

Chapter 2

The Rare-Earth Nickelates

2.1 Bulk Electronic, Magnetic, and Structural Properties

The rich phase diagram of rare-earth nickelates $R\text{NiO}_3$ (with R = rare-earth or Y), has been subject of interest in a great variety of studies since more than 20 years [1–3]. The phase space of bulk $R\text{NiO}_3$ spans from a Pauli paramagnetic metal to paramagnetic insulator to unconventional period-four antiferromagnet [Fig. 2.1]. The phase diagram's complexity originates from a fine balance between bandwidth and correlation energies that is mediated by the perovskite lattice distortions

The properties of rare-earth nickelates are determined by the ionic radius r_R of the rare-earth R . The ground state of the family member with the largest radius, LaNiO_3 , is paramagnetic metallic with space group $R\bar{3}c$ [Fig. 2.1a, b]. All other members exhibit a relatively sharp metal-insulator transition (MIT) with the transition temperature T_{MI} monotonically increasing with decreasing rare-earth ionic radius - from PrNiO_3 with ~ 130 K, to NdNiO_3 with ~ 200 K, to SmNiO_3 with ~ 400 K, up to YNiO_3 with ~ 560 K [6]. For PrNiO_3 and NdNiO_3 the MIT coincides with an antiferromagnetic phase transition, whereas the magnetic onset temperature T_N is lower than T_{MI} for smaller rare-earths, with an intermediate paramagnetic insulating phase. For $R \neq \text{La}$ the space group of the high-temperature metallic phase is of orthorhombic $Pbnm$ symmetry, which is reduced to monoclinic $P2_1/n$ when the nickelate undergoes the transition to the insulating state. For PrNiO_3 and NdNiO_3 the monoclinic distortion is relatively faint and only one Raman study [7] and recent state-of-the-art high-resolution powder x-ray and neutron diffraction have found clear evidence for its presence [8, 9].

Another parameter classifying the rare-earth nickelates is the so-called *tolerance factor* t [Fig. 2.1a]. The tolerance factor is generally used to characterize perovskite structures [10] and is defined as $t = d_{R-O}/\sqrt{2}d_{\text{Ni-O}}$, where d_{R-O} and $d_{\text{Ni-O}}$ are the ionic bond distances. The ideal undistorted perovskite structure manifests itself by $t = 1$. The ionic radii of the rare-earth ions of the $R\text{NiO}_3$ family, however, are generally not large enough to accommodate the cubic lattice. Hence, t is smaller than unity throughout the entire phase diagram of Fig. 2.1b, except for a small pocket

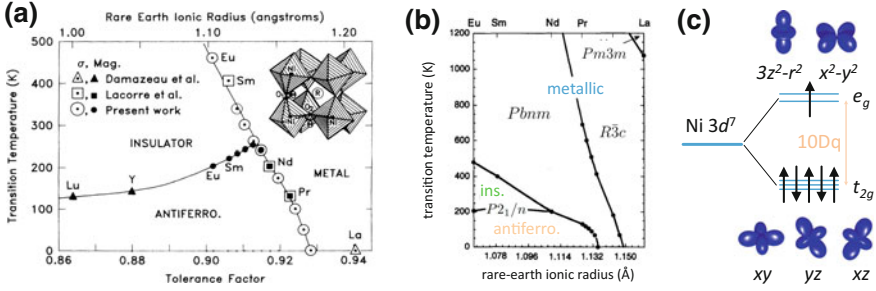


Fig. 2.1 Rare-earth nickelates in bulk. **a** Insulator-metal-antiferromagnet phase diagram of the $R\text{NiO}_3$ family as a function of the ionic radius of the rare-earth R or the tolerance factor. The data points in-between the $R\text{NiO}_3$ family members correspond to compounds with mixed rare-earth composition. The figure is reprinted with permission from Ref. [4] and includes data from references therein. Copyright (1992) by the American Physical Society. **b** Phase diagram of the crystallographic symmetries of the rare-earth nickelates. The figure is reprinted from Ref. [5] with permission from Elsevier Ltd. **c** Energy level diagram of the Ni ion in the $R\text{NiO}_3$ compound. The formal $\text{Ni}^{3+} 3d^7$ state is in low-spin configuration. An O_h symmetry crystal field ($10Dq$) splits the 5-fold degenerate orbitals into an e_g and t_{2g} manifold

corresponding to space group $Pm3m$ in the case of LaNiO_3 at very high temperatures. In first approximation, a reduction in the tolerance factor is accommodated by the tilts of the NiO_6 octahedra. In a simplified picture, the bending of the Ni-O-Ni angle (see inset in Fig. 2.1a) reduces the orbital overlap of Ni $3d$ and oxygen $2p$ and promotes the insulating state over the metallic one, rendering LaNiO_3 with the straightest bond angles metallic down to lowest temperatures.

In the ABO_3 stoichiometric composition the Ni ion formally exhibits a $3+$ valence with low-spin $3d^7$ ($t_{2g}^6 e_g^1$) configuration and one electron in the twofold degenerate e_g orbitals [Fig. 2.1c]. Naturally, this electron interacts with the crystal field environment and in correspondence to similar TMO systems [11] the degeneracy of the e_g levels is expected to be split by a Jahn–Teller distortions of the oxygen octahedra [6, 12, 13]. However, the fingerprints of such lattice distortion and the concurrent orbital order could not be detected in bulk and bulk-like samples [14]. Instead it was suggested that a charge disproportionation between adjacent Ni^{3+} ions of the form $\text{Ni}^{3+\delta}$ and $\text{Ni}^{3-\delta}$ could lift the degeneracy, in correspondence to the two inequivalent Ni sites of the monoclinic $P2_1/n$ ground state. The $P2_1/n$ structure exhibits two types of NiO_6 octahedra, one set is compressed and has short Ni-O bonds (SB), and the other set of octahedra is expanded and has long Ni-O bonds (LB) [Fig. 2.2a]. Generally, a charge transfer between the Ni ions should be suppressed by the on-site Coulomb repulsion U , however, in presence of a sizable Hund’s coupling a disproportionated can be stabilized if the system is close to the itinerant limit [15].

The picture relating the MIT and the concomitant structural transition to the occurrence of an order parameter equivalent to the Ni charge disproportionation was supported by resonant x-ray scattering experiments at the Ni K -edge at 8340 eV [14]. Staub et al. measured a modulated intensity of specific Bragg reflections when the

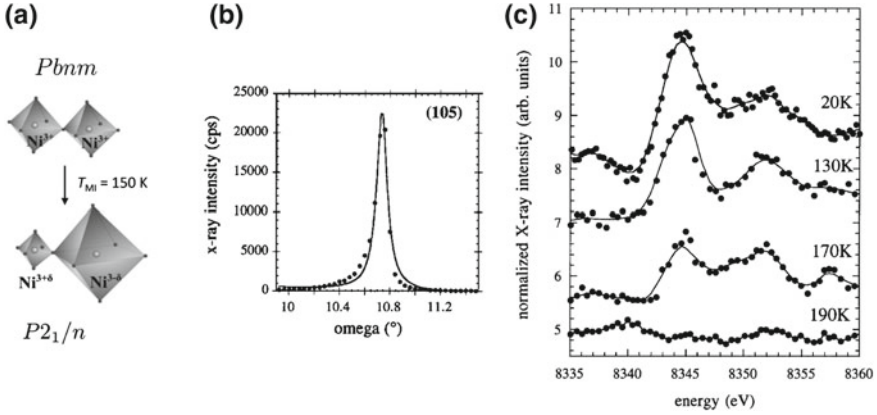


Fig. 2.2 Structural phase transition and charge order. **a** Nickelates with orthorhombic crystal symmetry (space group $Pbnm$) exhibit uniformly sized NiO_6 octahedra. Concomitant with the MIT the volume of one set of octahedra collapses while the other set expands, corresponding to space group $P2_1/n$. The structural transition of NdNiO_3 occurs at 150 K upon cooling [14]. Some theoretical models relate the transition to a charge disproportionation of Ni^{3+} ions to $\text{Ni}^{3+\delta}$ and $\text{Ni}^{3-\delta}$, whereas other models describe the transition in terms of a bond disproportionation without charge transfer between adjacent Ni ions. **b** Rocking scan of the $(105)_{\text{or}}$ Bragg reflection at 190 K. **c** Intensity of the $(105)_{\text{or}}$ reflection in dependence of the energy for selected temperatures below and above the MIT. Panel **b** and **c** are reprinted with permission from Ref. [14]. Copyright (2002) by the American Physical Society

incident x-ray energy was tuned through the Ni K -edge. This was interpreted as a signature of Ni being present in two different valence states. In the study reflections of $(h0l)_{\text{or}}$ and $(0hl)_{\text{or}}$ type with h and l odd [Fig. 2.2b] are considered (here orthorhombic indexing is used). In $Pbnm$ symmetry with a single Ni site the structure factor of these reflections is not sensitive to the considered resonance effects, i.e. in first approximation the peak intensity is independent of the energy.¹ In $P2_1/n$, on the other hand, the presence of two inequivalent Ni sites and their structure factors leads to a complex interference when the phase shifts of the x-ray wavefronts add up, with the real and imaginary part simultaneously playing a role in the scattered intensity. This yields the wiggly lineshape in Fig. 2.2c as the energy is scanned through the resonance. Note that it is difficult to detect the presence of slightly different structure factors in the corresponding K -edge absorption experiments [17]. In more detail, each Ni site exhibits a different core potential, slightly shifting the position of the absorption edge in the x-ray absorption spectrum (XAS). Since the absorption is proportional to the imaginary part of the scattering factor, which here is a simple superposition of the two, only the average of the two sites is measured. Thus possible differences between them are just washed out into a slightly broader spectrum.

¹Recently it has been shown by Lu et al. that also mere octahedral tilt distortions yield an energy dependence of the Bragg peaks at the Ni K -edge [16].

Also note that the occurrence of two inequivalent Ni sites basically doubles the size of the pseudocubic unit cell which can result in superstructure peaks of $\mathbf{q}_{CO} = (\frac{h}{2}, \frac{k}{2}, \frac{l}{2})$ (now pseudocubic indexing is used). However, the soft x-ray regime employed in this thesis (comprising e.g. the Ni L -edges with $2p \rightarrow 3d$ transition) does not provide sufficient momentum transfer to access this point in reciprocal space experimentally. Conversely, the momentum transfer in hard x-ray K -edge experiments is high, but the electronic transition corresponds to $1s \rightarrow 4p$, i.e. the states close to the Fermi level of $3d$ TMOs are not probed directly. Still, these experiments can be sensitive to the local electronic and crystallographic environment of the respective TMO ions with complex resonant lineshapes arising from details of the scattering tensor [16, 18–20].

From a theoretical point of view there are many studies that have reassessed the traditional interpretation of the charge-ordered state in terms of $\text{Ni}^{3+\delta}$ and $\text{Ni}^{3-\delta}$ valence states stabilized by Hund’s rule interactions [15, 22–25]. One set of models has invoked an unusual electron-phonon interaction that modulates the covalency of the Ni-O bond so that the charge transfer, δ , between adjacent Ni sites vanishes both above and below the MIT [21, 26–30]. The approach treats the nickelate as *negative charge transfer* material, as introduced by Mizokawa et al. [31, 32], and starts with a Ni $3d^8$ electron configuration with a ligand hole $\underline{L}$ at the oxygen [Fig. 2.3]. In the extreme limit the disproportionation then corresponds to

$$2 (\text{Ni } d^8 \underline{L})_{S=1/2} \rightarrow \text{Ni } (d^8 \underline{L}^2)_{S=0} + \text{Ni } (d^8)_{S=1}, \quad (2.1)$$

with the total spin S . Hence the charge disproportionation rather happens at the ligand oxygen state than at the Ni. Also in this picture the uniformly sized NiO_6 octahedra of the metallic phase split into sets of collapsed (SB, $d^8 \underline{L}^2$) and expanded octahedra (LB, d^8). In the strong-coupling limit the SB sites correspond to a Kondo insulator and the LB sites to a Mott insulator, which is why the transition has been called ‘site-selective Mott transition’ by the authors of Ref. [28]. This associates the MIT with a change of the covalency of the bonds rather than an actual charge transfer [12, 33]. Therefore the ground state has been coined *bond ordered* instead of *charge ordered*.

According to another model, the MIT of the more itinerant members with $R = \text{Nd}$ and Pr is caused by spin density wave formation, with charge/bond order as a secondary order parameter in some (but not all) lattice structures [36, 37]. However, the antiferromagnetic order of the nickelates with an unusually large periodicity is generally subject of an ongoing discussion. Whereas other perovskite TMOs show the tendency to form antiferromagnetic order via dominant next-nearest neighbor superexchange which leads to a doubling of the pseudocubic unit cell neutron studies of nickelates consistently found an unusual period-four antiferromagnetic order along the pseudocubic (111) body diagonal, i.e. the propagation vector was determined as $\mathbf{q}_0 = (1/4, 1/4, 1/4)$ [13, 38], corresponding to $(1/2, 0, 1/2)_{or}$ in orthorhombic notation. From the neutron powder diffraction data collinear ($\uparrow\uparrow\downarrow\downarrow$) and non-collinear ($\uparrow\rightarrow\downarrow\leftarrow$) spin configurations could not be discerned. What could be resolved, however, were the Ni magnetic moments corresponding to distinct Ni

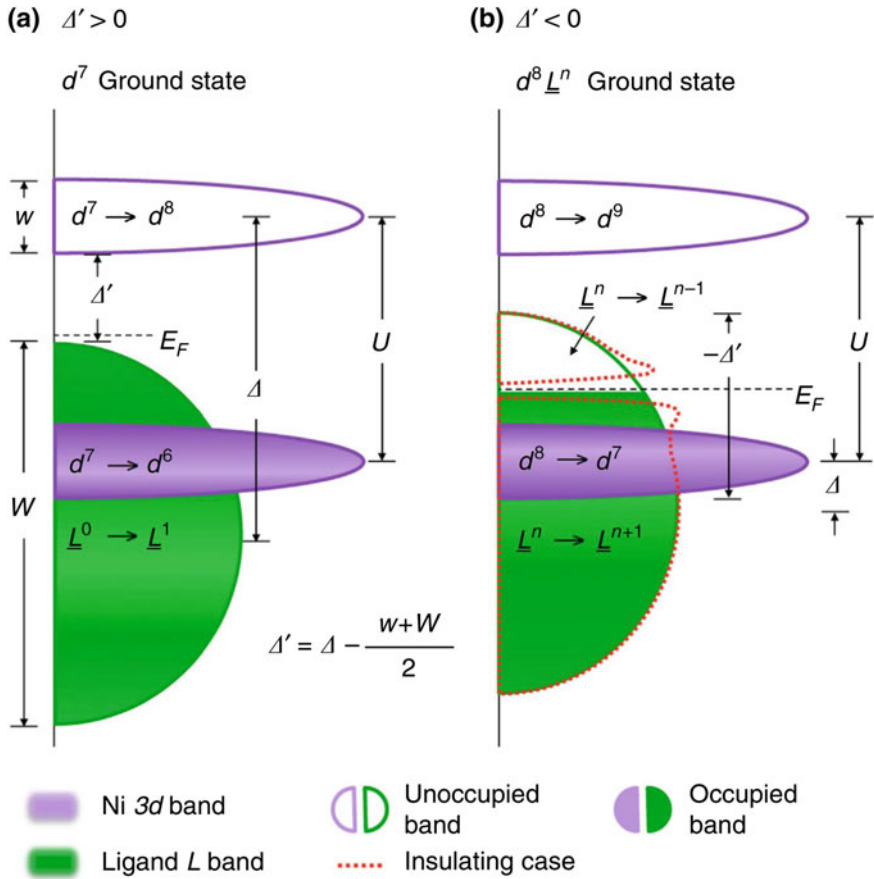


Fig. 2.3 Negative charge transfer gap character of nickelates. **a, b** Single electron excitation spectra in terms of charge removal and charge addition for different regimes of effective charge-transfer Δ' . The charge transfer energy, i.e. the cost for transferring an electron/hole from the ligand band to the Ni 3d band, is Δ . The (Hubbard) U is the cost needed to remove an electron from the occupied 3d band and to add it to the unoccupied 3d band. **a** Positive charge transfer compound ($\Delta' > 0$). The lowest energy removal states are ligand-based and the lowest energy addition states are transition metal based, leading to a charge transfer derived energy gap ($O\ 2p - Ni\ 3d$ like) and a $3d^7$ ground state. **b** In negative charge transfer compounds ($\Delta' < 0$), one hole per Ni is doped into the ligand band, giving a density of ligand holes n , L^n . The ground state is $d^8 \underline{L}^n$. The red-dashed contour bands are a cartoon-like demonstration of the opening of the gap in the mainly $O\ 2p$ continuum resulting in the MIT. Here, the lowest energy removal and addition states are both ligand-based, leading to an $O\ 2p - O\ 2p$ like gap. Ni-O hybridization are neglected to provide clear distinction between the regimes. The figure is reprinted from Ref. [21] and licensed under CC BY 4.0

sites of the SB and LB octahedra with 1.4 and 0.6 μ_B for $HoNiO_3$ and 1.4 and 0.7 μ_B for $YNiO_3$ [6, 39]. Early neutron studies investigating the larger rare-earths were not able to distinguish different moment sizes and detected 0.9 μ_B in case of $NdNiO_3$ and

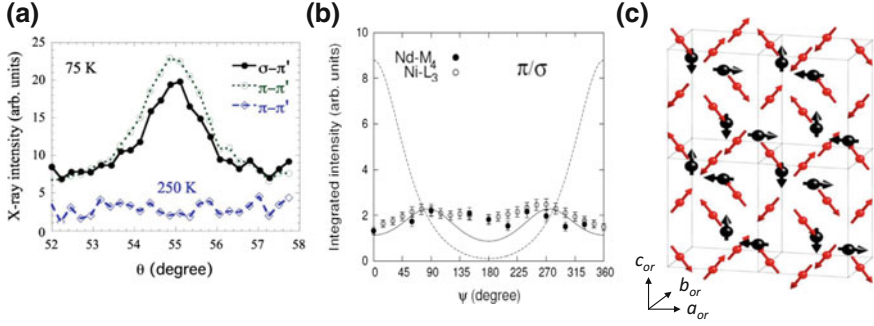


Fig. 2.4 Resonant magnetic x-ray scattering. **a** Rocking scans of the magnetic Bragg reflection of NdNiO₃ at $\mathbf{q}_0 = (1/4, 1/4, 1/4)$ below (75 K) and above (250 K) T_N for π and σ photon polarizations. The energy is tuned to the Ni L_3 edge. The figure is reprinted with permission from Ref. [34]. Copyright (2006) by the American Physical Society. **b** Azimuthal dependence of the π/σ ratio measured in resonance to the Ni L_3 (open circles) and the Nd M_4 edge (filled circles), respectively. The superimposed solid and dashed lines are the simulated dependencies of non-collinear ($\uparrow \rightarrow \downarrow \leftarrow$) and collinear ($\uparrow \uparrow \downarrow \downarrow$) spin order, respectively. The collinear order corresponds to spins oriented within the ab plane of the orthorhombic unit cell. The non-collinear spin configuration is shown in **c**. Ni ions and their corresponding spins are indicated in red color and Nd ions and spins in black. Dashed lines are the borders of the orthorhombic unit cells. Panel **b** and **c** are reprinted with permission from Ref. [35]. Copyright (2008) by the American Physical Society

PrNiO₃ [40] which is close to the purely ionic value of $1 \mu_B$ of Ni³⁺ but inconsistent with a charge/bond disproportionation scenario with SB and LB sites.

Scagnoli et al. addressed the open question of spin collinearity versus non-collinearity by magnetic resonant x-ray diffraction experiments on bulk-like NdNiO₃ films [34, 35]. As described in Chap. 3 the intensity of a magnetic Bragg reflection depends on the relative orientation between the incident x-rays and the local orientation of the magnetic moments. When the sample is rotated around the azimuthal angle ψ this relative orientation changes and from the modulation of the intensity the spin configuration can be deduced. The experimental results shown in Fig. 2.4b indicated an orthogonal spin spiral of the type ($\uparrow \rightarrow \downarrow \leftarrow$) and ruled out a collinear ($\uparrow \uparrow \downarrow \downarrow$) model.

2.2 Nickelate Heterostructures

Specifically designed heterostructures offer alternative routes to study the manifold physics of strongly correlated TMOs. Beside the possibility to stabilize chemical phases, which are hard or impossible to grow in bulk form,² structural distortions

²Note that the synthesis of large single crystals of rare-earth nickelates has not been achieved yet with common crystal growth methods, as an extremely high oxygen pressure at high temperatures would be required to stabilize Ni in its 3+ state of oxidation. Few exceptions are reported in Refs. [41, 42],

can be systematically influenced by the epitaxial relationship with the underlying substrate or a second-component material, confinement of the electron system can be realized through reduced layer thicknesses, and interfacial reconstructions and interactions might occur depending on the combination of different materials [43].

Heterostructures comprising rare-earth nickelates as component are particularly intriguing since the material class features a delicate competition between spin, charge, orbital, and lattice degrees of freedom. In such an environment a pronounced susceptibility to external control parameters influencing this competition comes naturally. Over the last years an impressive number of studies has demonstrated how the microscopic and macroscopic properties of nickelates can be widely influenced and controlled via epitaxial strain [44–48], external electric fields [49], chemical doping and electrolyte gating [2, 50, 51], light induced lattice distortions [52–54], reduced thickness of the active layer [55], spatial confinement of the conduction electrons through proximity to a band insulator [56], altered geometrical motifs of the underlying crystal lattice [3, 57–60], and interfacial exchange interactions [61, 62]. A recent review on the topic is given in Ref. [63]. A selection of the key findings in nickelate heterostructures is discussed in the following.

- **Suppressed order parameters:** Epitaxy and lattice mismatch to a substrate can have severe impact on the intrinsic lattice distortions of nickelates. This allows for a tuning of the strength of electronic and magnetic correlations and therewith the transition temperatures T_{MI} and T_{N} . Whereas the transitions of [001] oriented thin films under tensile strain are similar to bulk, T_{MI} and T_{N} can be suppressed down to lowest temperatures for sufficiently large compressive strain [45, 64]. Table A.1 and Table A.2 in Appendix A give an overview on the lattice parameters of nickelates and common oxide substrates. Substrates with larger lattice parameters induce tensile strain to the nickelate while smaller lattice parameters induce compressive strain.

In addition, femtosecond pump-probe experiments demonstrated a melting of the magnetic ground state and an increase of the electrical conductivity by five orders of magnitude through light pulses resonant with specific lattice vibrational modes [52–54]. These observations confirm a strong coupling between the lattice and the electronic degrees of freedom and provide a new way of dynamically controlling the nickelates' ground state.

- **Induced order parameters:** In bulk, the ground state of LaNiO_3 is paramagnetic metallic. Boris et al. have shown that LaNiO_3 layers in LaNiO_3 - LaAlO_3 superlattices as thin as two unit cells undergo a sequence of collective metal-insulator and antiferromagnetic transitions as a function of decreasing temperature, whereas samples with thicker LaNiO_3 layers retain bulk properties. The transition to the antiferromagnetic state was later confirmed by Frano et al. by REXS and the

(Footnote 2 continued)

with very small and heavily twinned crystals. The feasibility of stabilizing nickelates as powders or as films on a substrate up to a critical thickness, however, is long known. In specific cases the films resemble the bulk-like properties in other cases the epitaxy to the substrate alters the nickelate's properties.

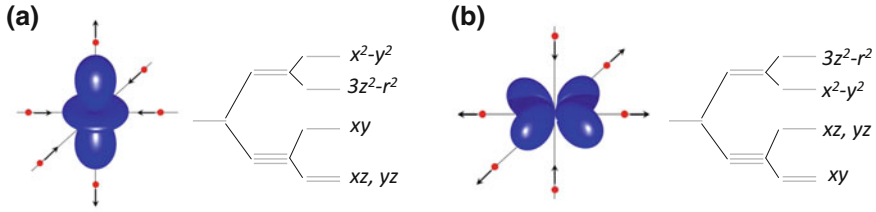


Fig. 2.5 Orbital polarization induced by tetragonal lattice distortions. **a** Tetragonal (D_{4h}) distortion of the NiO_6 octahedron lifting the degeneracy of the e_g and t_{2g} orbitals. A compression along the in-plane directions yields preferred occupation of the $d_{3z^2-r^2}$ orbital. **b** Elongation along the in-plane directions yields preferred occupation of the $d_{x^2-y^2}$ orbital

magnetic spin configuration in the heterostructures was revealed, as described in more detail later in the text.

- Separated order parameters:** For bulk NdNiO_3 and films grown under tensile strain on [001] oriented substrates the MIT and the antiferromagnetic transition coincide. Catalano et al. found T_{MI} and T_{N} widely separated in the particular case of NdNiO_3 grown on [111] oriented NdGaO_3 substrates [57]. Here NdNiO_3 resembles the bulk properties of SmNiO_3 . The study will be described further below.
- Orbital polarization:** Distortions of the local symmetry of the NiO_6 octahedra can lift the degeneracy of the Ni e_g orbitals [Fig. 2.5] [65, 66]. Benckiser et al. could resolve orbital polarization profiles in the atomic layers of LaNiO_3 - LaAlO_3 heterostructures and disentangle the influence of epitaxial strain from interfacial effects controlled by the chemical composition of the insulating blocking layers [67]. Along the pseudocubic [001] direction at the interface to a band insulator a reduced out-of plane orbital occupation was revealed. Later it was shown by Wu et al. that the occupation of the $d_{x^2-y^2}$ orbital can be enhanced by about 25% predominantly through the tensile strain imposed through substrate mismatch [68, 69].
- Orbital order:** Middey et al. suggest the presence of a novel type of orbital order in NdNiO_3 - LaAlO_3 superlattices composed of two Ni layers along the [111] direction [3]. The antiferro-orbital ordered state which manifests as staggered planes of Ni $d_{3z^2-r^2}$ and $d_{3x^2-r^2}$ orbitals is unattainable in bulk nickelates and nickelate based heterostructures grown along the [001] direction. Hence the altered geometric motif of the [111] oriented crystal structure (buckled honeycomb lattice) can induce novel orbital states when combined with the spatial confinement of the electronic system.
- Interfacial charge transfer:** Charge transfer and electronic reconstructions are common phenomenon at (polar) TMO heterointerfaces. Substantial effects have been observed in nickelate multilayer systems containing RXO_3 layers with $X = \text{Ti}$ [70]. Charge is transferred across the interface from Ti to Ni which yields 50% enhanced occupation of the $d_{3z^2-r^2}$ orbitals in case of LaTiO_3 - LaNiO_3 - LaAlO_3 tricomponent superlattices [71, 72]. This kind of orbital engineering based on

symmetry-breaking and polar fields thus leads to large orbital polarizations and provides the possibility to create unique electronic systems.

Another example for interfacial charge transfer are nickelate/manganite multilayers [61], allowing the Ni ion to adopt its preferred Ni^{2+} state by accepting an electron from the Mn. Such systems which can induce specific types of magnetic order in the nickelate will be discussed in more detail further below.

- **Stabilized non-equilibrium states:** Kim et al. designed [111] oriented NdNiO_3 - LaAlO_3 heterostructures where polar displacements of the Nd cations can be stabilized because the LaAlO_3 octahedral tilt pattern counteracts that in NdNiO_3 [73]. The result is a ferroelectric polarization in the metallic phase of NdNiO_3 . Such an exotic state corresponding to a polar metal contradicts Gauss's law which dictates that the net electric field inside a conductor is zero by effective charge screening. The study combining experiments and first-principles calculations is an intriguing example of atomic-scale engineering leading to the emergence of novel and unprecedented states.
- **Predicted multiferroicity:** The charge/bond ordered ground state of the nickelates together with the period-four antiferromagnetic order is in principal prone to so-called type II multiferroicity [74, 75]. In that case a ferroelectric polarization can occur in the magnetically ordered state due to magnetostriction effects and is expected to be strongest when the spin order is of collinear ($\uparrow\uparrow\downarrow\downarrow$) type. However, to this day no conclusive experimental evidence for multiferroicity in the nickelates has been presented.
- **Predicted superconductivity:** The high- T_c cuprates exhibit an electronic configuration of $\text{Cu } d^9$ with one hole in the $d_{x^2-y^2}$ orbital. The quasi-two-dimensional electronic structure in the CuO_2 planes and the strong antiferromagnetic correlations between the Cu 1/2 spins are believed to be essential for their high- T_c superconducting state. Chaloupka, Khaliullin and other pointed out that in LaNiO_3 - LaAlO_3 superlattices with a nickelate layer thickness of only one unit cell the $d_{3z^2-r^2}$ level could be pushed above the Fermi surface, leaving only the $d_{x^2-y^2}$ relevant [76, 77]. In consequence all aforementioned ingredients might be present in a nickelate heterostructure. From the experimental side, however, a superconducting transition has not yet been observed in nickelate based superlattices.

2.2.1 Orbital Control of Non-collinear Magnetic Order

Frano et al. have used REXS to probe the antiferromagnetic spin configuration of nickelate heterostructures under (i) tensile strain, (ii) compressive strain, and (iii) additional spatial confinement [Fig. 2.6] [78]. The methodology of extracting the spin order from the azimuthal dependence of the (1/4, 1/4, 1/4) reflection is similar to the experiments of Refs. [34, 35] mentioned above. The concept will be elucidated in detail in Chap. 3 and is employed for the magnetic REXS measurements of this thesis. The heterostructures investigated by Frano et al. were oriented along the

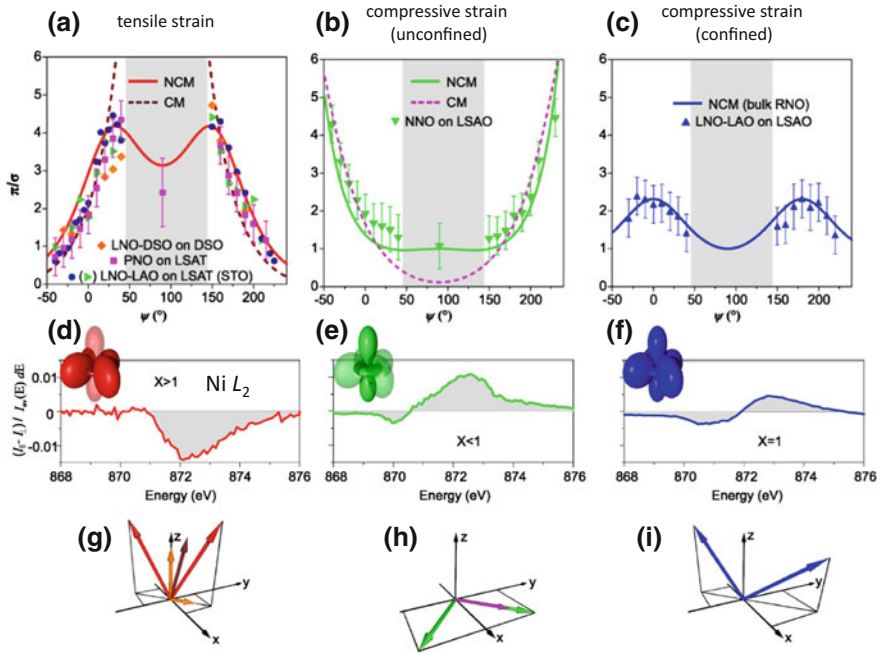


Fig. 2.6 Orbital polarization and its influence on the spin order. **a–c** Azimuthal dependencies of magnetic scattering intensities for π and σ polarized x-rays. The [001] oriented heterostructures are composed of LaNiO_3 (LNO), PrNiO_3 (PNO), NdNiO_3 (NNO), LaAlO_3 (LAO), and DyScO_3 (DSO) and grown on DSO, LSAT, and LSAO substrates. Gray shaded areas correspond to azimuthal angles ψ where the incident or outgoing beams are below the sample horizon. **d–f** X-ray linear dichroism. The normalized difference spectra $(I_{\parallel} - I_{\perp})/I_{av}(E)dE$ are obtained from the XAS around the Ni L_2 edge with incoming light polarization in and out of the (001) plane. The sign of the hole ratio X is stated in each panel. Insets with the color-coded solid and semitransparent e_g orbitals illustrate the corresponding imbalance of orbital occupancy, i.e. the orbital polarization. **g–i** Cartoons of the spin order influenced by orbital polarization. The axis x , y and z correspond to the pseudocubic [001] reference frame and the color-coding refers to panels (a)–(c). For simplicity only the first two spins of the period-four antiferromagnetic spin spiral are shown. The two omitted spins are the corresponding negative vectors. Spins of different color (orange and dark red in **g** and purple in **h**) are alternative spin configurations from the model calculations. The configuration of the blue spins in (i) is similar to the orthogonal ($\uparrow \rightarrow \downarrow \leftarrow$) spiral found in bulk-like nickelate films [34, 35]. The figure is adapted with permission from Ref. [78]. Copyright (2013) by the American Physical Society

[001] pseudocubic direction whereas the bulk-like nickelate films of Refs. [34, 35] were oriented along the [111] direction, coinciding with the $\mathbf{q}_0 = (1/4, 1/4, 1/4)$ magnetic propagation vector direction. Thus, Frano et al. had to use a tilted wedge scattering geometry in order to access the corresponding scattering plane. Fig. 2.6a–c show the ratio of the intensity of the $(1/4, 1/4, 1/4)$ reflection for π and σ polarized incident x-rays as a function of the azimuthal angles ψ . Since in the wedge geometry the illuminated sample area changes with ψ the ratio of the intensities was evaluated

for extracting the spin orientation. Model calculations (solid lines) then confirmed the non-collinearity of the spin spiral for nickelate heterostructures, but relative spin angles between the Ni sublattices and the spiral's polarization plane were revealed to be different than in the orthogonal ($\uparrow \rightarrow \downarrow \leftarrow$) spiral of the bulk [Fig. 2.6g, h].

In addition to the magnetic scattering (at the Ni L_3 edge), the x-ray linear dichroism, a measure of the orbital polarization, was recorded at the Ni L_2 edge [Fig. 2.6d–f]. Note that the intrinsically stronger L_3 edge XAS signal could not be evaluated due to large overlap with the La M_4 line. The change in the hole ratios X (further explanation in Chap. 3) indicate different relative occupations of the Ni e_g orbitals which in turn govern the local spin orientation via the spin-orbit coupling. Accordingly, the spiral polarization plane can be controlled by adjusting the Ni d -orbital occupation via two independent mechanisms: epitaxial strain and spatial confinement of the valence electrons.

2.2.2 Heterostructures Oriented Along the $[111]$ Direction

Studies exploring the $[111]$ crystallographic orientation of nickelates are sparse compared to research on $[001]$ heterostructures which is partly due to difficulties of synthesizing the materials along this highly polar direction. However, the occurrence of novel properties in $[111]$ heterostructures has been reported in Refs. [3, 57, 59, 61, 73, 79].

In Chap. 5 we will present magnetic REXS measurements on nickelate heterostructures grown on $[111]$ oriented substrates. Since one of the major results of the study by Frano et al. [78] was that orbital polarization controls the nickelates' magneto-crystalline anisotropy via the spin-orbit coupling the possible orbital polarization of $[111]$ heterostructures is of particular interest. A trigonal lattice distortion corresponding to epitaxial strain within the (111) plane as possibly imposed by a $[111]$ substrate mismatch does not lift the degeneracy of the e_g manifold [Fig. 2.7]. Thus no orbital polarization and therewith no major effect on the spin configuration is expected for such heterostructures. However, other effects that might have an impact on the magnetic configuration of $[111]$ heterostructures are to be discussed.

Important experiments investigating induced magnetic order in $[111]$ oriented nickelates were performed on superlattices consisting of LaNiO_3 sandwiched by layers of ferromagnetic LaMnO_3 [61, 62]. Gibert et al. found an unusual exchange bias effect implying an interface induced magnetic structure in the otherwise non-magnetic LaNiO_3 . Induced magnetism in LaNiO_3 heterostructures has been reported before [56], however it is pointed out in Ref. [61] that the observed exchange bias provides a unique tool to probe the interfacial coupling between LaNiO_3 and LaMnO_3 . Moreover, the exchange bias effect is exclusively present in $[111]$ heterostructures because here the interfacial coupling is enhanced as compared to $[001]$ interfaces. The enhanced coupling does not only apply to structural properties, but also the charge transfer between Mn and Ni is more pronounced across the $[111]$ interface [80]. First-principles simulations of superlattices with different periodicities indicate

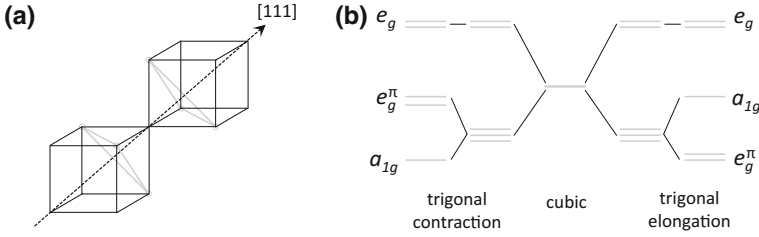


Fig. 2.7 Orbital polarization for trigonal distortions. **a** Two pseudocubic unit cells with the [111] direction and two (111) planes indicated. Trigonal (D_{3d}) lattice distortions within the (111) plane of a heterostructure can be induced by the compressive or tensile strain mismatch to a [111] oriented substrate. **b** The t_{2g} levels are split into a e_g^π doublet and an a_{1g} singlet while the e_g manifold is unaffected and stays degenerate

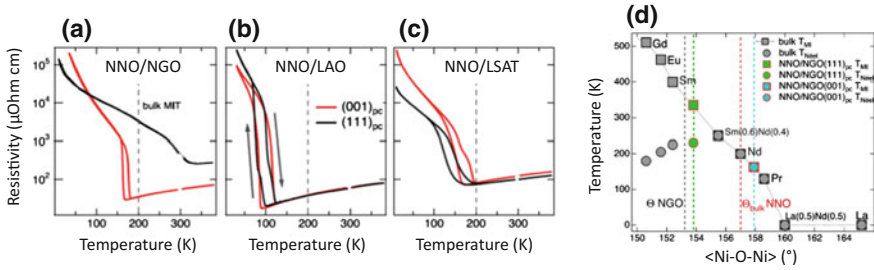


Fig. 2.8 Enhanced T_{MI} in [111] oriented NdNiO_3 on NdGaO_3 . **a–c** Electrical transport of NdNiO_3 in the [001] and the [111] orientation on various substrates (red and black curve, respectively). Only the system NdNiO_3 on NdGaO_3 shows a distinct behavior for the [111] orientation with the metal-insulator transition shifted to ~ 325 K. The dashed vertical lines represent $T_{\text{MI}} = T_{\text{N}}$ of bulk NdNiO_3 . **d** T_{MI} and T_{N} as a function of the Ni-O-Ni bond angle. Panel **a–d** are adapted from Ref. [57] and licensed under CC BY 3.0

a spin density wave like modulation of the Ni magnetic moments with a ferromagnetic coupling of the Ni moments at the interface to the Mn. Recently, the follow-up study showed that the interlayer magnetic coupling depends on the exact thickness of the LaNiO_3 layer [62]. Specifically for $N = 7$ atomic layers of Ni, negative and positive exchange bias occurs, as well as antiferromagnetic interlayer coupling in different temperature windows.

Interestingly, nickelate films show similar behavior in electronic transport when grown on [001] and [111] oriented LaAlO_3 (or LSAT) substrates, whereas the specific combination of NdNiO_3 on [111] oriented NdGaO_3 substrate significantly enhances T_{MI} up to 335 K [Fig. 2.8a–c] [57]. This strengthening of the electronic correlations gives rise to an unprecedented paramagnetic insulating phase, since now T_{MI} and T_{N} are widely separated. Catalano et al. attributed the effect to a structural modification of the NdNiO_3 imposed by the NdGaO_3 substrate which is possible for NdNiO_3 - NdGaO_3 due to a close matching of the lattice constants as well as the B-O-B tilt angles. A highly increased propagation length of the substrate's octahedra

tilts across the [111] interface was suspected and it is proposed that the octahedra tilt angles of the NdGaO_3 propagate throughout the whole 17 nm thick NdNiO_3 film. This would be in contrast to findings for [001] oriented heterostructures where the propagation length is usually only of the order of a few unit cells [81]. Thus, the enhanced octahedral interconnectivity of the [111] interface and the tilt propagation [Fig. 5.3c] is an important issue, that is addressed by scanning transmission electron microscopy imaging of the octahedral oxygen positions within the scope of this thesis (see Chap. 5).

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