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Ab initio calculations on the formation of $\text{La}_{1-x}\text{Ni}_2$ compounds

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Abstract

First principle calculations have been performed to compare the stability of the stoichiometric LaNi_2 compound, crystallizing in the cubic C15 structure, with that of the C15 superstructure compound $\text{La}_{15}\text{Ni}_{32}$ and the tetragonal $\text{La}_7\text{Ni}_{16}$ which both contain La vacancies. These results show that LaNi_2 is not stable against decomposition in the two neighbouring phases La_2Ni_3 and LaNi_3 of the La–Ni phase diagram, which means that LaNi_2 cannot be formed. The formation of La vacancies allows the relaxation of the stresses caused by too short La–La distances and lowers the enthalpy of formation. The $\text{La}_7\text{Ni}_{16}$ phase is more stable than the cubic $\text{La}_{15}\text{Ni}_{32}$, but the enthalpy of formation of $\text{La}_{15}\text{Ni}_{32}$ lies only slightly above the critical value for stability. This small difference may explain that, with very pure lanthanum, the formation of a cubic $\text{La}_{15}\text{Ni}_{32}$ phase is not observed, but can be stabilized by the presence of impurities present in commercial La.

1. Introduction

The RNi_2 compounds ($R = \text{Y}$, lanthanide) were believed for a long time to crystallize in the MgCu_2 type cubic structure (C15). Several authors reported the existence of a cubic C15 LaNi_2 compound when quenched from the melt with cell parameters ranging from 7.262 to 7.365 Å [1–4]. Nevertheless extra lines in the x-ray diffraction (XRD) pattern of LaNi_2 have been observed [3], indicating a two-phase alloy at this composition. The deviation from the ideal 1:2 stoichiometry was first reported in [5] where it was shown that the cubic phase LaNi_x exists in the homogeneity range $2.17 \leq x \leq 2.21$ when annealed between 660 and 730 °C. The existence of superstructure lines corresponding to a doubling of the cell parameter was then reported for $\text{LaNi}_{2.17}$ and $\text{CeNi}_{2.16}$ [6]. In [5] the existence of a second $\text{LaNi}_{2.286}$ phase, obtained for larger Ni content and after annealing at temperatures lower than 730 °C, was reported for the first time. Above 730 °C the $\text{LaNi}_{2.28}$ phase decomposes into $\text{LaNi}_{2.21}$ and LaNi_3 . Its XRD pattern was indexed according to an orthorhombic structure ($a = 6.890$ Å,

$b = 7.146 \text{ \AA}$, $c = 8.312 \text{ \AA}$). A single-crystal study [7] allowed one to refine this phase in a tetragonal structure with the space group $I42m$ and cell parameters $a = 7.355 \text{ \AA}$ and $c = 14.51 \text{ \AA}$, which means a doubling of the cell along the c axis. The formula of this phase $\text{LaNi}_{2.286}$ can be expressed as $\text{La}_7\text{Ni}_{16}$, which means—compared to the ideal cubic $\text{La}_8\text{Ni}_{16}$ cell—that one La atom is missing among 8. In [8] the La–Ni phase diagram from LaNi to LaNi_5 has been re-investigated, showing that only $\text{LaNi}_{2.286}$ exists around the 1:2 composition, whereas in [9] the existence of both cubic $\text{LaNi}_{2.17}$ and tetragonal $\text{LaNi}_{2.286}$ phases have been found. These discrepancies could be due to the purity of the La metal since the cubic $\text{LaNi}_{2.17}$ phase can only be obtained from a commercial La (99.9%) and not from high purity La provided by Ames Laboratory.

The existence of ordered rare earth vacancies has also been observed in the other $\text{R}_{1-x}\text{Ni}_2$ compounds, leading to a doubling of the cubic cell parameters [10]. The amount of ordered vacancies is correlated to the size of the rare earth element, i.e. it decreases with the decrease of the rare earth radius due to the lanthanide contraction [11]. *Ab initio* calculations performed on $\text{Y}_{1-x}\text{Ni}_2$ have already shown that the $\text{Y}_{0.95}\text{Ni}_2$ phase, containing ordered Y vacancies, has a lower free enthalpy of formation than the ideal C15 stoichiometric structure [12]. The preferential stability of this phase has been confirmed by the consideration of the two neighbouring phases in the Y–Ni phase diagram, YNi and YNi_3 . Owing to the particular structural behaviour of the $\text{La}_{1-x}\text{Ni}_2$ system, compared to the other RNi_2 compounds, we have performed *ab initio* total energy calculations of cubic $\text{La}_{15}\text{Ni}_{32}$ and tetragonal $\text{La}_7\text{Ni}_{16}$ compared to the ideal LaNi_2 cubic compound in order to gain a better understanding of the existence of ordered rare earth vacancies in the $\text{R}_{1-x}\text{Ni}_2$ series. The results of the calculation will first be presented for the La–Ni compounds, including the two neighbouring La_2Ni_3 and LaNi_3 phases, then discussed in relation to the calculations previously performed for the Y–Ni compounds [12].

2. Computational set-up for calculations

The *ab initio* calculations of the total energy and of the electronic structure have been performed using the program package VASP [13], which allows one to minimize the total energy with respect to the volume and shape of the unit cell, and to the atomic positions, which are not fixed by space group symmetry. For a detailed description of the computational procedure used for the present calculations we refer to [12] and [14]. For the La atoms the projector augmented plane wave method was used instead of the ultrasoft potential method, which is not suitable for lanthanides. The set of k points, used for the total energy calculations, was adapted to the size of the primitive cell. As an example, a $7 \times 7 \times 7$ k -point mesh was used for LaNi_2 , a $2 \times 2 \times 2$ for $\text{La}_{15}\text{Ni}_{32}$ and a $3 \times 3 \times 3$ for $\text{La}_7\text{Ni}_{16}$. A finer grid was used for the DOS calculations, $13 \times 13 \times 13$ for LaNi_2 and $5 \times 5 \times 5$ for $\text{La}_7\text{Ni}_{16}$.

3. Results and discussion

3.1. Structural model

For stoichiometric LaNi_2 we have considered the ideal cubic MgCu_2 structure (C15, space group $Fd\bar{3}m$), where the La and Ni positions are fixed by symmetry. For the compounds with La vacancies we have considered the two possible structures derived from the cubic C15 structure: the cubic superstructure of C15 with formula unit $\text{La}_{15}\text{Ni}_{32}$ (space group $F\bar{4}3m$), which implies a doubling of the cell parameter ($a = 14.75 \text{ \AA}$), and a body-centred tetragonal structure for $\text{La}_7\text{Ni}_{16}$ ($I42m$), which implies a doubling and a small contraction of the c axis

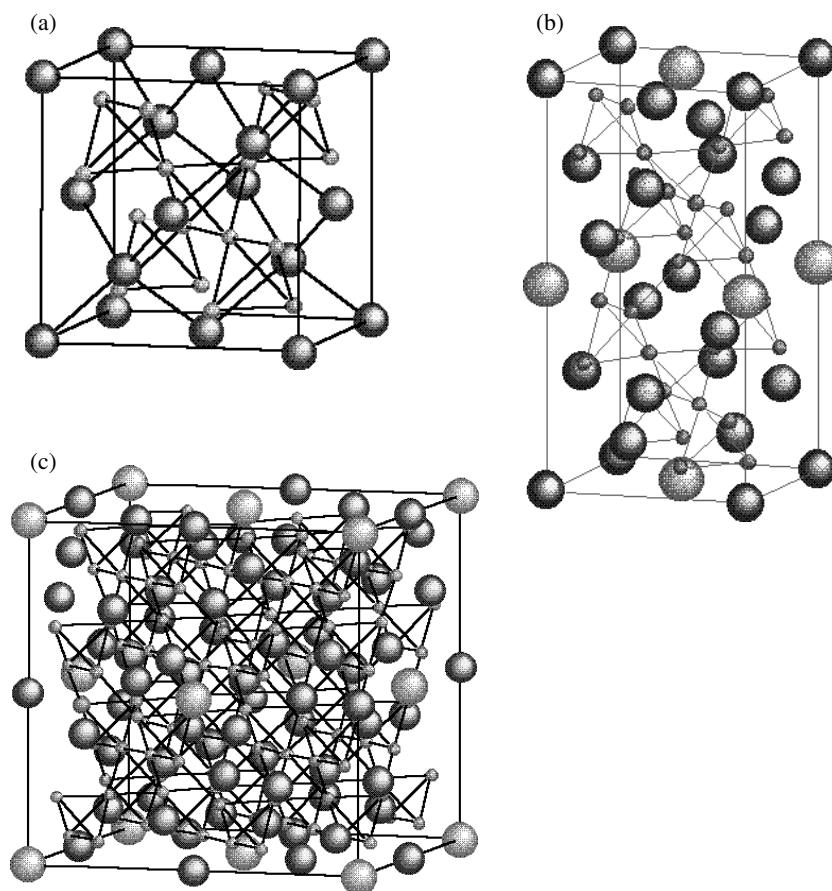


Figure 1. Models of the crystal structures of (a) LaNi_2 , (b) $\text{La}_7\text{Ni}_{16}$ and (c) $\text{La}_{15}\text{Ni}_{32}$. The La vacancies are indicated by the large gray balls, the La atoms by the medium one and the Ni by the small one.

($a = 7.355 \text{ \AA}$ and $c = 14.51 \text{ \AA}$). These different structures are compared in figure 1. For the cubic C15 superstructure phase $\text{La}_{15}\text{Ni}_{32}$, the atomic positions of $\text{Y}_{15}\text{Ni}_{32}$ [12] were taken as starting parameters for the relaxation in the *ab initio* total energy calculations. As in the case of $\text{Y}_{15}\text{Ni}_{32}$ the La 4a sites are considered as fully unoccupied in the calculations. This corresponds to $\text{La}_{0.938}\text{Ni}_2$ which is not far from the experimental $\text{La}_{0.922}\text{Ni}_2$ value. For the tetragonal $\text{La}_7\text{Ni}_{16}$, we have taken the structural model, which was refined for a single-crystal compound in [7]. The La vacancies are located at the 2b sites of space group $I\bar{4}2m$. As can be seen in figure 1, the difference of symmetry between these two structures leads to two different locations of the La vacancies within the cell. For the computation, the primitive cell has been considered, leading to 6 atoms for LaNi_2 , 47 atoms for $\text{La}_{15}\text{Ni}_{32}$ and 23 atoms for $\text{La}_7\text{Ni}_{16}$.

3.2. Enthalpy of formation

Since LaNi_2 , $\text{La}_{15}\text{Ni}_{32}$ and $\text{La}_7\text{Ni}_{16}$ have different stoichiometries it is necessary to consider their enthalpies of formation per atom to compare the structural stability of these phases:

$$\Delta H(\text{La}_{1-y}\text{Ni}_y) = E(\text{La}_{1-y}\text{Ni}_y) - (1 - y)E(\text{La}) - yE(\text{Ni}) \quad (1)$$

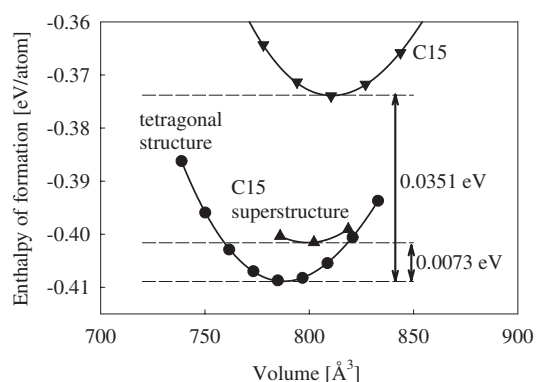


Figure 2. Comparison of the enthalpy of formation versus volume of LaNi_2 , $\text{La}_{15}\text{Ni}_{32}$ and $\text{La}_7\text{Ni}_{16}$ (see text). The volume corresponds to the primitive unit cell of the C15 superstructure (46 atoms for the tetragonal structure, 47 for the C15 superstructure and 48 for C15).

with $E(\text{La}_{1-y}\text{Ni}_y)$ the total equilibrium energy of the phase, and $E(\text{La}) = -4.870$ eV/atom and $E(\text{Ni}) = -5.420$ eV/atom the total equilibrium energy of the constituent elements, also calculated with VASP. For each phase, the total energy was calculated for different volumes around the equilibrium volume. Then the minimum total energy, as well as the equilibrium volume, was determined by interpolation. The minimum total energies thus obtained are $E(\text{LaNi}_2) = -16.831$ eV, $E(\text{La}_{15}\text{Ni}_{32}) = -265.356$ eV and $E(\text{La}_7\text{Ni}_{16}) = -130.209$ eV, leading to $\Delta H(\text{LaNi}_2) = -0.3738$ eV/atom, $\Delta H(\text{La}_{15}\text{Ni}_{32}) = -0.4016$ eV/atom and $\Delta H(\text{La}_7\text{Ni}_{16}) = -0.4089$ eV/atom. In figure 2 the enthalpy of formation versus volume of LaNi_2 , $\text{La}_{15}\text{Ni}_{32}$ and $\text{La}_7\text{Ni}_{16}$ are compared, showing that the two phases with La vacancies are much more stable than the stoichiometric phase ($\Delta H(\text{La}_7\text{Ni}_{16}) - \Delta H(\text{LaNi}_2) = -0.0351$ eV/atom), whereas the difference between $\text{La}_7\text{Ni}_{16}$ and $\text{La}_{15}\text{Ni}_{32}$ is about five times smaller (-0.0073 eV).

It is also interesting to compare the calculated volume of formation of each phase according to the equation

$$\Delta V(\text{La}_{1-y}\text{Ni}_y) = V(\text{La}_{1-y}\text{Ni}_y) - (1-y)V(\text{La}) - yV(\text{Ni}) \quad (2)$$

leading to $\Delta V(\text{LaNi}_2) = -2.855 \text{ \AA}^3$, $\Delta V(\text{La}_{15}\text{Ni}_{32}) = -2.297 \text{ \AA}^3$ and $\Delta V(\text{La}_7\text{Ni}_{16}) = -1.853 \text{ \AA}^3$.

This means that the loss of volume due to the formation decreases with increasing number of vacancies. This can be explained by the displacement of the La and Ni atoms around the vacancies in order to obtain a more compact structure. The decrease (compared to LaNi_2) is 0.56 \AA^3 for $\text{La}_{15}\text{Ni}_{32}$ and 1.002 \AA^3 for $\text{La}_7\text{Ni}_{16}$, following the amount of La vacancies.

3.3. Structural stability relative to the neighbouring phases in the La–Ni phase diagram

In order to compare the stabilities of the discussed phases around the composition 1:2 (LaNi_2 , $\text{La}_{15}\text{Ni}_{32}$ and $\text{La}_7\text{Ni}_{16}$) with those of the neighbouring stable compounds of the La–Ni phase diagram (La_2Ni_3 and LaNi_3), we have also calculated the enthalpy of formation of La_2Ni_3 (orthorhombic, space group $Cmca$) and of LaNi_3 (rhombohedral, space group $R\bar{3}m$). The calculated enthalpies are $\Delta H = -0.3916$ eV/atom for La_2Ni_3 and $\Delta H = -0.3836$ eV/atom for LaNi_3 . The diagram thus obtained in figure 3 clearly shows that the C15 structure is unstable against decomposition in the two neighbouring phases La_2Ni_3 and LaNi_3 , lying about 14 meV (d_1 in the figure) above the critical line connecting La_2Ni_3 and LaNi_3 (broken line).

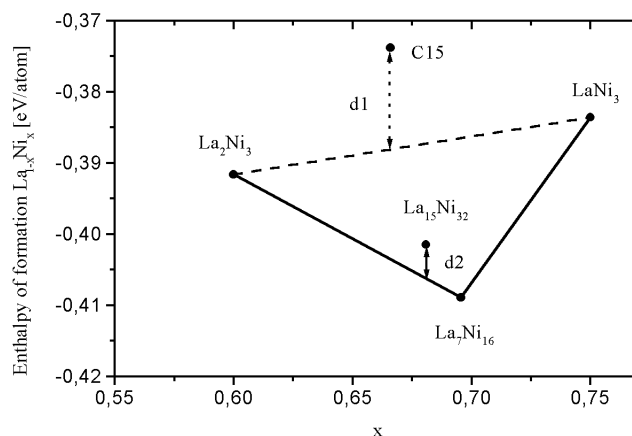


Figure 3. Enthalpy of formation of the $\text{La}_{1-x}\text{Ni}_x$ phases near the composition 1:2 (see text).

This means that LaNi_2 cannot crystallize in the C15 structure. On the contrary, both the $\text{La}_{15}\text{Ni}_{32}$ and $\text{La}_7\text{Ni}_{16}$ phases are stable against decomposition in the two neighbouring phases La_2Ni_3 and LaNi_3 , since their formation enthalpies clearly lie below this critical line. But, as the figure shows, the $\text{La}_{15}\text{Ni}_{32}$ phase is not stable against decomposition in $\text{La}_7\text{Ni}_{16}$ and La_2Ni_3 , i.e. $\text{La}_7\text{Ni}_{16}$ should be the only stable phase around the composition 1:2. However, the difference $d_2 \approx 5$ meV between the formation enthalpy of $\text{La}_{15}\text{Ni}_{32}$ and the critical line between $\text{La}_7\text{Ni}_{16}$ and La_2Ni_3 is very small and near the intrinsic errors of the *ab initio* calculations. This could explain that, under certain conditions (e.g. due to some impurities contained in La), the cubic $\text{La}_{15}\text{Ni}_{32}$ phase can also be stabilized.

3.4. Relaxation of the atoms in the $\text{La}_7\text{Ni}_{16}$ and $\text{La}_{15}\text{Ni}_{32}$ phases

The *ab initio* calculations, performed in the present study, include the relaxation of those atomic position, which are not fixed by the crystal symmetry. Table 1 shows the calculated atomic positions in $\text{La}_7\text{Ni}_{16}$, compared to the experimental ones and those derived from the C15 structure described in the $I42m$ space group. The differences between the calculated and experimental atomic positions are within or close to the experimental errors, and it must be mentioned that there are also errors in the calculation, mainly due to an approximate exchange-correlation potential compared to the real one governing the crystalline structure, so that small deviations between calculated and experimental structural parameters may be meaningless. However, what is most interesting are the deviations of the calculated (or experimental) atomic positions of $\text{La}_7\text{Ni}_{16}$ from the ideal C15 values. These deviations are very pronounced for some of the parameters and much larger than the errors in the experimental and/or calculated values. The La3 atoms, which are close to the vacancies, are displaced from their ideal positions by 0.65 Å, and the Ni by 0.07, 0.023 and 0.11 Å for Ni 1–3, respectively. The La3 atoms are shifted towards the vacancies whereas the Ni2 and Ni3 are shifted out of the way. Table 2 shows the atomic positions calculated for $\text{La}_{15}\text{Ni}_{32}$ in the cubic $F\bar{4}3m$ space group, compared with those derived from the C15 structure. Experimental data are not available for this compound, since its structure was not completely resolved. The La2 atoms are closest to the La vacancies, and show a displacement of 0.67 Å, whereas La3 is displaced by only 0.08 Å and La4 by 0.24 Å. The Ni3 atom is displaced by 0.1 Å, whereas Ni1, 2 and 4 are displaced by 0.02–0.03 Å.

Table 1. Experimental and calculated atomic positions for $\text{La}_7\text{Ni}_{16}$ compared with the ideal values for LaNi_2 (C15), described in the tetragonal $I\bar{4}2m$ space group. For LaNi_2 (C15) all parameters are fixed by symmetry.

Atom	$I\bar{4}2m$ S.G	General position	$\text{La}_7\text{Ni}_{16}$ calculated	$\text{La}_7\text{Ni}_{16}$ experiment	C15
La vacancy	2b	0, 0, 1/2	Fixed	Fixed	Fixed
La1	2a	0, 0, 0	Fixed	Fixed	Fixed
La2	4d	0, 1/2, 1/4	Fixed	Fixed	Fixed
La3	8i	x, x, z	$x = 0.3042$ $z = 0.1027$	$x = 0.3043(3)$ $y = 0.1025(2)$	$x = 0.25$ $z = 0.125$
Ni1	8i	x, x, z	$x = 0.3819$ $z = 0.3146$	$x = 0.3816(7)$ $y = 0.3136(5)$	$x = 0.375$ $z = 0.3125$
Ni2	8i	x, x, z	$x = 0.1393$ $z = 0.3014$	$x = 0.1413(6)$ $y = 0.3014(5)$	$x = 0.125$ $z = 0.3125$
Ni3	16j	x, y, z	$x = 0.1318$ $y = 0.3827$ $z = 0.4344$	$x = 0.1328(7)$ $y = 0.3848(6)$ $y = 0.4335(4)$	$x = 0.125$ $y = 0.375$ $z = 0.4375$

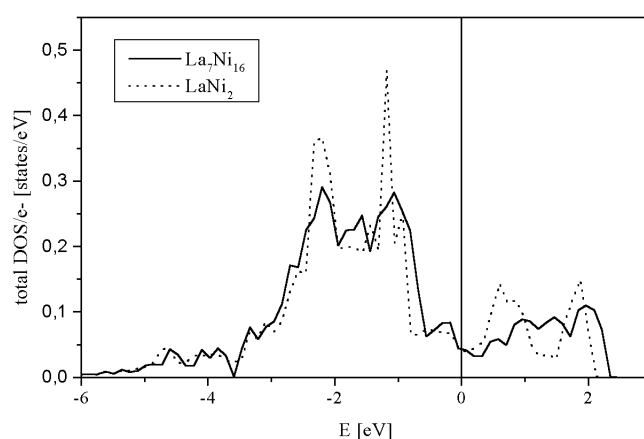
Table 2. Calculated atomic positions of $\text{La}_{15}\text{Ni}_{32}$, compared with LaNi_2 (C15) and described in the cubic $F\bar{4}3m$ space group. For LaNi_2 (C15) all parameters are fixed by symmetry.

Atom	Site	General position	$\text{La}_{15}\text{Ni}_{32}$ calculated	C15
Vacancies	4a	0.0.0	Fixed	Fixed
La1	4b	1/2, 1/2, 1/2	Fixed	Fixed
La2	16e	x, x, x	$x = 0.0986$	$x = 0.125$
La3	16e	x, x, x	$x = 0.6281$	$x = 0.625$
La4	24g	$x, 1/4, 1/4$	$x = 0.0165$	$x = 0.0$
Ni1	16e	x, x, x	$x = 0.3114$	$x = 0.3125$
Ni2	16e	x, x, x	$x = 0.8117$	$x = 0.8125$
Ni3	48h	x, x, z	$x = 0.0660$ $z = 0.8083$	$x = 0.0625$ $z = 0.8125$
Ni4	48h	x, x, z	$x = 0.0612$ $z = 0.3128$	$x = 0.0625$ $z = 0.3125$

The interatomic distances calculated for the three structures are compared in table 3. The distances between the vacancies and the neighbouring La and Ni atoms are very similar in both $\text{La}_7\text{Ni}_{16}$ and $\text{La}_{15}\text{Ni}_{32}$. The main difference is observed for the distances between the lanthanum atoms, which become larger as the number of vacancies increases. Concerning the La–Ni and Ni–Ni distances, we have reported only the minimum, maximum and average distances, due to the large number of different distances in $\text{La}_7\text{Ni}_{16}$ and $\text{La}_{15}\text{Ni}_{32}$. They are not very different in these two phases and lie around the mean values calculated for the C15 structure. Nevertheless one can notice the existence of very short Ni–Ni distances (2.46 Å) in $\text{La}_7\text{Ni}_{16}$, close to Ni metal. The main effect of the existence of La vacancies is therefore to increase the La–La distances, which would be strongly compressed in the ideal C15 structure (3.20 Å) compared to pure La (3.76 Å). In contrast, the Ni–Ni distances are larger in LaNi_2 (2.616 Å) than in Ni metal (2.48 Å). This opposite behaviour between La and Ni atoms is related to the fact that the ratio of the La/Ni radii (1.515) is significantly larger than the ideal 1.225 ratio calculated for the C15 structure.

Table 3. Selected calculated interatomic distances in LaNi_2 , $\text{La}_{15}\text{Ni}_{32}$ and $\text{La}_7\text{Ni}_{16}$.

Atom 1	Atom 2		$d(\text{LaNi}_2)$	$d(\text{La}_{15}\text{Ni}_{32})$	$d(\text{La}_7\text{Ni}_{16})$
La	La		3.204	3.382	3.497
				3.319	3.415
				3.273	
Vacancies	La			2.519	2.521
Vacancies	Ni			3.145	3.237
					3.146
La	Ni	Maximum		3.284	3.355
		Mean	3.068	3.029	2.995
		Minimum		2.830	2.826
Ni	Ni	Maximum		2.633	2.898
		Mean	2.616	2.595	2.592
		Minimum		2.533	2.457

**Figure 4.** Total electronic DOS of C15 LaNi_2 and tetragonal $\text{La}_7\text{Ni}_{16}$.

3.5. Electronic density of states

Figure 4 shows the total electronic density of states (DOS) of C15 LaNi_2 and tetragonal $\text{La}_7\text{Ni}_{16}$. The main effect of the lowering of symmetry due to La vacancies on the DOS is a broadening of the fine structures. This can be related to the distribution of the interatomic distances in the tetragonal phase. The Fermi level is, in both cases, close to a minimum of the DOS. This result, like that for the Y–Ni system, indicates that the stabilization of a phase which contains Y or R vacancies is related to a geometrical effect allowing stress relaxation rather than to an electronic effect [12, 15].

3.6. Comparison of $\text{La}_{1-x}\text{Ni}_2$ with the other $\text{R}_{1-x}\text{Ni}_2$ phases

The stabilization of the $\text{Y}_{1-x}\text{Ni}_2$ phases has previously been studied by similar *ab initio* calculations, using the VASP program [12]. There it was shown that both YNi_2 and $\text{Y}_{15}\text{Ni}_{32}$ are stable against decomposition in the neighbouring compounds in the Y–Ni phase diagram (YNi_3 and YNi), but YNi_2 is not stable against decomposition in $\text{Y}_{15}\text{Ni}_{32}$ and YNi . In the case of the La–Ni compounds the stoichiometric LaNi_2 phase is even unstable against

decomposition in the neighbouring compounds in the La–Ni phase diagram (La_2Ni_3 and LaNi_3). In addition, experimental studies showed the existence of two possible structures containing La vacancies [5]: a cubic one, with a structure close to that of $\text{Y}_{15}\text{Ni}_{32}$, and a tetragonal one, which contains twice as many vacancies. The present calculations show that both phases are stable against decomposition in the neighbouring phases and display a lowering of the enthalpy of formation about three times larger than for the corresponding Y–Ni compounds. In both the Y–Ni and La–Ni systems the existence of R vacancies induces an increase of the R–R distances (which are too short in the ideal C15 structure) and leads therefore to stress relaxation. The amount of rare earth vacancies necessary to stabilize a $\text{R}_{1-x}\text{Ni}_2$ compound near the 1:2 stoichiometry is strongly dependent on the rare earth size. A systematic experimental study of RNi_2 compounds [11] has shown that the amount of ordered vacancies decreases as the size of the rare earth decreases. For LuNi_2 a 1:2 stoichiometric compound with the C15 structure has been obtained [11]. It has also been observed that a reversible order–disorder transition can occur at high temperatures or under high pressure [16], corresponding to the redistribution of the ordered vacancies within the structure. Since the La atoms have a larger atomic radius (1.877 Å) than the Y atoms (1.81 Å), the stresses in the C15 structure would be larger for the La compound, and therefore a larger amount of vacancies is necessary to stabilize the structure. As a consequence, $\text{La}_{1-x}\text{Ni}_2$ crystallizes preferentially in a tetragonal structure with more vacancies than the cubic C15 superstructure of the other $\text{R}_{1-x}\text{Ni}_2$ compounds. It is a characteristic that in many RM_2 systems, where M is a 3d transition metal, the behaviour of the La-containing compounds is different from the other RM_2 compounds of the series. Two examples for this are: (i) LaFe_2 and LaCo_2 can—in contrast to the other RFe_2 and RCo_2 compounds—only be obtained under high pressure and (ii) LaCu_2 crystallizes in an AlB_2 hexagonal structure more symmetric than the CeCu_2 type orthorhombic structure [14] which is the stable structure of the other RCu_2 compounds.

4. Conclusion

In this study we have compared the enthalpy of formation of cubic C15 LaNi_2 with that of the C15 superstructure compound $\text{La}_{15}\text{Ni}_{32}$ and tetragonal $\text{La}_7\text{Ni}_{16}$ by *ab initio* total energy calculations, showing that the stoichiometric LaNi_2 compound is not stable. The formation of La vacancies allows relaxation of the stresses caused by the compression of the La atoms in the C15 structure, and leads to stable structures. According to these calculations the tetragonal $\text{La}_7\text{Ni}_{16}$ phase is the only stable phase around the 1:2 composition, but the formation enthalpy of cubic $\text{La}_{15}\text{Ni}_{32}$ lies only slightly above the critical value of stability. Since the calculations are based on the assumption of 100% pure La, this allows us to understand why only for very pure La is the $\text{La}_7\text{Ni}_{16}$ phase the only stable one around the composition 1:2. The presence of interstitial impurities could induce a sufficient lowering of the enthalpy of formation, stabilizing also the experimentally observed cubic $\text{La}_{1-x}\text{Ni}_2$ phase.

Acknowledgments

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