on-site Coulomb repulsion term and Boltzmann theory, we demonstrate how the interplay of quantum confinement and epitaxial strain allows to selectively design n- and p-type thermoelectric response in (LaNiO$_3$)$_3$/(LaAlO$_3$)$_1$ (001) superlattices. In particular, varying strain from −4.9 to +2.9 % tunes the Ni orbital polarization at the interfaces from −6 to +3 %. This is caused by an electron redistribution among Ni 3$d_{x^2−y^2}$- and 3$d_{z^2}$-derived quantum well states which respond differently to strain. Owing to this charge transfer, the position of emerging cross-plane transport resonances can be tuned relative to the Fermi energy. Already for moderate values of 1.5 and 2.8 % compressive strain, the cross-plane Seebeck coefficient reaches $\sim$ −60 and +100 µV/K around room temperature, respectively. This provides a novel mechanism to tailor thermoelectric materials.

Transition metal oxides are attractive for thermoelectric applications owing to their chemical and thermal stability and environmental friendliness as well as to the prominent role of electronic correlations [1, 2]. Considerable experimental and computational [3] research aims at finding oxide thermoelectrics with improved performance, mostly among bulk materials by doping [4–7] or strain [8]. An alternative strategy is to exploit heterostructuring and dimensional confinement [9–16]. This is promoted by the advancement of growth techniques that allow to design transition metal oxide superlattices (SLs) with atomic precision [17–24].

One system that has been in the focus of intensive research comprises the correlated metal LaNiO$_3$ (LNO) and the wide-gap band insulator LaAlO$_3$ (LAO). Following the initial proposal of Chaloupka and Khaliullin [25], significant effort was concentrated on controlling the degree of Ni $e_g$ orbital polarization which is absent in bulk LNO. For instance, Wu et al. reported an orbital polarization of −3 to +8 % in (LNO)$_{4}/$(LAO)$_{4}/$(001) SLs on YAlO$_3$, LaSrAlO$_4$, and SrTiO$_3$ (STO) [26]. Simulations for ultrathin (LNO)$_{3}/$(LAO)$_{1}/$(001) SLs revealed a similar variation of the orbital polarization between −4 and +2 % for LAO and STO substrates [27]. Variation of the spacer material [26, 28] or the crystallographic orientation [29] allows for even higher values.

Several studies have shown that a single or a double LNO layer confined in LAO along the [001] direction undergoes a metal-to-insulator transition (MIT) for tensile strain [19, 27, 30] and exhibits magnetic order [20, 31–33]. The origin of this MIT is, however, not related to orbital polarization, as initially proposed, but to a disproportionation into two inequivalent Ni sites [27]. With increasing LNO thickness, e.g., in (LNO)$_{3}/$(LAO)$_{3}/$(001) SLs on STO ($n = 3, 5, 10$) [16, 27, 30] or (LNO)$_{4}/$(LAO)$_{4}/$(001) SLs on STO [21, 34], the metallic behavior of the nickelate is restored.

While the confinement- and strain-induced opening of a small band gap in (LNO)$_{3}/$(LAO)$_{1}/$(001) SLs enhances strongly the thermoelectric response, the thermoelectric performance of (LNO)$_{3}/$(LAO)$_{3}/$(001) SLs was found to be impeded by (i) the two-dimensional metallic nature of the LNO region and (ii) the too thick insulating LAO spacer layer that prohibits vertical transport [16]. On the other hand, efficient thermoelectric energy conversion requires both n- and p-type materials that are structurally and electronically compatible. To this end, the selective control of interface layer stacking was recently proposed as a strategy to achieve n- and p-type response in polar (LNO)$_{3}/$(STO)$_{1}/$(001) SLs [15]. Designing the thermoelectric response necessitates quantum control over the spectral transmission function asymmetry around the Fermi energy [35, 36]. However, the distinct use of transport resonances, which are attractive for thermoelectric applications [37], has been limited to model studies [38, 39] and materials realizations are lacking so far.

In this Letter we explore the thermoelectric properties of (LNO)$_{3}/$(LAO)$_{1}/$(001) SLs from first principles. The single LAO spacer layer induces the formation of distinct Ni-derived quantum well (QW) states, while at the same time permitting electronic transport. This leads to the emergence of sharp cross-plane transport resonances associated with the 3$d_{z^2}$-derived QW states. Moreover, by using strain the orbital polarization and thus the relative position and occupation of 3$d_{x^2−y^2}$- and 3$d_{z^2}$-derived QW states can be tuned. Interestingly, this mechanism allows to precisely shift the transport resonances relative to the Fermi energy. Thereby, considerable n- and p-type thermoelectric response can be obtained in one and the same materials combination by moderately varying the control parameter epitaxial strain between −1.5 and −2.8 %. We thus exemplify how to control and optimize the thermoelectric properties of oxide heterostructures by varying layer thickness, confinement, and epitaxial strain. This opens a new area of application for the design of orbital polarization, which is intensively pursued in artificial transition metal oxides.

Methodology. We performed first-principles calculations in the framework of spin-polarized density functional theory [41] (DFT) as implemented in Quantum Espresso [42]. The generalized gradient approximation was used for the exchange-correlation functional as parametrized by Perdew, Burke, and Ernzerhof [43]. Static correlation effects were
considered within DFT+$U$ [44] using $U = 4$ and $J = 0.7$ eV for Ni $3d$, in line with previous work by us and others [15, 16, 27, 40, 45, 46]. In order to take octahedral tilts fully into account, 40-atom $\sqrt{2}a \times \sqrt{2}a \times c$ supercells were used to model the (LNO)$_3$/(LAO)$_1$ (001) SLs. Epitaxial strain is considered by varying the in-plane lattice parameter $a$ from 3.65 to 3.95 Å. The out-of-plane lattice parameter $c(a)$ was optimized in each case (Fig. 1), as were the atomic positions.

All structures exhibit an antiferrodistortive $a^-a^-c^-$ octahedral rotation pattern and ferromagnetic order (see Supplemental Material). The Brillouin zone was sampled by an $8 \times 8 \times 4$ $k$-point grid [47] and 5 mRy smearing [48]. The BoltzTraP code [49] was used to obtain converged energy- and spin-resolved transmission functions $T_\sigma(E)$ in Boltzmann theory (using a denser $64 \times 64 \times 16$ $k$ point grid) and thermoelectric quantities according to Sivan and Imry [35], an approach we have employed also in previous studies [15, 16, 36, 50, 51]; it is described in the Supplemental Material.

Interplay of structure and orbital polarization. Figure 1 shows the optimized (LNO)$_3$/(LAO)$_1$ (001) SL structures and cell heights $c(a)$ for several in-plane lattice parameters $a$, modeling the growth on a variety of substrates imposing compressive strain [such as ScAlO$_3$ (3.60 Å), YAlO$_3$ (3.716 Å), or LAO (3.79 Å)] or tensile strain [such as STO (3.905 Å), DyScO$_3$ (3.94 Å), or GdScO$_3$ (3.976 Å)] [55, 56]. The relaxed $c(a)$ parameters for discrete $a$ values were fitted to $c(a) = c_0 \tanh \{a(a - a_i)\} + c_1$, rendering $c_0 = 0.934 \AA$, $c_1 = 15.86 \AA$, $a = 4.818/\AA$, and $a_i = 3.773 \AA$ (inflexion point). With the pseudocubic lattice parameter of LNO, $a_{LNO} = 3.838 \AA$ [40], this corresponds to degrees of epitaxial stain $\epsilon = a/a_{LNO} - 1$ ranging from $-4.9$ to $+2.9\%$.

The strong octahedral rotations around the $c$ axis present for compressive strain are continuously reduced while shifting to tensile strain. This is reflected in part in the basal $B$-$O$-$B$ bond angles that increase from 153° to 161° (Ni) and from 161° to 165° (Al; 180° implying the absence of any rotation). In contrast, while almost no octahedral rotations around the $a$ axes are present for strong compressive strain, they appear at $a \approx 3.80 \AA$, signaled by a sudden decrease of the apical bond angles that increase from $150°$ to $180°$.

Figure 1. Top and side views of optimized (LNO)$_3$/(LAO)$_1$ (001) SLs for $a = 3.65$, 3.79, and 3.95 Å, ranging from compressive (left) to tensile (right) epitaxial strain. Below, several optimized $c(a)$ values are shown, together with a fitted curve. Moreover, $B$-$O$-$B$ bond angles and $O$-$B$ distances are provided as functions of the substrate lattice parameter $a$. Green (red) circles mark DFT (XRD) results for bulklike LNO films on LAO and STO. [40] Pseudocubic lattice parameters of LAO, LNO, and STO are 3.79, 3.838, and 3.905 Å, respectively.
B-O-B bond angles (stronger tilts) from ~ 175° to 165°. This onset is located close to the inflection point $\alpha_0$ of the $\epsilon(\alpha)$ curve; the relaxation pattern around this point has been carefully checked to avoid local minima. The basal O-Ni-O and O-Al-O distances increase from 3.7 to 4.0 Å, whereas the apical O-Al-O and interfacial O-Ni-O distances decrease from 3.95 to 3.78 Å and from 4.2 to 3.9 Å, respectively. The central apical O-Ni-O distance is almost constant (~ 4 Å). Comparison of the nickelate region to DFT and x-ray diffraction (XRD) results for 100–200 Å thick LNO films grown on LAO and STO substrates [40] reveals major similarities, e.g., the strong variation of the apical bond angles with $\alpha$ (Fig. 1). Similar to the (LNO)$_3$(LAO)$_3$ (001) SLs and at variance with the (LNO)$_3$(LAO)$_3$(001) SLs [16], the present system shows no tendency towards an in-plane Ni-site disproportionation and remains metallic for all considered substrate lattice constants.

We quantify the octahedral regularity $R$ and the Ni 3$d_{e_g}$ orbital polarization $P$ (from O-B-O distances $d$ and Ni orbital occupations $n$) shown in Fig. 2 by the expressions

$$ R = \frac{d_{basal}-d_{apical}}{d_{basal}+d_{apical}}, $$

$$ P = \frac{n(3d_{2\times \text{y}^2})-n(3d_z)}{n(3d_{2\times \text{y}^2})+n(3d_z)}. $$

Positive (negative) values of $R$ denote a compression (elongation) in the [001] direction, while positive (negative) values of $P$ imply a preferential occupation of the in-plane $3d_{2\times \text{y}^2}$ (out-of-plane $3d_z$) orbitals. We reduce projection errors arising from the tilts of the octahedra by applying a simple correction scheme to the ‘Cartesian’ orbital occupations (see Supplemental Material). While $P$ is almost constant in the central LNO layer (~ +1 %), it changes from ~ -6 % (compressive strain) to ~ +3 % (tensile strain) in the interfacial LNO layers. Likewise, $R$ of the interfacial NiO$_6$ octahedra shows the strongest strain dependence and varies between -6 and +1.25 %. Experiments on (LNO)$_3$(LAO)$_3$(001) SLs found a similar variation of $P$ with strain [26]. We thus conclude from Fig. 2 that the interfacial Ni orbital polarization can be designed considerably by strain, displaying the strongest variation around $\alpha = 3.80$ Å.

The evolution of the electronic structure with epitaxial strain is shown exemplarily for $\alpha = 3.70$ and 3.80 Å in Fig. 3. As previously observed in (LNO)$_3$(STO)$_3$(001) and (LNO)$_3$(LAO)$_3$(001) SLs [15, 16], distinct Ni $3d_{2\times \text{y}^2}$ and $3d_z$-derived QW states form within the band gap of the spacer material due to confinement. While the $3d_{2\times \text{y}^2}$-derived QW states are restricted to single LNO layers and show almost no influence of the LAO spacer layer, the $3d_z$-derived QW states extend over the entire QW and split up strongly. Consequently, the two sets of states have a distinct response to a variation of the substrate lattice parameter: With increasing strain, the $3d_{2\times \text{y}^2}$ ($3d_z$-) derived QW states are shifted to lower (higher) energies. This impacts the band occupations: Figure 3 shows that the strong increase of $P$ in the interfacial LNO layers with strain (Fig. 2) is caused by a charge transfer from the localized 2nd $3d_z$-derived QW state to the set of dispersive $3d_{2\times \text{y}^2}$-derived QW states. (More information can be found in the Supplemental Material.)

Thermoelectric response exploiting transport resonances. The single LAO spacer layer allows for a significant cross-plane electronic transmission (Fig. 3). In particular, resonances emerge, which originate from the $3d_z$-derived QW states and whose position can be shifted considerably with respect to the Fermi energy $E_F$ by epitaxial strain. We empha-
electricity is strongly improved in the (LNO)$_3$/(LAO)$_1$ (001) SL with respect to bulk LNO and (LNO)$_3$/(LAO)$_1$ (001) SLs [16] owing to the reduction to a single LAO spacer layer. The system attains $S$ and $ZT_{|\sigma|}$ values that are similar in magnitude to those of metallic (LNO)$_1$/(LAO)$_1$ (001) SLs at $a_{\text{LAO}}$ or (LNO)$_3$/(STO)$_1$ (001) SLs at $a_{\text{STO}}$ [15, 16]. Only (LNO)$_1$/(LAO)$_1$ (001) SLs at $a_{\text{STO}}$, which undergo a MIT for tensile strain [27], show better values that are comparable to the best oxide thermoelectrics [16]. Another beneficial feature of the LAO layers is that they are expected to scatter LNO phonons due to the high mass difference, thereby reducing the detrimental cross-plane lattice thermal conductivity.

**Summary.** By combining density functional theory calculations with an on-site Coulomb repulsion term and Boltzmann theory in the constant relaxation time approximation, we explored the thermoelectric properties of (LaNiO)$_3$/(LaAlO)$_3$ (001) superlattices and the impact of different substrate lattice parameters. Variation of epitaxial strain between $-4.9$ and $+2.9$ % causes an electron redistribution among Ni 3$d_{x^2-y^2}$ and 3$d_{z^2}$-derived quantum well states that results in a considerable change in the orbital polarization ($-6$ to $+3$ %). Concomitantly, sharp cross-plane transport resonances emerging from the 3$d_{z^2}$-derived quantum well states, induced by the confinement due to the single LaAlO$_3$ spacer layer, can be shifted relative to the Fermi energy. Already slight variation of the control parameter epitaxial strain between $-1.5$ and $-2.8$ % is sufficient to selectively induce a considerable $n$- and $p$-type thermoelectric response ($-60$ and $+100$ $\mu$V/K) in one and the same oxide superlattice. This constitutes an interesting mechanism and a concrete materials realization in an oxide system of current interest that calls for further experimental and theoretical exploration. We expect that the results can be extended to a broader class of oxide heterostructures.

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