I. INTRODUCTION

Materials that are located at the crossover between itinerant and localized electronic behavior often exhibit rich phase diagrams, including different forms of electronic order (charge, orbital, magnetic) and metal-insulator transitions. Moreover, exotic properties such as non-Fermi liquid behavior or high-temperature superconductivity can typically be found in this regime, and in many cases a strong coupling between electronic and lattice degrees of freedom, such as, e.g., the Jahn-Teller effect can be observed.

An interesting example to study the crossover between localized and itinerant electronic behavior is found in the series of perovskite-structure rare-earth nickelates, $\text{RNiO}_3$, where $R$ can be any rare-earth ion ranging from Lu to La. All members of this series (except LaNiO$_3$) exhibit a metal-insulator transition (MIT) as a function of temperature, which is accompanied by a structural distortion that lowers the space group symmetry of the crystal structure from orthorhombic $\text{Pbnm}$ in the high temperature metallic phase to monoclinic $\text{P}2_1/\text{n}$ in the low temperature insulating phase. In addition, all systems (except LaNiO$_3$) order antiferromagnetically at low temperatures. The corresponding phase diagram (based on experimental data taken from Refs. [10-12] [14-16]) is depicted in Fig. 1, where the temperature dependence of the phase boundaries is shown as a function of the average (Ni-O-Ni) bond angle. It can be seen that the transition temperature for the MIT, $T_{\text{MIT}}$, decreases monotonously with increasing (Ni-O-Ni) bond angle, whereas the antiferromagnetic (AFM) transition temperature, $T_N$, increases up to $R=$Sm but then becomes identical to $T_{\text{MIT}}$. Thus, for $R$ from Lu to Sm, the AFM transition occurs at lower temperatures than the MIT, whereas for $R=$Nd and Pr, $T_N$ coincides with $T_{\text{MIT}}$. In contrast, LaNiO$_3$ is a paramagnetic metal at all temperatures, and exhibits a slightly different, rhombohedrally-distorted perovskite structure with $\text{R}$3c symmetry.

The rare-earth nickelates allow us to study the transition from itinerant paramagnetic behavior to a localized AFM state in a quasicontinuous fashion using simple stoichiometric bulk systems, i.e., without the need...
Ni is still under debate. In the simplest picture, the nominal also schematically shown in Fig. 3. within a [001]-type plane (in pseudocubic notation) is the MIT octahedra, 

ment of alternating long bond (LB) and short bond (SB) by changing the Ni-O bond lengths accordingly. This of their volumes while the other half reduce their volumes inequivalent. One half of the NiO$_6$ octahedra become as NiO$_6$ octahedra differ by $\sim 12\%$. The crystal structure is visualized using VESTA.

to introduce dopants or substitutional atoms. Moreover, the nickelates are also highly tunable by pressure, strain, electromagnetic fields, or doping, and are potentially multiferroic (see, e.g., Refs. [5] and [20]). Consequently, the perovskite rare-earth nickelates have received considerable attention during recent decades.

Apart from the exact mechanism underlying the MIT, the magnetic order observed in the nickelates is also not yet fully resolved and poses numerous open questions. All systems from $R=$ Lu to Pr exhibit the same antiferromagnetic wave-vector $k = [1/4, 1/4, 1/4]$ relative to the underlying simple cubic perovskite structure (with approximate cubic lattice constant $a_c$). Furthermore, it is known from experiment that the magnetic moments vary between the LB and SB Ni sites. However, the exact magnetic structure is not yet established, due to the lack of sufficiently large single crystals. There are several possible arrangements that cannot be distinguished within the experimental resolution. As a result, it is still under debate whether the magnetic order is collinear or not. Moreover, below $\sim 10$ K, the magnetic moments of the rare-earth ions also order. However, while Ref. [31] reports a different magnetic periodicity of the rare earth moments relative to the Ni moments in HoNiO$_3$, Ref. [15] suggests the same periodicity of Ni and Dy moments in DyNiO$_3$.

In order to gain further insights into the underlying mechanisms, and also to enable quantitative predictions about the physical properties of rare-earth nickelates, a first principles-based computational approach is very desirable. However, an accurate quantitative description of the complex interplay between the various factors that are believed to control the MIT in these materials, i.e., structural properties, electronic correlation effects, and hybridization between the Ni 3$d$ states and the surrounding O ligands, is rather challenging.

Several previous studies have reported that both struc-
Here, we present a systematic study of the whole nickelate series with rare-earth ions Lu, Er, Ho, Y, Dy, Gd, Sm, Nd, Pr and La, using the DFT+U approach. In particular we address the interplay between the strength of the Hubbard $U$, different magnetic orders, the size of the rare-earth cation $R$, and the resulting structural parameters. Our results thus fill an important gap and further clarify the capabilities of the DFT+U approach for quantitative predictions of the physical properties of rare-earth nickelates. Our work can also serve as starting point for further studies using more advanced electronic structure methods such as, e.g., DFT+DMFT.

Our findings show that the amplitude of the bond-disproportionation distortion is strongly influenced by the size of $U$ and also by the specific magnetic order, but that in principle good agreement with available experimental data can be obtained for $U \approx 2\, \text{eV}$. Moreover, the trends across the series agree well with experiment. Furthermore, our calculations show that a magnetic order with the experimentally observed wave-vector is energetically favored for relatively small $U$ values (also around $U \approx 2\, \text{eV}$), and that the energy gain relative to ferromagnetic order increases from Lu to Pr, consistent with the observed trend of the magnetic ordering temperature.

The remainder of this article is organized as follows. First, in Sec. II, we introduce the symmetry-based decomposition of distortion modes and discuss its application to the experimental structure of LuNiO$_3$. In Sec. III we then briefly describe our computational setup and list all relevant parameters used in the DFT+U calculations. The presentation of our main results is divided into two parts. We start in Sec. IV by discussing calculations for LuNiO$_3$ based on the experimental structure taken from Ref. [12] Hereby, we investigate the stability of different magnetic phases for different interaction parameters $U$ and $J$ without relaxing the structural degrees of freedom. We then start to incorporate structural effects by varying the amplitude of the breathing mode distortion while keeping all other structural parameters fixed to the experimental values. Finally, our results of the full structural relaxations across the nickelate series are presented in Sec. V and in Sec. VI we summarize our main results and discuss their implications.

II. DESCRIPTION OF STRUCTURAL DISTORTIONS USING SYMMETRY-BASED MODE DECOMPOSITION

For a systematic and quantitative discussion of the various structural distortions that are present in the $Pbnm$ and $P2_1/n$ crystal structures of the rare-earth nickelates, we use a symmetry-based mode decomposition as described by Perez-Mato et al. Thereby, the atomic positions within a distorted crystal structure (low-symmetry structure), $\mathbf{r}_j^\text{dist}$, are written in terms of the positions in a corresponding non-distorted reference structure (high-symmetry structure), $\mathbf{r}_j^0$, plus a certain number of inde-
TABLE I. Mode decomposition of several structures obtained for LuNiO$_3$. The top three lines are based on available experimental data corresponding to different temperatures: $T = 643$ K ($Pbnm$) $T = 533$ K ($P2_1/n$), and $T = 295$ K ($P2_1/n$). The bottom five lines correspond to results of our structural relaxations for different magnetic orders (NM: nonmagnetic, FM: ferromagnetic, T-AFM: $T$-type antiferromagnetic) and using different values for the parameters $U$ and $J$.

| $Pbnm$ modes | additional $P2_1/n$ modes |
|---------------|----------------------------|
|               | $R_1^+\overline{4}$ | $R_1^+\overline{2}$ | $M_3^+\overline{1}$ | $M_3^+\overline{5}$ | $R_1^+\overline{4}$ | $R_1^+\overline{2}$ | $M_3^+\overline{1}$ | $M_3^+\overline{5}$ |
| exp. 643 K ($Pbnm$) | 0.811 | 0.117 | 0.449 | 0.018 | 0.626 | – | – | – |
| exp. 533 K ($P2_1/n$) | 0.821 | 0.124 | 0.452 | 0.025 | 0.617 | 0.077 | 0.001 | 0.013 |
| exp. 295 K ($P2_1/n$) | 0.826 | 0.124 | 0.445 | 0.031 | 0.616 | 0.077 | 0.002 | 0.007 |
| NM $U = 0$, $J = 0$ eV | 0.845 | 0.129 | 0.487 | 0.023 | 0.625 | – | – | – |
| FM $U = 5$, $J = 1$ eV | 0.875 | 0.126 | 0.476 | 0.027 | 0.623 | 0.094 | 0.006 | 0.023 |
| $T$-AFM $U = 0$, $J = 0$ eV | 0.861 | 0.130 | 0.480 | 0.026 | 0.622 | 0.037 | 0.001 | 0.002 |
| $T$-AFM $U = 2$, $J = 1$ eV | 0.870 | 0.129 | 0.480 | 0.034 | 0.625 | 0.081 | 0.008 | 0.019 |
| $T$-AFM $U = 5$, $J = 1$ eV | 0.879 | 0.124 | 0.475 | 0.037 | 0.623 | 0.124 | 0.009 | 0.029 |

The bottom five lines correspond to results of our structural relaxations for different magnetic orders (NM: nonmagnetic, FM: ferromagnetic, T-AFM: $T$-type antiferromagnetic) and using different values for the parameters $U$ and $J$. The amplitudes $A_m$ can thus be viewed as distinct order parameters for the different structural distortions present in the low-symmetry structure. This allows to clearly identify the most relevant structural degrees of freedom, and, in particular, for the case of the rare-earth nickelates, to systematically distinguish between the various octahedral tilt distortions and the breathing mode related to the MIT.

The mode displacement vectors $\vec{d}_{im}$ are constructed such that each mode $m$ has a well-defined symmetry, i.e., it corresponds to a specific irreducible representation (irrep) of the high-symmetry space group. Here, we use the ideal cubic perovskite structure as high-symmetry reference structure. Thus, all distortion modes are labeled according to the irreps of space-group $Pm3m$. Note that an irrep can involve distortion vectors with multiple degrees of freedom, e.g., corresponding to displacement patterns of different inequivalent atoms. All distortion modes corresponding to the same irrep can then be grouped together to define a total mode amplitude of that symmetry.

Balachandran and Rondinelli have presented such a symmetry-based mode decomposition for the low-temperature $P2_1/n$ structure of various nickelates, based on available experimental data. Eight different irreps of the high-symmetry $Pm3m$ space group can occur within $P2_1/n$. Five of them, corresponding to symmetry labels $R_1^+$, $M_2^+$, $X_2^+$, $R_2^+$, and $M_2^-$, are already allowed within the high-temperature $Pbnm$ structure. The first two of these, $R_1^+$ and $M_2^+$, correspond to out-of-phase and in-phase tilts of the oxygen octahedra, and, as shown by Balachandran and Rondinelli, only the distortions corresponding to $R_1^+$, $M_2^+$, and $X_2^+$ have consistently non-negligible mode amplitudes throughout the nickelate series. In contrast, the amplitude of the $M_2^-$ mode, which corresponds to a staggered Jahn-Teller distortion of the oxygen octahedra that is found, e.g., in many manganites, is negligibly small.

The low-temperature $P2_1/n$ structure allows for three additional irreps, labeled $R_1^+$, $R_1^-$, and $M_3^+$. Here, only the $R_1^+$ mode, which describes the breathing mode distortion with alternating LB and SB octahedra, has a non-negligible amplitude. The three most relevant distortion modes found in the rare-earth nickelates, i.e., the octahedral tilt modes $R_1^+$ and $M_3^+$ ($Pbnm$ symmetry), as well as the $R_1^+$ breathing mode (within $P2_1/n$) are visualized in Fig. 4.

In Table I, we list the distortion mode amplitudes for LuNiO$_3$ at the three different temperatures measured in Refs. 11 and 12. We use ISODISTORT to calculate the distortion mode amplitudes. All mode amplitudes are given in Å and are normalized to the cubic high-symmetry parent structure (not to the 20 atom $Pbnm$ unit cell). Note that the data at room temperature is identical (except for the different normalization) to the corresponding data in the paper of Balachandran and Rondinelli.

If one compares the experimental data from Ref. 12 obtained approximately 50 K above and below the MIT (first and second row of Table I), one can see that the largest $Pbnm$ mode amplitude, i.e., $R_1^+$, does almost not change during the MIT. The $R_1^+$ amplitude is 0.811 Å within the high-temperature $Pbnm$ phase and 0.821 Å within the low-temperature $P2_1/n$ phase. This value corresponds to maximal displacements of individual oxygen atoms by 0.58 Å. Similar behavior can be observed for the other two main modes, $M_3^+$ and $X_2^+$. Finally, the bond-disproportionation mode in the low-temperature phase, $R_1^-$, exhibits an amplitude of 0.077 Å, which corresponds to a displacement of each oxygen atom by 0.044 Å.
III. COMPUTATIONAL METHOD

DFT calculations are performed using the projector augmented wave (PAW) method implemented in the “Vienna Ab initio Simulation Package” (VASP). We use the generalized gradient approximation (GGA) in the form proposed by Perdew, Burke, and Ernzerhof (PBE) as exchange correlation functional. For an improved treatment of the strong local electron-electron interaction we use PAW potentials corresponding to a 3+ valence state with f-electrons frozen into the core and, depending on the rare-earth cation, the corresponding 5p and 5s states are also included as valence electrons. Thus, we neglect the ordering of the rare-earth f magnetic moments, which only occurs at very low temperatures. The kinetic energy cut-off for the plane-wave basis is set to 550 eV.

For Ni, the 3p semicore states are included as valence electrons in the PAW potential. For the rare-earth atoms, we use PAW potentials corresponding to a 3+ valence state with f-electrons frozen into the core and, depending on the rare-earth cation, the corresponding 5p and 5s states are also included as valence electrons. Thus, we neglect the ordering of the rare-earth f magnetic moments, which only occurs at very low temperatures. The kinetic energy cut-off for the plane-wave basis is set to 550 eV.

We consider four different types of magnetic order: FM, T-AFM, E-AFM, and A-AFM order, which are depicted in Fig. 5. The rather common A-type AFM order (A-AFM) corresponds to an alternating (↑↓↓↓) alignment of Ni magnetic moments along the Cartesian z direction, and parallel alignment perpendicular to z. The E-type AFM order (E-AFM) corresponds to an ↑↑↓↓ alignment along both x and y directions, and alternating moments, i.e. ↑↑↑↑, along the z direction. The T-AFM order, which corresponds to the experimentally observed AFM wave vector, \( k = \left[ \frac{1}{4}, \frac{1}{4}, \frac{1}{4} \right] \), exhibits an ↑↑↓↓ pattern along all three Cartesian directions. As shown by Giovannetti et al. using DFT+U calculations, this T-AFM order is energetically nearly indistinguishable from the other two magnetic order patterns (one collinear and one noncollinear) that are compatible with the experimental neutron data. In the following, we therefore use the (relatively simple) T-AFM structure as representative for the experimentally observed magnetic order. Both T-AFM and bond-disproportionation are also illustrated in Fig. 3 within a \([001]\)-type layer.

For the examination of the different magnetic order patterns, different unit cell sizes are used. For the FM and A-AFM order, we use a 20 atom unit cell consisting of \( \sqrt{2} \times \sqrt{2} \times 2 \) (pseudo-) cubic perovskite units. This cell also corresponds to the primitive crystallographic unit cells for both the \( Pbnm \) and \( P2_1/n \) structures. For the E-AFM magnetic structure, this unit cell is doubled along the \( a \) direction (40 atoms), and for the special T-AFM order the cell is doubled once more, this time along the \( c \) direction (80 atoms). A k-point mesh with 10×10×8 grid points along the three reciprocal lattice directions is used for the 20 atom \( Pbnm \) and \( P2_1/n \) unit cells to perform Brillouin zone integrations. For the 40 atom E-AFM cell we use an appropriately reduced 5×10×8 k-point grid and for the 80 atom T-AFM cell a 5×10×4 grid. For accurate structural relaxations, the forces acting on all atoms are minimized until all force components are smaller than \( 10^{-4} \) eV/Å. Local magnetic moments are obtained by integrating the spin density within the PAW spheres (LORBIT=11).
For values $U > 2 \text{ eV}$ the FM state is most favorable, while the simple $A$-AFM state is higher in energy over the whole range of $U$ values. We also note that for $U = 0$ we were not able to stabilize the $T$-AFM state within our calculations.

The bottom panel of Fig. 6 shows the effect of varying the Hund’s coupling parameter $J$ for fixed $U = 5 \text{ eV}$. Consistent with the results shown in the top panel, at this $U$ value the FM state is favored for $J = 0$. If $J$ is increased, the FM state becomes even more favorable compared to all three AFM orderings. The same trend can be observed for other values of $U$ (not shown). Increasing $J$ lowers the energy of the FM state relative to the various AFM orderings.

It appears that the $T$-AFM state, i.e., the state that is compatible with the experimental observations, is only favorable for small values of $U$ and $J$. Furthermore, within this range of $U$ and $J$, the energy difference between $T$-AFM and the closely related $E$-AFM state is rather small. On increasing both $U$ and $J$, the FM states becomes lower in energy than all considered AFM orderings.

We note that nonmagnetic DFT calculations with $U = 0$ for LuNiO$_3$ in both the low temperature $P2_1/n$ and the high temperature $Pbnm$ structures (taken from Ref. 12) result in a metallic system. By adding the local Coulomb interaction $U$ we are able to stabilize the $T$-AFM order, which then results in an insulating ground state. FM order also results in an insulating ground state for $U > 0 \text{ eV}$. Thus, magnetic order and a small value of $U$ (around 1 eV or larger) is needed to obtain an insulating ground state in the experimental low temperature structure.

To investigate how sensitive the energy differences between different magnetic states depend on small variations in the crystal structure, in particular the $R_1^T$ breathing mode, we now use the mode decomposition of the experimental $P2_1/n$ structure and tune the amplitude of the $R_1^T$ mode while keeping all other structural degrees of freedom fixed to their experimental values. The result is shown in Fig. 6 which shows the total energy (top) and the magnetic moments on the Ni sites (bottom) as function of the $R_1^T$ mode amplitude for different magnetic orderings and two different $U$ values ($U = 2 \text{ eV}$ on the left and $U = 5 \text{ eV}$ on the right) together with $J = 1 \text{ eV}$. In each case, the energy exhibits a minimum at a finite value of the $R_1^T$ amplitude, which indicates the value predicted by DFT+$U$ for a given magnetic order (with all other structural parameters fixed to experimental values). The black vertical dashed line indicates the $R_1^T$ amplitude in the experimental structure, $R_1^T = 0.077 \text{ Å}$. Note that the experimental structure was determined in the paramagnetic insulating phase.

One observes that the energy of the FM state (green triangles) is always lower than that of the AFM states (magenta squares and blue circles). However, the energy difference between FM and AFM order is smaller for $U = 2 \text{ eV}$ than for $U = 5 \text{ eV}$, consistent with the results shown.

![Graph showing energy differences between different magnetic states](image)

**FIG. 6.** Effect of $U$ (top) and $J$ (bottom) on the energy differences between different magnetically ordered states, calculated for LuNiO$_3$ using the experimentally observed $P2_1/n$ structure. For each $U$ and $J$, the energies of three different AFM states are given relative to the FM state, normalized to a unit cell containing 4 Ni sites. The $T$-AFM order (magenta squares) is energetically favored only for rather small $U$ values. Increasing $J$ (bottom) also favors the FM state.

### IV. CALCULATIONS FOR LUNIO$_3$ BASED ON THE EXPERIMENTALLY OBSERVED STRUCTURE

We start by performing calculations for LuNiO$_3$ in the experimentally determined $P2_1/n$ structure at $T = 533 \text{ K}$ and analyze the influence of the Hubbard and Hund’s rule interaction parameters, $U$ and $J$, on the relative stability of different magnetic configurations. We consider the FM case as well as three different AFM configurations ($A$-AFM, $E$-AFM, and $T$-AFM, see Sec. III for more details). Fig. 6 shows the calculated total energies of the three AFM configurations relative to the FM state. All energies are normalized to a 20 atom unit cell. A negative value indicates that the corresponding AFM state is lower in energy, whereas a positive value indicates that the FM state is lower in energy.

The top panel of Fig. 6 depicts the case with $J = 0$. It can be seen that for small values of $U$, the $T$-AFM and $E$-AFM states have very similar energies, and for $U < 2 \text{ eV}$, both are lower in energy than the FM state.
in Fig. 6 (note that the top panel in Fig. 6 corresponds to \( J = 0 \) whereas Fig. 7 is obtained using \( J = 1 \) eV, and that increasing \( J \) favors the FM state). Furthermore, it is apparent that the AFM states couple much stronger to the \( R_1^+ \) breathing mode than the FM state, with a much deeper energy minimum relative to zero mode amplitude and a position of the energy minimum at significantly larger \( R_1^+ \) amplitude.

The predicted mode amplitude for T-AFM and \( U = 2 \) eV (\( R_1^+ = 0.076 \) Å) agrees very well with the experimental value, whereas the FM state results in an amplitude (\( R_1^+ = 0.050 \) Å) that is much smaller than what is observed experimentally. Increasing \( U \) increases the predicted mode amplitudes for both FM and AFM order, and for \( U = 5 \) eV the amplitude obtained for FM order (\( R_1^+ = 0.082 \) Å) is close to the experimental value, whereas both AFM states exhibit significantly larger amplitudes (\( R_1^+ \approx 0.11 \) Å). There is only a small difference between the two different AFM orderings, and in particular the positions of the energy minima are very similar. For \( U = 2 \) eV, T-AFM is slightly lower in energy than A-AFM, whereas for \( U = 5 \) eV, A-AFM is lower.

The bottom panels of Fig. 7 show the local magnetic moments of the Ni cations for the different magnetic orderings as a function of the \( R_1^+ \) amplitude. For \( U = 5 \) eV, all moments have the same value of \( \sim 1.1 \mu_B \) at zero \( R_1^+ \) amplitude. In contrast, for \( U = 2 \) eV, the SB and LB moments differ already for \( R_1^+ = 0 \) in the two AFM cases, while they are both equal to \( \sim 0.9 \mu_B \) in the FM case. It thus appears that for \( U = 2 \) eV, the magnetic moments are much more susceptible to the small symmetry breaking resulting from the presence (albeit with very small amplitude) of the two other \( P2_1/n \) modes, i.e., \( R_3^+ \) and \( M_5^- \). We note that if these additional modes as well as the small monoclinic tilt of the unit cell are also removed, i.e., if the underlying crystal structure has exact \( Pbnm \) symmetry, then the difference between the LB and SB moments also vanishes in the case of A-AFM order. However, this is not the case for the T-AFM ordering, since T-AFM order by itself breaks the \( Pbnm \) symmetry, leading to two symmetry-inferior Ni sites.

With increasing \( R_1^+ \) amplitude, the moments of the SB sites decrease and the moments of the LB sites increase. Thereby, the size of the NiLB moments is rather independent of the magnetic order, and seems to converge to a value of around 1.4 \( \mu_B \) (1.6 \( \mu_B \)) for \( U = 2 \) eV (\( U = 5 \) eV). In contrast, the decrease of the NiSB moments depends more strongly on the magnetic order. For T-AFM order, the NiSB moments vanish completely for \( R_1^+ \) amplitudes larger than \( R_1^+ = 0.04 \) Å (\( R_1^+ = 0.06 \) Å) for \( U = 2 \) eV (\( U = 5 \) eV). This means that, for both \( U \) values, the NiSB moments in the T-AFM state are zero at the experimental \( R_1^+ \) amplitude. For the A-AFM and FM cases, the SB moments seem to only asymptotically converge to zero, with the residual moment in the FM case about twice as large as in the A-AFM case. These results are con-
sistent with earlier studies that also found nonvanishing magnetic moments on the SB sites for LuNiO$_3$ with FM order and vanishing Ni$_{SB}$ moments for NdNiO$_3$ with T-AFM order (for not too large $U$).

We note that the behavior of the SB moments for larger $R^+_1$ amplitudes is consistent with a picture where the Ni$_{SB}$ moment is simply induced by the effective field created by the magnetic moments on the neighboring Ni$_{LB}$ sites. In the FM case, each SB site is surrounded by six LB nearest neighbors with parallel alignment of their magnetic moments. In the A-AFM case, only four of the six neighboring LB moments are parallel to each other, and thus the effective field at the SB site is reduced. For the T-AFM case, exactly half of the neighboring LB moments are aligned parallel to each other, while the other half is aligned antiparallel, leading to a cancellation of the effective field on the SB site. We also performed some calculations where we initiated the magnetic moments according to $G$-type AFM order. In this case, all LB moments are parallel to each other and thus the effective field at the SB site is the same as for FM order. As a result, the calculations converge to the FM solution even if the SB moments are initiated antiparallel to the LB moments.

It appears that DFT+$U$ is able to correctly describe the bond-disproportionated state in LuNiO$_3$, resulting in $R^+_1$ amplitudes that are consistent with the experimentally obtained structure. However, the precise value of the $R^+_1$ amplitude depends strongly on the type of magnetic order that is imposed in the calculation, and also on the value used for the Hubbard interaction parameter $U$. The complex T-AFM state, which is consistent with the available experimental data and is also stable within the calculations, is lower in energy than the FM and A-AFM states for small values of $U$ (and $J$). However, the calculations seem to favor the FM solution for $U$ values larger than $U = 2$ eV. Furthermore, the $R^+_1$ breathing mode results in a strong energy lowering of the AFM states and also leads to a strong disproportionation between the magnetic moments on the two different Ni sites (for all magnetic orderings). For T-AFM, the local magnetic moments on the Ni$_{SB}$ sites vanish completely at the experimental $R^+_1$ amplitude.

We note that while different magnetic structures assumed in the refinements of the available experimental data generally lead to different values for the local magnetic moments, most studies indeed report a significant difference between Ni$_{LB}$ and Ni$_{SB}$ moments (see, e.g., Refs. 15 and 34). Furthermore, our T-AFM calculations show that the Ni$_{SB}$ moments can be zero, in spite of the fact that the integrated charges inside the PAW spheres differ only very little between the two different Ni sites (consistent with previous DFT-based studies). Thus, the SB moments can vanish completely even though the integrated charges do not correspond to a naive picture of full charge disproportionation within atomic spheres. The results presented in this section are also in good agreement with a recent DFT+$U$ study by Varignon et al. focusing on the members of the nickelate series with large $R^+_1$ amplitudes, which suggests that a value of $U = 2$ eV gives the best overall agreement with experimental observations, both regarding magnetic order and the magnitude of the bond disproportionation.

V. STRUCTURAL RELAXATIONS FOR THE WHOLE NICKELATE SERIES

Next, we perform full structural relaxations within the low-temperature $P2_1/n$ symmetry across the whole series of nickelates with $R$ from Lu to La. We again compare different values of $U$ and $J$ and different magnetic orderings. However, we will focus mainly on the FM and T-AFM cases, since other AFM orderings give results similar to T-AFM. In addition, we also perform nonmagnetic (NM) structural relaxations with $Pbnm$ symmetry and using $U=0$. The larger symbols not connected by lines indicate various experimental results: Lu-Y (red crosses with circle at 60 K above $T_{MIT}$), Dy (blue diamond) from Ref. 15, Nd (orange asterisk) from Ref. 16, Pr (purple star) from Ref. 17, and La (black three-pointed star) from Ref. 17.
ture with $R3c$ space group symmetry\cite{ref17}.

Generally, our calculated lattice parameters agree very well with available experimental data across the whole series, with maximal deviations of the unit cell volume of a few percent or less. For example, for LuNiO$_3$ the NM calculation results in a unit cell volume that deviates by $-1.5\%$ from the experimental high temperature structure\cite{ref12} whereas the volume obtained in the FM calculation with $U = 5\text{ eV}$ and $J = 1\text{ eV}$ differs by only $+0.2\%$ from that of the experimental $P2_1/n$ structure at $\sim 60\text{ K below }T_{\text{MIT}}$\cite{ref12}.

In Table\[ref1\] we list the amplitudes of all distortion modes obtained for LuNiO$_3$ in different settings. It can be seen that the $R_1^+$ mode is the only mode which depends very strongly on $U$, $J$, and the type of magnetic order. All other relevant mode amplitudes agree well with the experimental data, except maybe for a slight overestimation of the $R_4^+$ mode (and perhaps also $X_5^+$), in particular for the FM/AFM cases and increasing $U$.

As discussed in Sec.\[ref11\] the $R_1^+$ mode is the most prominent distortion mode in the nickelate series and describes the out-of-phase octahedral tilts around the in-plane direction (Glazer tilt $a^- a^- c^+$, see Fig.\[ref4\]). The evolution of the $R_1^+$ amplitude across the nickelate series, calculated for different settings and compared to experimental data, is depicted in Fig.\[ref8\]. Experimental data for $R=\text{Lu, Er, Ho, and Y}$ is taken from the two papers by Alonso et al.\cite{ref10,ref12} for $R=\text{Dy}$ from Muñoz et al.\cite{ref15} for $R=\text{Nd}$ from García-Muñoz et al.\cite{ref19} and for $R=\text{Pr}$ from Medarde et al.\cite{ref21}. Note, that the structural data is generally measured at different temperatures and that Alonso et al.\cite{ref10,ref12} have obtained data both above and below the MIT transition, i.e., both within the metallic high temperature $Pbnm$ phase and the insulating low temperature $P2_1/n$ phase. However, we note that in all these cases, there is only a rather small difference in the $R_1^+$ amplitude between the two phases (see also Table\[ref1]\ for the case with $R=\text{Lu}$).

The amplitude of the $R_1^+$ mode is monotonically decreasing across the series from Lu to La, consistent with the increasing radius of the $R$-cation. Furthermore, the $R_1^+$ amplitude is slightly smaller for the NM calculation with $U = 0$, compared to both FM and T-AFM calculations with $U = 5\text{ eV}$ and $J = 1\text{ eV}$, while there is only a negligible difference between FM and T-AFM. Overall, there is rather good agreement, both qualitatively and quantitatively, between the calculated and experimentally measured mode amplitudes. The best agreement is obtained for the NM case with $U = 0$, whereas the magnetic relaxations with $U = 5\text{ eV}$ lead to a slight overestimation of the octahedral tilt distortion compared to the experimental data.

Next, we discuss the $R_1^+$ breathing mode amplitude. We first note that, in contrast to the calculations for the fixed experimental structure presented in the previous section, the T-AFM magnetic order is stable within the fully relaxed structure even in the case with $U = 0\text{ eV}$. Moreover, in contrast to the FM and A-AFM (and NM) cases, in the T-AFM case all compounds from $R=\text{Lu}$ to La develop a finite $R_1^+$ amplitude already for $U = 0\text{ eV}$. Although the resulting amplitudes are about two to three times smaller than the experimentally observed $R_1^+$ amplitudes, this nevertheless indicates that T-AFM strongly supports the $R_1^+$ mode. For larger $U$ values, a finite $R_1^+$ amplitude emerges from the relaxations for all considered magnetic orderings.

In the following, we compare results for two different values of $U$, a smaller value of $U = 2\text{ eV}$ and a larger value of $U = 5\text{ eV}$, in both cases with $J = 1\text{ eV}$. The corre-

![Figure 9](image-url)

**FIG. 9.** $R_1^+$ mode amplitude for the relaxed structures with $U = 2\text{ eV}$ (top) and $U = 5\text{ eV}$ (bottom), in both cases using $J = 1\text{ eV}$. The relaxed mode amplitudes are given for the FM (green circles) and T-AFM (magenta squares) cases, as well as for the ‘$R_1^+$-only” relaxation with FM order (blue triangles). The large disconnected symbols (same in both panels) indicate different experimental values: brown crosses for Lu-Y from Ref.\[ref12\], red plus symbols for Lu-Y from Ref.\[ref11\] at $T = 290\text{ K}$, blue diamond for Dy from Ref.\[ref15\], orange asterisk for Nd from Ref.\[ref46\] and purple star for Pr from Ref.\[ref47\].
sponding $R^+_1$ mode amplitudes for FM and T-AFM cases are shown in Fig. 9 (top: $U = 2$ eV; bottom: $U = 5$ eV) together with available experimental data. Furthermore, to assess whether the slight overestimation of the $R^+_1$ octahedral tilt mode in the magnetically ordered +$U$ calculations (cf. Fig. 8) affect the calculated $R^+_1$ amplitude, we also consider a third case. Here, we use the $Pbnm$ structure obtained for the NM case (with $U = 0$), and then relax only the $R^+_1$ amplitude using FM order and $U = 5$ eV (while keeping all other mode amplitudes fixed). In the following, this relaxation is referred to as “$R^+_1$-only”. The corresponding data is also shown in Fig. 9.

It can be seen that there are significant differences in the calculated $R^+_1$ mode amplitudes for the various cases, similar to what has been found in the previous section for LuNiO$_3$. The calculated $R^+_1$ mode amplitudes are consistently larger for T-AFM (magenta) compared to the FM case (green), and the larger $U$ value results in a larger $R^+_1$ amplitude across the whole series. Furthermore, in all cases we obtain a decrease of the $R^+_1$ amplitude across the series from $R$=Lu towards $R$=La. This decrease is most pronounced for the FM case with $U = 5$ eV. The “$R^+_1$-only” relaxations (blue) result in reduced $R^+_1$ amplitudes compared to the full FM relaxations at $U = 5$ eV. As suggested above, this can be related to the reduced octahedral tilt distortion ($R^+_1$ mode) in the underlying NM structures.

Rather good agreement with the experimental data is obtained in the T-AFM case using $U = 2$ eV, in particular for the compounds at the beginning of the series. However, the decrease towards $R$=Pr appears weaker than for the experimental data. For FM order and $U = 5$ eV, the agreement is also good, including the decrease of the $R^+_1$ towards the end of the series. Note that a slightly smaller $U$ value would also slightly reduce the $R^+_1$ amplitude and probably further improve the comparison of the FM case with the experimental data.

Another fact that becomes apparent from Fig. 9 is that the rather large scattering of the experimental results for different members of the series, or even for the same compound measured at different temperatures (see, e.g., the data for $R$=Ho or Dy in Fig. 9). This can be attributed to difficulties in sample preparation, which is only possible under high pressure, leading to very small sample sizes and thus low experimental resolution. Nevertheless, it seems that the decrease in $R^+_1$ amplitude for $R$=Nd and in particular $R$=Pr compared to the compounds at the beginning of the series can indeed be inferred from the experimental data.

We now have a closer look at the $U$ dependence of the $R^+_1$ amplitude across the series. For this, we focus on the two “end-members” of the nickelate series, LuNiO$_3$ and PrNiO$_3$, and perform full structural relaxations for various $U$ values and both FM and T-AFM magnetic orders. Here, we use $J = 0$, so that the limiting case with $U = 0$ can be continuously incorporated. The results are depicted in the top panel of Fig. 10. We note that while the $R^+_1$ amplitude is very sensitive to the choice of $U$, the influence of $J$ is much weaker, and therefore we present only results for varying $U$.

In agreement with the results shown in Fig. 9, the T-AFM state leads to an overall larger $R^+_1$ amplitude compared to the FM state. Furthermore, the $R^+_1$ amplitude is consistently larger for LuNiO$_3$ than for PrNiO$_3$ (with the same magnetic order). In all cases, the $R^+_1$ amplitude is monotonously increasing with $U$ up to about 3-4 eV. For larger $U$, the $R^+_1$ amplitude starts to decrease and can even vanish completely at large $U$. The value of $U$ where the turnaround from increasing to decreasing $R^+_1$ amplitude occurs, depends both on the $R$ cation and the magnetic order. It is lowest for Pr and FM order and highest for Lu and T-AFM order (in fact, in this latter case the turnaround does not occur up to $U = 8$ eV).

The collapse of the breathing mode at large $U$ has also been observed in earlier DFT calculations for NdNiO$_3$ by Prosandeev et al. It can be related to a qualitative change in the electronic structure beyond a certain $U$ value. This is illustrated in Fig. 11 which shows pro-
Projected densities of states (DOS) for relaxed LuNiO₃ with FM order for \( U = 0, U = 4 \) eV, and \( U = 7 \) eV (in all cases with \( J = 0 \)). Here, the element-resolved DOS are summed over all atoms of a given type, i.e., the Ni DOS contains the contributions from both LB and SB sites.

For \( U = 0 \), the Ni \( d \) states (red and blue) are situated just above the oxygen \( p \) states (green). The system is slightly metallic and no breathing mode appears in the relaxed structure. With increasing \( U \), the occupied Ni \( d \) states are pushed down in energy relative to the oxygen \( p \) states, and a gap opens between the top of the valence band with predominant O \( p \) character and the conduction bands with strong Ni \( d \) character. This is indicative of a charge transfer insulator with strong hybridization between the ligand \( p \) and transition metal \( d \) states. This is also the regime that supports the breathing mode in the relaxed structure. The site splitting between the two nickel sites can be observed as two distinct peaks (at energies of approximately 1.5 eV and 3 eV) in the unoccupied minority spin Ni \( e_g \) DOS for \( U = 4 \) eV (middle panel of Fig. 10).

However, for \( U = 7 \) eV, the occupied Ni \( d \) states are pushed completely below the oxygen \( p \) states, i.e., the system has entered a negative charge transfer regime. This leads to reduced hybridization between O \( p \) and Ni \( d \) states, and the unoccupied part of the majority spin states has now essentially pure O \( p \) character, i.e., it now clearly corresponds to two ligand holes. Interestingly, this regime does not support the breathing mode distortion, as seen from the top panel of Fig. 10. Thus, it appears that the bond disproportionation in the nickelates depends strongly on the degree of hybridization between the Ni \( d \) and O \( p \) states and requires a mixed character of the nominal Ni \( e_g \) bands. On the other hand, if the “ligand hole” character of the unoccupied states becomes too dominant, the bond disproportionation becomes unfavorable. This is very much in line with the interpretation of “charge order” in terms of hybridized Ni-centered \( e_g \)-like Wannier functions, as discussed by Varignon et al. [20].

Finally, in the bottom panel of Fig. 10, we compare the relative stability of the FM and T-AFM states for the two “end-members” LaNiO₃ and PrNiO₃ in the fully relaxed structures as a function of \( U \) (and using \( J = 0 \)). Here, a negative (positive) value indicates that the T-AFM (FM) state is energetically favored. One can see that, while for LaNiO₃ the FM state is more favorable than T-AFM over essentially the whole range of \( U \) (with a nearly vanishing energy difference for \( U = 0 \)), for the case of PrNiO₃ the energy difference \( E_{T\text{-AFM}} - E_{FM} \) exhibits a nonmonotonous behavior with a minimum at around \( U = 1 \) eV. Most strikingly, the T-AFM state is favored in PrNiO₃ for \( U \) values up to \( U \approx 3 \) eV. Thus, in the small \( U \) regime (below 3-4 eV) the T-AFM state becomes more favorable for increasing size of the R cation, i.e., when going from Lu to Pr. This is consistent with the experimentally observed trend for the magnetic ordering temperature. We point out that, even though here we show only data for the two end members of the series, we have verified that the corresponding trends evolve continuously throughout the series.

The results for the energy difference between T-AFM and FM for LuNiO₃ are similar to the ones presented in Fig. 6 for the experimental structure, although in the experimental structure the T-AFM state is lower in energy than FM for \( U < 2 \) eV. This is due to the small structural differences between the experimental and relaxed structures, which slightly shift the energetics of the different magnetic orderings. Additionally, we note that in our calculations the T-AFM ordering is found to be stable in LaNiO₃ within \( Pbnm \) symmetry. This is in agreement with a very recent theoretical work by Subedi [28] where it is also shown that the stability of the T-AFM ordering disappears if the correct \( R\bar{3}c \) symmetry is considered. This shows that also LaNiO₃ is very close to a transition between the breathing mode phase with AFM ordering and the metallic \( R\bar{3}c \) phase. Together with the differences found for LuNiO₃ in the experimental and relaxed structures, it also demonstrates that the energy differences between different magnetic states are rather sensitive to small changes in the underlying crystal structure, indicating a subtle interplay between magnetism and structure in the rare-earth nickelates.
VI. SUMMARY

We have presented a systematic DFT+$U$ study for the whole series of perovskite structure rare-earth nickelates. Our goal was to assess if and to what extent the structural and magnetic properties of these compounds can be described within the DFT+$U$ approach. In order to distinguish different structural distortions, we have used a symmetry-based mode decomposition. Based on this decomposition, the transition from the metallic $Pbnm$ structure at high temperatures to the insulating $P2_1/n$ structure at lower temperatures can mainly be related to a single octahedral “breathing mode” corresponding to irrep $R_1^+$ of the cubic reference structure.

We find that essentially all structural parameters apart from this $R_1^+$ mode amplitude are rather well described already within nonmagnetic DFT calculations with $U = 0$. In particular, this is the case for the important $R_1^+$ mode describing the degree of out-of-phase octahedral rotations around the orthorhombic $a$ axis, which decreases strongly from $R=$Lu towards $R=$La. However, in order to obtain a nonzero $R_1^+$ mode amplitude in agreement with the experimentally observed $P2_1/n$ low temperature structures, both magnetic order and a nonzero value of $U$ are required within the calculations. Thereby, the obtained amplitudes of the breathing mode strongly depend on the value of $U$ and also on the magnetic order imposed in the calculation. For not too large $U$, the $R_1^+$ amplitude increases with increasing $U$ and it is significantly larger for the more realistic $T$-$AFM$ order than for the FM case. For the case with $T$-$AFM$ order, very good overall agreement with the experimentally determined structures across the whole series is achieved for $U = 2\text{ eV}$ and $J = 1\text{ eV}$. Similar good agreement can also be achieved for FM order using a larger $U$ value of around $5\text{ eV}$. However, if $U$ is further increased, and once the occupied Ni $d$ states are pushed energetically below the O $2p$ manifold, the $R_1^+$ mode vanishes again and the system becomes metallic.

Both our calculations as well as the available experimental data indicate a decrease of the $R_1^+$ amplitude across the series from $R=$Lu towards $R=$Pr. This decrease seems to be somewhat weaker in our computational results compared to experiment. Here, we note that, in order to simplify the analysis, we have always compared results obtained with the same values for $U$ and $J$ across the whole series. However, the use of a constant $U$ value for the whole nickelate series might not be fully appropriate. Considering the strong effect of $U$ on the $R_1^+$ amplitude, even a small decrease of $U$ from $R=$Lu towards $R=$Pr would result in a noticeably stronger decrease of the $R_1^+$ amplitude across the series. Since the octahedral rotations ($R_2^+$ and $M_1^+$ modes) decrease towards $R=$Pr, and thus the hybridization between the Ni $d$ and O $p$ states increases, potentially leading to enhanced screening, the correct $U$ value for $R=$Pr could indeed be slightly smaller compared to $R=$Lu. Therefore, in order to clarify how large (or small) these effects really are, first principles calculations of $U$ across the series would be of great interest.

On the other hand, it should also be noted that the available experimental data is quite sparse. In particular, data for the compounds in the middle of the series, i.e., for $R=$Gd and Sm, is currently not available. Furthermore, an unexpectedly large breathing mode amplitude has been reported for HoNiO$_3$ at $60\text{ K}$ below the MIT\cite{26} and for DyNiO$_3$ at $2\text{ K}$\cite{30} (see Fig. 3), and systematic measurements of the temperature dependence of the $R_1^+$ amplitude are also lacking. In particular, considering the strong influence of the magnetic state on the $R_1^+$ amplitude obtained in the calculation, it would be of interest whether there is a noticeable change in the $R_1^+$ amplitude (or some other structural parameters) when the nickelate compounds (with $R$ from Lu to Sm) undergo the transition to the AFM phase. Indeed, some anomalies of the phonon frequencies at the magnetic transition temperature have already been observed in SmNiO$_3$ thin films using Raman scattering\cite{27}.

While the overall trends and orders of magnitude seem to be well captured within the DFT+$U$ calculations, some deficiencies also become apparent. For example, the imposed $T$-$AFM$ ordering, which is compatible with the experimental data, is only energetically favored (compared to the FM state) for a relatively small range of $U$ values. For the case of LuNiO$_3$, it is even hardly favored at all (only for $U = 0$ in the fully relaxed structure). Nevertheless, in the small $U$ regime, the $T$-$AFM$ state becomes more and more energetically favored with increasing radius of the rare-earth cation (see bottom panel of Fig. 10), consistent with the experimentally observed trend of the magnetic ordering temperature. Our calculations also show that the $T$-$AFM$ order generally couples much stronger to the breathing mode distortion than the FM order.

Overall, we find that the best agreement with experimental observations across the whole series, regarding both structure and magnetic order, is achieved if a relatively small value of $U \approx 2\text{ eV}$ is used in the calculations. This is consistent with the work of Varignon et al.\cite{22} and in contrast to what has been suggested by Prosandeev et al.\cite{23}. However, one should note that even for $U = 2\text{ eV}$, the stability of the FM state seems to be overestimated, in particular for the small rare-earth cations such as Lu.

To conclude, our results give a clear picture of the predictive capabilities of the DFT+$U$ approach in the rare-earth nickelate series, and also provide a solid starting point for the use of more advanced computational methods, such as, e.g., DFT+DMFT. Furthermore, they can also be used as reference for future experimental investigations regarding the temperature dependence of the structural parameters and trends across the series.
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