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Lanthanide Contraction in $RENi_5$ (RE = La, Ce, Nd, Sm, Eu, Gd, Tb, Yb) Compounds Studied with Band Structure Calculations

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Full potential linearized augmented plane wave band structure calculations were performed for hexagonal $RENi_5$ (RE = rare earth) compounds in order to investigate reproducibility of lanthanide contraction by *ab initio* studies. The a and c parameters were optimised using a paraboloid fit, starting from the same initial values for all compounds studied. The trend in lattice parameters across the RE series obtained from the calculations was found to be in general agreement with experimental data. A comparison of results obtained by generalized gradient approximation and generalized gradient approximation with additional Coulomb correlations calculations is presented for several double counting schemes.

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1. Introduction

$RENi_5$ (RE = rare earth) compounds have been intensively studied because of their potential for applications. These materials are good candidates for hydrogen storage materials [1, 2]. In particular, $LaNi_5$ finds widespread use e.g. in nickel-metal hydride batteries [1]. Doped $CeNi_5$ has similar properties [1]. Moreover, $PrNi_5$ is employed in low-temperature physics to obtain very low temperatures by adiabatic demagnetisation [3].

The $RENi_5$ compounds crystallise in the $CaCu_5$ hexagonal crystal structure [4] (space group $P6/mmm$ (D^1_{6h}), No. 191). The RE atom occupies the high symmetry 1a (0 0 0) Wyckoff position, whereas the Ni atoms occupy the 2c ($\frac{1}{3}$ $\frac{2}{3}$ 0) and 3g ($\frac{1}{2}$ 0 $\frac{1}{2}$) positions. In agreement with a phenomenon known as lanthanide contraction [5], the lattice parameter a decreases with increasing atomic number across the rare-earth series [4], while the c parameter remains almost unchanged [4]. We found it of interest to investigate whether this behaviour can be reproduced by *ab initio* calculations and which approach would yield the best results. Although some data concerning band structure calculations for selected $RENi_5$ compounds exist (see, for example, Refs. [6, 7]), no attempt of predicting the lanthanide contraction for these materials by an *ab initio* study has been reported to the authors' knowledge. However, conclusions regarding reproducibility of the lanthanide contraction by first principle calculations could be useful for prediction of structural properties of intermetallic compounds with a non-trivial crystal structure (i.e., not cubic), especially in view of potential applications for which details of the crystal structure play a crucial role, such as hydrogen storage materials.

2. Details of calculations

FP-LAPW [8] band structure calculations were performed using 2k9 version of the Wien2K [9] FP-LAPW code with 133 k-points in the irreducible Brillouin zone. Perdew–Burke–Ernzerhof [10] exchange-correlation potential ($V_{\rm xc}$) was used since it is known to give more reliable results than local spin density approximation (LSDA-type) $V_{\rm xc}$ in case of lattice parameters and bulk modulus calculations. Calculations were performed for all compounds starting from the same values of lattice parameters: $a = 4.895$ Å, $c = 3.969$ Å. These values were selected as approximate averages of the experimental data across the whole $RENi_5$ series. The starting a and c values corresponded to the middle point on a 3×3 grid and a and c were varied by 3%. The optimised a and c values were obtained from a paraboloid fit of total energy vs. lattice parameter $E(a, c)$ on the 3×3 grid. Muffin-tin radii $R_{\rm MT}$ of 2.5 a.u. (atomic unit) for the rare earths and 2.17 a.u. for Ni were chosen as values allowing to have the same $R_{\rm MT}$ values for all calculations. A value of U equalling 6 eV, typical for the rare earths, was assumed for the $4f$ states within the generalized gradient approximation with U (GGA+U) approach. Around mean field (AMF) and fully localised limit (FLL) approaches were used to account for double-counting (see Ref. [11]).

The only difference in the initial conditions for all calculations was the choice of the particular RE atom in the $RENi_5$ unit cell.

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3. Results and discussion

The Table shows the optimised lattice parameters a and c across the $RENi_5$ series. The optimised lattice parameters and the cube root of the cell volume are also shown in Fig. 1 as function of the RE^{3+} radius to present the regularity of the lanthanide contraction trend [5]. Experimental data are compared with calculation results obtained within GGA and several GGA+U approaches with different double counting schemes. The series of calculations for the eight RE compounds selected required the number of compounds × the number of GGA/GGA+U approaches × 9 point (a, c) grid = 288 band structure calculations, for which it was not always possible to obtain converged results without ghost-bands using the same starting parameters (R_{MT}, cut-off energy for core states, etc.). We preferred not to tune each parameter in order to preserve the consistency across the series of calculations (the same initial conditions in all cases, only the RE atom changed). Only the results with no doubt about the quality of calculations are presented in the Table.

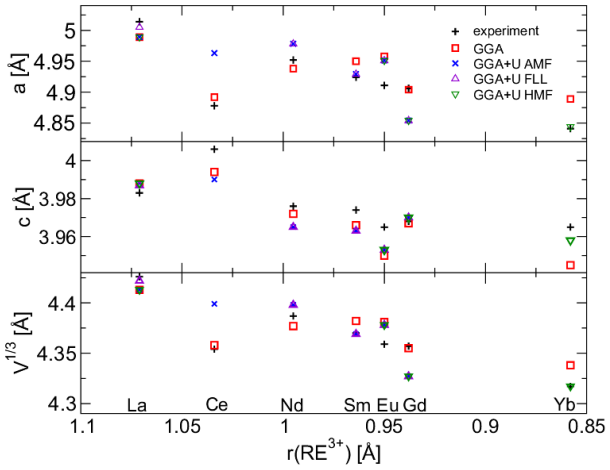

Fig. 1. Optimised lattice parameters a and c and cube root of the optimised atomic cell volume ($V^{1/3}$) for $RENi_5$ compounds as function of trivalent rare earth radius ($r(RE^{3+})$). The $r(RE^{3+})$ values were taken from Ref. [5].

There is not a large difference between the GGA and GGA+U results for $LaNi_5$ and $SmNi_5$. However, GGA gives better agreement with experimental lattice parameters than GGA+U for $NdNi_5$, $CeNi_5$, $GdNi_5$, and $TbNi_5$. This result can be explained by the fact that the value of $U = 6$ eV requires a careful tuning to give good agreement with spectroscopic data. As a predictive method, the use of the bare GGA seems, however, more reasonable, as it yields the most regular contraction trend and overall the best agreement with the experimental data. The difference between the particular double counting schemes is small for $RENi_5$ with RE = Nd, Sm, Eu and Tb. GGA+U with the HMF double counting scheme gives good agreement with the experimental lattice parameters for $YbNi_5$. The trivalent configuration of Eu known from experiment for $EuNi_5$ [12] is particularly difficult to reproduce within DFT band structure calculations, which is the reason of a large discrepancy between the theoretical and experimental lattice parameters for this compound. However, the calculations within the GGA approach were able to reproduce the deviation of the a and c parameters of $CeNi_5$ from the regular trend due to the mixed valency of cerium in this compound [13].

It is to be noted that the agreement between theory and experiment is satisfactory separately for the a and c parameters (Fig. 1).

TABLE

Experimental [4] and calculated lattice parameters a and c for the $RENi_5$ series. Different double counting schemes within the GGA+U approach are denoted by the superscript.

Compound	$a_{\mathrm{exp}}/a_{\mathrm{calc}}/a_{\mathrm{calc}}^{\mathrm{AMF}}/a_{\mathrm{calc}}^{\mathrm{FLL}}/a_{\mathrm{calc}}^{\mathrm{HMF}}$ [Å]	$c_{\mathrm{exp}}/c_{\mathrm{calc}}/c_{\mathrm{calc}}^{\mathrm{AMF}}/c_{\mathrm{calc}}^{\mathrm{FLL}}/c_{\mathrm{calc}}^{\mathrm{HMF}}$ [Å]
$LaNi_5$	5.014/4.989/4.989/5.005/4.989	3.983/3.988/3.988/3.987/3.988
$CeNi_5$	4.878/4.892/4.963/–/–	4.006/3.994/3.990/–/–
$NdNi_5$	4.952/4.938/4.978/4.978/–	3.976/3.972/3.965/3.965/–
$SmNi_5$	4.924/4.950/4.929/4.929/–	3.974/3.966/3.963/3.963/–
$EuNi_5$	4.911/4.958/4.951/4.951/4.951	3.965/3.950/3.953/3.953/3.953
$GdNi_5$	4.906/4.904/4.854/4.854/4.854	3.968/3.967/3.970/3.970/3.970
$TbNi_5$	4.894/4.872/–/4.902/–	3.966/3.966/–/3.960/–
$YbNi_5$	4.841/4.889/–/–/4.844	3.965/3.945/–/–/3.958

4. Conclusions

The lanthanide contraction is in general reproduced by our calculations despite a non-trivial crystal structure. Differences between equilibrium lattice parameters obtained from GGA and GGA+U calculations are noticeable, the GGA calculations give better agreement between calculated and experimental lattice parameters for $CeNi_5$, $NdNi_5$, and $TbNi_5$. The opposite situation is en-

countered for $YbNi_5$, where the GGA+U approach with the HMF scheme gives better results. The choice of a particular double counting scheme within the GGA+U approach has small impact on equilibrium lattice parameters.

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