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***Ab initio* studies of the formation of a $Y_{1-x}Ni_2$ superstructure with ordered Y vacancies**

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Received 19 August 1998

Abstract. *Ab initio* total-energy calculations have been performed to study the structural stability of $Y_{1-x}Ni_2$. In the literature (Villars P and Calvert L D 1985 *Pearson's Handbook of Crystallographic Data for Intermetallic Phases* (Materials Park, OH: American Society for Metals)) YNi_2 is often considered to show the cubic Laves phase structure, but x-ray diffraction experiments of Latroche *et al* (*J. Less-Common Met.* **161** L27) showed that YNi_2 crystallizes in a superstructure of C15 with ordered Y vacancies with a stoichiometry of approximately $Y_{0.95}Ni_2$. The total-energy calculations for the superstructure and for the ideal C15 structure, as well as for the neighbouring phases in the Y–Ni phase diagram YNi and YNi_3 , confirm that the formation of the superstructure with Y vacancies is favoured against the formation of the pure C15 compound YNi_2 . The calculated relaxation of the atoms around the vacancies is also in good agreement with the experimental results (Latroche *et al*), demonstrating that the relaxation of strains in the Y sublattice is the driving mechanism for formation of vacancies. In addition, the electronic properties of the vacancy superstructure have been examined.

1. Introduction

Deviations from the ideal cubic C15 structure (MgCu₂ type, space group $Fd\bar{3}m$) in RNi_2 compounds have been reported in the literature since 1988. Paul-Boncour *et al* [1] observed superstructure lines in $LaNi_{2.18}$ and $CeNi_{2.16}$, which were indexed on the basis of a C15 unit cell with doubled lattice parameter a . In 1989 Deutz *et al* [2] reported a superstructure phase of $TmNi_2$ which was described within the cubic space group $F\bar{4}3m$, also with doubled lattice parameter a . The first detailed analysis of the C15 superstructure with doubled lattice parameter was performed by Latroche *et al* [3] for YNi_2 . They showed that a single phase compound can only be obtained with stoichiometry 0.95:2 and described it within space group $F\bar{4}3m$ with the 4a sites only partially occupied by the Y atoms (the refinement gave an occupation factor of about 0.25 instead of one for these sites). A systematic investigation of the $R_{1-x}Ni_2$ compounds revealed that this kind of defect superstructure is also present for $R = Pr, Nd, Gd, Tb, Dy, Ho$ and Er ; however the occupancy factor of the Y 4a sites increases with decreasing radius of the R atom from 0.12 for Pr to 0.68 for Er and reaches 1 for Lu [4].

An interesting property of the $Y_{1-x}Ni_2$ and $R_{1-x}Ni_2$ compounds is a reversible transition from the superstructure with ordered Y vacancies to disordered (statistically distributed) vacancies at high temperatures, which was first detected by anomalies in the transport properties and the thermal expansion, and later directly observed by the vanishing of the additional x-ray diffraction lines of the superstructure above the transition temperature [5]. Furthermore

high-pressure x-ray diffraction experiments (also reported in [5]) showed that there is also a pressure-induced transition from ordered to disordered vacancies in $Y_{1-x}Ni_2$ at room temperature between 14 and 27 GPa. More detailed high-pressure studies on $Y_{1-x}Ni_2$ and other $R_{1-x}Ni_2$ are in progress and will be reported soon.

The aim of the present work was to study the formation of a $Y_{1-x}Ni_2$ superstructure with ordered Y vacancies by performing *ab initio* total-energy calculations for the ideal C15 structure, for the vacancy superstructure and for the neighbouring compounds in the Y–Ni phase diagram YNi and YNi_3 .

2. Computational set-up for the *ab initio* total-energy calculations

Ab initio calculations of the total energy and of the electronic structure were performed using the Vienna *ab initio* simulation package VASP [6, 7]. VASP performs an iterative solution of the Kohn–Sham equations of local-density-functional (LDF) theory based on residuum-minimization and optimized charge-density mixing routines [7] and allows us to use generalized gradient corrections. In the present calculations we use the exchange–correlation functional based on the quantum Monte Carlo calculations of Ceperley and Alder, as parametrized by Perdew and Zunger [8], and the gradient corrections proposed by Perdew *et al* [9]. The electronic eigenstates are expanded in terms of plane waves; the electron–ion interaction is described in terms of ultrasoft pseudopotentials [10, 11]. VASP allows for the calculations of the Hellmann–Feynman forces acting on the atoms and of the stresses on the unit cell. Hence the total energy may be optimized with respect to the volume and shape of the unit cell and to the positions of the atoms within the cell, with no other restrictions than those imposed by space-group symmetry. For Brillouin-zone (BZ) integrations we used the Methfessel–Paxton technique [12] with a modest smearing of the one-electron levels (0.1 eV). Convergence of the results with respect to the k -point mesh for BZ integrations, the fast-Fourier-transform meshes used for the representation of the wave-functions, charge densities and potentials, and with respect to the cut-off energy of the plane-wave basis set, was carefully tested.

For the total-energy calculations of the $Y_{1-x}Ni_2$ superstructure (with doubled cubic lattice parameter) a $2 \times 2 \times 2$ k -point mesh was found to be sufficient; a finer mesh ($5 \times 5 \times 5$) was used for calculating the electronic density of states. The total-energy and band structure calculations for the pure C15 phase (YNi_2) were performed using the same supercell (containing eight primitive cells, i.e. 48 atoms) with the same k -point meshes, in order to achieve better convergence of the energy and band structure differences between $Y_{1-x}Ni_2$ and YNi_2 . For the total-energy calculation of the neighbouring compounds YNi (eight atoms in the primitive cell) and YNi_3 (12 atoms in the primitive cell) a $5 \times 5 \times 5$ k -point mesh was sufficient. For all other technical details we refer to [7].

While for transition metals with a nearly full d band ultrasoft pseudopotentials allow us to achieve convergence with respect to the plane-wave basis set at a modest cut-off energy of 150 to 200 eV [11], special problems arise for transition metals with only partially filled d bands such as Y. Total-energy calculations for pure Y show that without generalized gradient corrections (GGCs) the equilibrium atomic volume ($V_Y(\text{exp}) = 32.98 \text{ \AA}^3$ at 0 K) is strongly underestimated ($V_Y(\text{LDA}) = 29.5 \text{ \AA}^3$), even if the Y 4p ‘semicore states’ are treated as valence electrons ($V_Y(4p\text{-LDA}) = 30.1 \text{ \AA}^3$). The best prediction for the equilibrium atomic volume is achieved with GGC and treating the Y 4p states as valence electrons: $V_Y(4p\text{-GGC}) = 32.80 \text{ \AA}^3$. For these reasons throughout this study generalized gradient corrections are used and the Y 4p states are treated as valence electrons. Details of the construction of the Y pseudopotentials have been given in [13].

3. Results and discussion

3.1. Structural model

As reported in [3] it is possible to obtain a single phase compound of 'YNi₂' with stoichiometry 0.95:2, which can be described within the $F\bar{4}3m$ space group with five non-equivalent Y and four non-equivalent Ni sites, whereas in the C15 phase there is only one Y and one Ni site. Hence there are now nine atomic position parameters, which are not fixed by space-group symmetry, whereas within the C15 symmetry all atomic position parameters are fixed. According to a Rietveld analysis of the x-ray diffraction pattern [3] the occupation of the 4a sites by Y is 0.25 (i.e. 25%), which corresponds to the stoichiometry Y_{0.95}Ni₂. For modelling this vacancy superstructure in the *ab initio* calculations we will assume that the occupancy of the 4a sites is exactly 0. This simplification allows us to keep the computational effort at a reasonable level, while it can still give an answer to the question of whether there is a tendency towards the formation of a superstructure with ordered vacancies. The completely empty 4a sites correspond to a stoichiometry of Y_{0.9375}Ni₂ (or Y₁₅Ni₃₂). The original cubic superstructure cell with fully occupied 4a sites contains 192 atoms; with empty 4a sites it contains 188 atoms. In figure 1 the original superstructure cell is shown; the 4a sites are indicated by the big black symbols. For the total-energy calculations the primitive cell of the face-centred cube was used, which contains 48 atoms with occupied 4a sites (16 Y and 32 Ni), i.e. C15 symmetry) or 47 with empty 4a sites (15 Y and 32 Ni).

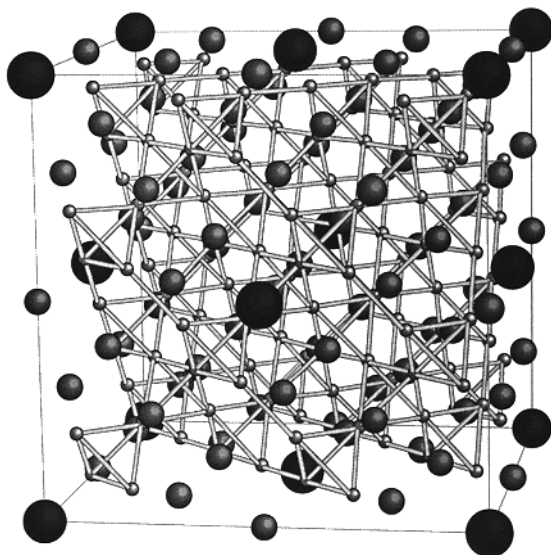


Figure 1. The cubic superstructure cell containing 192 atoms. The Y 4a positions are marked by the big black symbols. The tetrahedral Ni framework is indicated by the bonds.

As already mentioned above, in the case of empty 4a sites the C15 symmetry is lowered so that there are now nine free atomic position parameters. These parameters must be allowed to relax within the *ab initio* calculations, i.e. the total energy must be minimized with respect to these parameters in order to obtain correct results for the total energy. The calculated values for the relaxed atomic positions can then be compared with the results of the Rietveld analysis of the x-ray diffraction pattern [3].

3.2. Enthalpy of formation and volume of formation of the vacancy superstructure compared with the C15 structure

Since the vacancy superstructure and the C15 structure have different stoichiometries one has to compare the enthalpies of formation per atom $\Delta H(Y_{1-y}Ni_y) = E(Y_{1-y}Ni_y) - (1-y)E(Y) - yE(Ni)$ for structural stability considerations, i.e. one has to take into account also the equilibrium total energies of the elements which were also calculated with VASP: $E(Y) = -6.259$ eV at an equilibrium volume of 32.80 \AA^3 and $E(Ni) = -5.420$ eV with at an equilibrium volume of 11.00 \AA^3 (all values per atom).

This gives for $Y_{15}Ni_{32}$ ($y = 15/47$):

$$\Delta H = E(Y_{15/47}Ni_{32/47}) - (15/47)E(Y) - (32/47)E(Ni) = (1/47)E(Y_{15}Ni_{32}) + 5.688 \text{ eV}$$

and for $Y_{16}Ni_{32}$ ($y = 16/48 = 1/3$):

$$\Delta H = E(Y_{16/48}Ni_{32/48}) - (16/48)E(Y) - (32/48)E(Ni) = (1/48)E(Y_{16}Ni_{32}) + 5.700 \text{ eV}$$

In figure 2 these calculated enthalpies are shown as a function of the volume of the primitive cell of the face-centred superstructure cube for both the vacancy superstructure ($Y_{15}Ni_{32} \equiv Y_{0.9375}Ni_2$) and the C15 structure ($Y_{16}Ni_{32} \equiv YNi_2$). As can be seen the enthalpy of formation of the vacancy superstructure ($\Delta H = -0.501$ eV) lies about 0.012 eV below that of the C15 structure ($\Delta H = -0.489$ eV) at the corresponding equilibrium volumes. This is a clear hint that the vacancy superstructure is more stable than the C15 structure; however in order to clarify the question of the structural stability exactly one has also to look at the neighbouring phases in the Y-Ni phase diagram (see section 3.3).

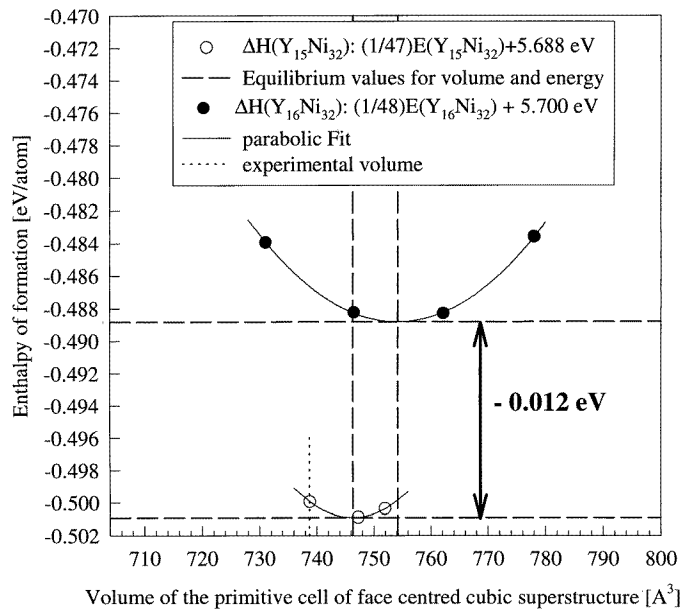


Figure 2. Enthalpy of formation for the vacancy superstructure and for the C15 structure as a function of the unit cell volume.

A further interesting point besides the enthalpy of formation is the comparison of the volumes of formation per atom $\Delta V(Y_{1-y}Ni_y) = V(Y_{1-y}Ni_y) - (1-y)V(Y) - yV(Ni)$ which

can be calculated with the equilibrium volumes shown in figure 2 ($V(Y_{15}Ni_{32}) = 746.3 \text{ \AA}^3$, $V(Y_{16}Ni_{32}) = 754.1 \text{ \AA}^3$) and with the equilibrium volumes of the elements (see above). We note at once that the difference of the volume of the ideal C15 compound and the vacancy superstructure (7.9 \AA^3) is much smaller than the atomic volume of the one missing Y atom (32.8 \AA^3). In terms of the volume of formation we find

$$Y_{15}Ni_{32}: \Delta V = (1/47)V(Y_{15}Ni_{32}) - (15/47)V(Y) - (32/47)V(Ni) = -2.078 \text{ \AA}^3$$

$$Y_{16}Ni_{32}: \Delta V = (1/48)V(Y_{16}Ni_{32}) - (16/48)V(Y) - (32/48)V(Ni) = -2.556 \text{ \AA}^3.$$

This means that the formation of the vacancy superstructure is not accompanied by a volume reduction corresponding to the change in the stoichiometry. The empty space created by the formation of the vacancies is rather used to relax internal strains in the Y sublattice (all Y–Y distances except those around the vacancies increase), as will be discussed in more detail in section 3.4.

In a recent paper [14] *ab initio* calculations were performed to study the structural stability of YCu_2 . Although Cu is the right-hand neighbour of Ni in the periodic table, YCu_2 crystallizes in the orthorhombic $CeCu_2$ structure, which has a completely different atomic arrangement compared to the C15 structure or to the vacancy superstructure of C15 (compared to the pronounced difference between the C15 and the $CeCu_2$ structures the difference between C15 and its vacancy superstructure is very small). The result was that the formation of the $CeCu_2$ structure is mainly caused by electronic effects and cannot be understood in terms of the different size of the Cu and Ni atoms. Within the present work we compared also for YCu_2 the (hypothetical) C15 structure with its vacancy superstructure in the same way as for YNi_2 . The result is that also in the case of YCu_2 the formation of the vacancy superstructure would be energetically favourable compared to the C15 structure. The enthalpy differences are as pronounced as those found for YNi_2 : the enthalpy of formation per atom of the vacancy superstructure $Y_{15}Cu_{32}$ ($\Delta H = -0.197 \text{ eV}$) lies about 0.011 eV below that of the C15 phase $Y_{16}Cu_{32}$ ($\Delta H = -0.186 \text{ eV}$), but considerably above the enthalpy of the $CeCu_2$ -type compound YCu_2 ($\Delta H = -0.303 \text{ eV}$ [14]). The corresponding volumes of formation per atom are $\Delta V = -0.922 \text{ \AA}^3$ for $Y_{15}Cu_{32}$ and $\Delta V = -1.486 \text{ \AA}^3$ for $Y_{16}Cu_{32}$.

As a test for the calculations the same procedure was performed for the well known C15 compound YAl_2 with the expected result that—in contrast to the systems with Ni and Cu—the enthalpy of formation per atom of the vacancy superstructure $Y_{15}Al_{32}$ ($\Delta H = -0.517 \text{ eV}$) lies about 0.035 eV above that of the C15 phase $Y_{16}Al_{32}$ ($\Delta H = -0.552 \text{ eV}$). The corresponding volumes of formation per atom are $\Delta V = -0.973 \text{ \AA}^3$ for $Y_{15}Al_{32}$ and $\Delta V = -1.532 \text{ \AA}^3$ for $Y_{16}Al_{32}$.

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

For the determination of the enthalpy of formation of the neighbouring phases in the Y–Ni phase diagram it was necessary to calculate also the total energy of YNi (FeB type) and YNi_3 (NbBe₃ type) with the following results: $E(YNi) = -12.718 \text{ eV}$ at an equilibrium volume of $41.118 \text{ \AA}^3 \text{ fu}^{-1}$ and $E(YNi_3) = -24.362 \text{ eV}$ at an equilibrium volume of $58.974 \text{ \AA}^3 \text{ fu}^{-1}$.

These total-energy values for YNi and YNi_3 together with the total energies of the elements, already given in section 3.2, yield the following enthalpies of formation per atom:

$$YNi: \Delta H = -0.520 \text{ eV} \text{ and } YNi_3: \Delta H = -0.461 \text{ eV}.$$

There is a remarkable uncertainty concerning experimental data for the heat of formation for

all the three compounds YNi , YNi_2 and YNi_3 :

$$\text{YNi} : \Delta H^{exp} \approx -0.38 \text{ eV [15]} \text{ or } \Delta H^{exp} \approx -0.36 \text{ eV [16]}$$

$$\text{YNi}_2 : \Delta H^{exp} \approx -0.40 \text{ eV [15]} \text{ or } \Delta H^{exp} \approx -0.32 \text{ eV [16]}$$

$$\text{YNi}_3 : \Delta H^{exp} \approx -0.38 \text{ eV [15]} \text{ or } \Delta H^{exp} \approx -0.30 \text{ eV [16]}.$$

In view of this uncertainty and of the general tendency of the local density approximation (even with GGC) to overestimate binding energies, the agreement between theory and experiment can be considered as satisfactory.

In figure 3 the calculated enthalpies of formation for the four neighbouring $\text{Y}_{1-y}\text{Ni}_y$ compounds YNi , YNi_2 (C15), $\text{Y}_{15}\text{Ni}_{32}$ (vacancy superstructure) and YNi_3 are shown as a function of y . The figure can be interpreted as follows:

Both the C15 phase YNi_2 and the vacancy superstructure $\text{Y}_{15}\text{Ni}_{32}$ are stable against decomposition into the neighbouring phases YNi and YNi_3 , but YNi_2 is not stable against the formation of $\text{Y}_{15}\text{Ni}_{32}$ and YNi . Therefore the ideal C15 phase YNi_2 cannot be a stable phase in the Y–Ni phase diagram. Instead of YNi_2 the vacancy superstructure is a stable phase, but it should be emphasized that the calculations were performed only for completely empty 4a sites. It is possible that a superstructure phase with partially occupied 4a sites is even more favourable. However, the tendency towards the formation of a vacancy superstructure instead of the C15 phase YNi_2 is confirmed by the *ab initio* calculations.

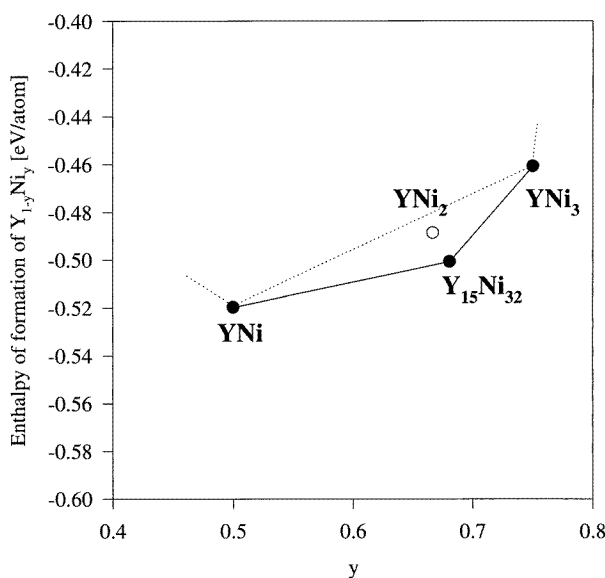


Figure 3. Enthalpies of formation for the four neighbouring $\text{Y}_{1-y}\text{Ni}_y$ compounds YNi , YNi_2 (C15), $\text{Y}_{15}\text{Ni}_{32}$ (vacancy superstructure) and YNi_3 . The full line shows a part of the convex polygon connecting the stable compounds.

3.4. Relaxation of the atoms in the vacancy superstructure $\text{Y}_{15}\text{Ni}_{32}$

In this section the relaxation of the atoms in the vacancy superstructure $\text{Y}_{15}\text{Ni}_{32}$ will be discussed. As already mentioned above, this relaxation is a result of the calculation of the total energy, which has to be minimized with respect to the nine free atomic position parameters not

Table 1. Comparison of calculated atomic positions for the vacancy superstructure $Y_{15}Ni_{32}$ ($\equiv Y_{0.9375}Ni_2$) with experimental values for $Y_{0.95}Ni_2$ and the ideal C15 values.

Atom at site of space group $F\bar{4}3m$	General position	$Y_{15}Ni_{32}$ (calculation)	$Y_{0.95}Ni_2$ (experiment)	C15
Y1 at 4a (vacancy)	(000)	fixed	fixed	fixed
Y2 at 4b	$(\frac{1}{2} \frac{1}{2} \frac{1}{2})$	fixed	fixed	fixed
Y3 at 16e	(xxx)	$x = 0.0986$	$x = 0.1000$	$x = 0.125$
Y4 at 16e	(xxx)	$x = 0.6270$	$x = 0.6280$	$x = 0.625$
Y5 at 24g	$(x \frac{1}{4} \frac{1}{4})$	$x = 0.0134$	$x = 0.0099$	$x = 0$
Ni1 at 16e	(xxx)	$x = 0.3115$	$x = 0.3109$	$x = 0.3125$
Ni2 at 16e	(xxx)	$x = 0.8117$	$x = 0.8141$	$x = 0.8125$
Ni3 at 48h	(xxz)	$x = 0.0669$	$x = 0.0669$	$x = 0.0625$
		$z = 0.8073$	$z = 0.8062$	$z = 0.8125$
Ni4 at 48h	(xxz)	$x = 0.0623$	$x = 0.0634$	$x = 0.0625$
		$z = 0.3124$	$z = 0.3133$	$z = 0.3125$

Table 2. Comparison of all nearest Y–Y and vacancy–Y distances for the vacancy superstructure $Y_{15}Ni_{32}$ ($\equiv Y_{0.9375}Ni_2$) with the experimental values for $Y_{0.95}Ni_2$ and the ideal C15 ($Y_{16}Ni_{32}$) values.

	$Y_{15}Ni_{32}$ (calc.)	$Y_{0.95}Ni_2$ (exp.)	$Y_{16}Ni_{32}$ (calc.)	Difference $Y_{15}Ni_{32}$ (calc.)- $Y_{16}Ni_{32}$ (calc.)	Deviation $Y_{15}Ni_{32}$ (calc.) - $Y_{0.95}Ni_2$ (exp.)
Distance of vacancy (Y1) to four Y3 neighbours	2.460 Å	2.486 Å	3.118 Å	-21.1%	-1.0%
Distance of Y3 to three Y5 neighbours	3.318 Å	3.307 Å	3.118 Å	+6.4%	+0.3%
Distance of Y5 to two Y4 neighbours	3.220 Å	3.170 Å	3.118 Å	+3.3%	+1.6%
Distance of Y4 to one Y2 neighbour	3.167 Å	3.181 Å	3.118 Å	+1.6%	-0.4%

fixed by the space group symmetry $F\bar{4}3m$. It is important to note that the ideal C15 positions were taken as the starting values for the *ab initio* calculations, i.e. no experimental results for the starting values were used. In table 1 these atomic positions are compared with the experimental values determined by the Rietveld analysis of the x-ray data of $Y_{0.95}Ni_2$ [3] as well as with the ideal values of the C15 structure. The deviation between the experimental and calculated cubic lattice parameter ($a_{exp} = 14.350 \text{ \AA}$, $a_{calc} = 14.399 \text{ \AA}$) is only 0.3%. The calculated lattice parameter for the C15 structure is 14.449 \AA .

There is good agreement between experiment and theory concerning the relaxation of the vacancy superstructure. The change of the position of the atoms Y3, which are the nearest neighbours of the vacancy, and also of Y5, which are the nearest Y neighbours of Y3, is most pronounced. The relaxation of the other Y atoms and all Ni atoms except Ni3 (the nearest Ni neighbours of the vacancy) are much smaller. However, also the relaxation of Ni3, which leads to a slight distortion of the Ni tetrahedra surrounding the vacancy, is much less pronounced than that of Y3 and Y5. This means that the relaxation of the structure caused by the removal of Y1 concerns mainly the Y sublattice. In table 2 the experimental and calculated values for all nearest Y–Y or vacancy–Y distances are listed and compared with the C15 values. In the diamond-type Y sublattice each Y atom as well as the vacancy (originally

Y1) is surrounded by a (distorted) tetrahedron formed by four Y atoms or by three Y atoms and a vacancy.

As can be seen from the calculated and experimental values in table 2, the relaxation of the Y sublattice results in clearly larger Y–Y distances compared to the C15 structure, i.e. the available space for all Y atoms is increased by the formation of the vacancies. The mean difference between the calculated Y–Y distances of the vacancy superstructure and the C15 structure is about +3.8%, whereas the lattice parameter is about 0.3% smaller for the vacancy superstructure. For illustrating the relaxation of the vacancy superstructure the atomic surroundings of the vacancy (including the atoms Y3, Y5, Ni3 and Ni2) are shown in figure 4 and compared with the C15 structure.

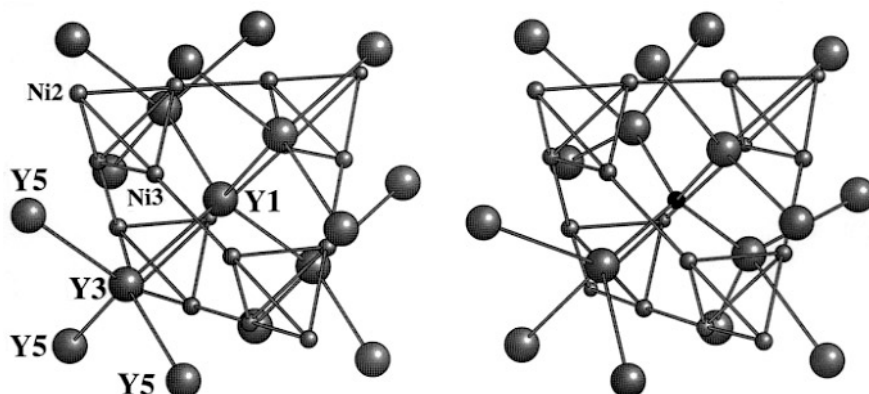


Figure 4. The atomic surroundings of the vacancy (Y1), including the atoms Y3, Y5, Ni3 and Ni2, in the ideal C15 structure (left) and in the relaxed vacancy superstructure (right).

The increase of the Y–Y distances compared to the ideal C15 structure is largest between the nearest neighbours (Y3) and next-nearest neighbours (Y5) to the vacancy ($d_{Y3-Y5} = 3.318 \text{ \AA}$ compared to 3.118 \AA in the ideal C15 structure and $d_{Y-Y} = 3.59 \text{ \AA}$ in the pure Y metal) and decreases with increasing distance. However, we have to note that the calculation predicts $d_{Y3-Y5} > d_{Y5-Y4} > d_{Y4-Y2}$, while the experimental data (obtained by Rietveld analysis of x-ray powder diffraction data) yield $d_{Y4-Y2} > d_{Y5-Y4}$. The difference has probably to be attributed to the difference in stoichiometry: at a partial occupation of the 4a sites of 25%, one of the four 4a sites in the cubic supercell remains occupied, resulting in a different distortion of the lattice compared to completely empty 4a sites.

The reason for the formation of the Y vacancies is that the distances between the large holes in the tetrahedral network formed by the Ni atoms accommodating the Y atoms are so small that a compression of the Y–Y distances of 13% compared to pure Y would be necessary. This causes a very large local strain which can be released by the formation of vacancies and the accompanying distortion of the Ni framework allowing for an increase of all Y–Y distances. Our work demonstrates that these strains and the related distortions may be calculated quantitatively from first principles.

As already mentioned in the introduction a systematic experimental investigation of the $R_{1-x}Ni_2$ compounds revealed that a vacancy superstructure is also present for the RNi_2 compounds with $R = Pr, Nd, Gd, Tb, Dy, Ho$ and Er [4]. However, with decreasing radius of the R atoms there should be a tendency towards the formation of the C15 structure, since the size ratio r_R/r_{Ni} approaches the ideal one for the C15 structure (1.225) with decreasing radius r_R (lanthanide contraction). This is reflected by the occupancy factor of the Y 4a sites which can

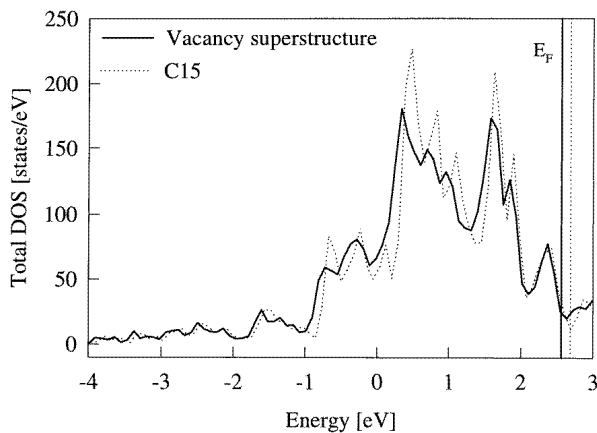


Figure 5. Total electronic density of states of the vacancy superstructure $Y_{0.9375}Ni_2$ ($Y_{15}Ni_{32}$) and the ideal C15-type YNi_2 ($Y_{16}Ni_{32}$).

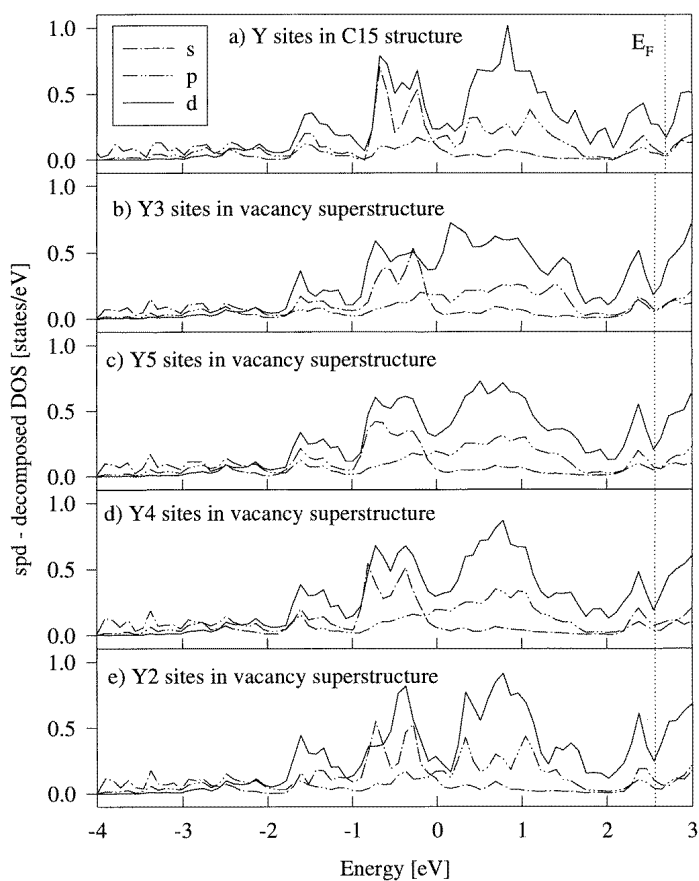


Figure 6. Local and angular-momentum-decomposed densities of states on the Y sites in (a) ideal C15-type YNi_2 and in the vacancy superstructure $Y_{15}Ni_{32}$ arranged in order of increasing distances from the vacancy: (b) Y3 sites, (c) Y5 sites, (d) Y4 sites, (e) Y2 sites.

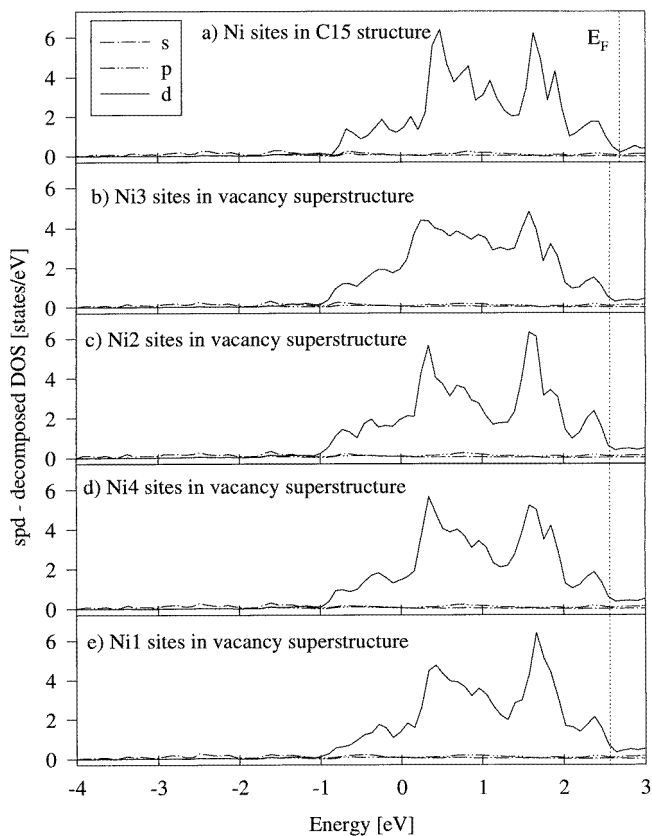


Figure 7. Local and angular-momentum-decomposed densities of states on the Ni sites in (a) ideal C15-type YNi_2 and in the vacancy superstructure $\text{Y}_{15}\text{Ni}_{32}$ arranged in order of increasing distances from the vacancies: (b) Ni3 sites, (c) Ni2 sites, (d) Ni4 sites, (e) Ni1 sites. (The difference in the distances of Ni2 and Ni4 to the vacancies is very small, see table 1).

take values between 0 (completely empty 4a sites) and 1 (ideal C15 structure): it increases from 0.12 for Pr to 0.68 for Er and reaches 1 for Lu [4]. Furthermore the temperature of the transition from the vacancy superstructure to the C15 symmetry (disordered vacancies) decreases with decreasing r_R [5], which seems also to reflect the tendency towards the formation of the C15 structure.

3.5. Electronic structure

In our recent work on the relative stabilities of the CeCu_2 and C15 phases of YNi_2 and YCu_2 we have emphasized the competition between space-filling and electronic effects in determining the stable crystal structure [14]. Figure 5 shows a comparison of the total electronic densities of states of the defect phase $\text{Y}_{15}\text{Ni}_{32}$ and of the ideal C15 compound YNi_2 (treated in a $\text{Y}_{16}\text{Ni}_{32}$ supercell), calculated on a $5 \times 5 \times 5$ k -point mesh and plotted on the same energy scale. In both phases the Fermi level is pinned in a minimum of the DOS and there are only relatively modest changes in the DOS near the bottom of the band and close to the Fermi level. At energies between about 0.5 and 3 eV below the Fermi level, however, we observe a systematic shift and broadening of the bands induced by the vacancy formation. These changes arise mostly from the modification of the d DOS on the Ni sites, as can be seen

from Figures 6 and 7, where the angular-momentum-decomposed DOS is depicted for the different Y and Ni sites and compared with the ideal C15 results. The modifications of the DOS are most pronounced for the Y and Ni sites which are closest to the vacancies, i.e. for Ni3 and Y3. The downshift of the d states is mostly a consequence of the reduced repulsive interactions.

4. Conclusion

The formation of an ordered vacancy superstructure in C15-type $Y_{1-x}Ni_2$ compounds has been studied using *ab initio* local-density-functional calculations (including generalized gradient corrections) for supercells allowing for a minimal vacancy concentration of $x = 0.0625$, i.e. only slightly higher than found experimentally ($x = 0.05$) [3]. We have shown that the creation of vacancies lowers the total energy of the C15 phase, increasing its stability relative to the neighbouring YNi (FeB-type) and YNi_3 (NbBe₃-type) compounds. The relaxation of the atoms in the supercell from their ideal C15 positions leads to atomic coordinates in good agreement with the experimental structure refinement [3]. The relaxation leads to an increase of all Y–Y distances and releases internal strains on the Y sublattice. This is the driving mechanism for the formation of a vacancy superstructure which is also reflected in a slight modification of the density of states. The calculated energy gain by the vacancy formation is 0.012 eV/atom, corresponding to a temperature of 140 K. Even if the vacancy formation on other Y sites requires a higher energy, a temperature-driven transition to disordered vacancies is well compatible with this energy. However, vacancies on other sites than 4a or 4b would break the symmetry of the supercell and thus require calculations for ensembles of at least 188 atoms per cell. Such studies would be possible only with extreme computational effort, since we have to treat ten electrons per Ni atom and nine electrons per Y atom as valence electrons.

Acknowledgment

This work was supported by the Austrian Science Foundation FWF (project: P-11581-PHY).

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