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Electronic structure and magnetism of YCo_5, YNi_5 and YCo_3Ni_2

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Abstract. Dependences of the magnetic moment on the lattice constant for binary and pseudo-binary compounds YCo_5, YNi_5 and $Y(Co_{0.6}Ni_{0.4})_5$ with a hexagonal $CaCu_5$-type structure are studied by an *ab initio* calculation on a self-consistent linear muffin-tin orbital method within the atomic sphere approximation. It is found that Co moments in YCo_5 decrease abruptly at a critical lattice constant smaller than the observed one. On the other hand, Ni moments in YNi_5 are shown to appear at a lattice constant a little larger than the observed one. Similar calculations are carried out for the ordered compound YCo_3Ni_2, where Co and Ni atoms occupy the 3g and 2c sites, respectively. It is shown that Co and Ni atoms in this compound lose their moments at a lattice constant slightly smaller than the observed one. It is also found that the Co atom on the 3g site in YCo_5 and YCo_3Ni_2 has two magnetic states, a high-moment state and a low-moment or non-magnetic state, depending on the lattice constant. The present results explain the concentration dependence of the the bulk moment observed for $Y(Co_{1-x}Ni_x)_5$ and $La(Co_{1-x}Ni_x)_5$.

1. Introduction

Intermetallic compounds of rare-earth and 3d transition-metal atoms have recently been studied intensively [1]. In particular the intrinsic magnetic properties of the 3d-rich intermetallics are discussed in the itinerant electron model based on the calculated electronic structures [2]. For instance, YCo_5 with a hexagonal $CaCu_5$-type structure is known as a strong ferromagnet. Co atoms in YCo_5 occupy two crystallographically different sites, 3g and 2c. By the neutron diffraction measurements, magnetic moments of Co on 3g and 2c sites are observed as 1.72 and 1.77 μ_B/atom, respectively [3]. These local moments have also been obtained theoretically by the spin-polarized band calculations [4–6].

A complete series of solid solutions exists for $Y(Co, Ni)_5$ and $La(Co, Ni)_5$. Observed bulk moments of $Y(Co_{1-x}Ni_x)_5$ [7–9] and $La(Co_{1-x}Ni_x)_5$ [8, 10, 11] decrease linearly with increasing Ni concentration x below $x = 0.4$. The deviation from the linear concentration dependence of moments becomes significant for $x > 0.4$. YNi_5 and $LaNi_5$ are strongly exchange-enhanced Pauli paramagnets. It is noted that only YNi_5 is paramagnetic among Ni-rich Y–Ni compounds except YNi_2. The moment induced on the Ni atom in $GdNi_5$ by Gd moments was observed as 0.16 μ_B/atom [12].

In order to study these magnetic properties, the electronic structures of YCo_5, YCo_3Ni_2 and YNi_5 are calculated by the self-consistent linear muffin-tin orbital (LMTO) method

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within the atomic sphere approximation (ASA). Preliminary results have already been reported by the present authors [13]. In section 2, details of the calculations are given. Section 3 contains the calculated results on the volume dependence of magnetization. In section 4, two magnetic states of Co atom on the 3g site are discussed with the density-of-states curves calculated in the non-magnetic state. Our conclusions and discussion are given in section 5.

2. Details of calculation

The $CaCu_5$ structure is a hexagonal Bravais lattice with six atoms in a unit cell. This structure is quite close packed and the packing fraction is 67% if the space is filled up by touching rigid spheres. The construction of the touching spheres gives an ideal c/a ratio $\sqrt{2/3}$ and an ideal ratio 0.764 between the radii of Cu and Ca atoms. The electronic structure was calculated by the LMTO method in the ASA, including the combined correction to the ASA [14]. The parametrization of von Barth and Hedin [15] was used for the exchange–correlation potential obtained within the local-spin-density approximation.

The spin–orbit interaction was not included although the calculations are scalar relativistic, including mass velocity and Darwin terms. The irreducible 1/24 Brillouin zone was sampled at 216 *k*-points. The convergence in charge density was achieved so that the root mean square of moments of the occupied partial density of states is smaller than 10^{-5}. A basis set of functions with angular momenta up to $l = 3$ on all sites was adopted. The radii of the atomic spheres used in the ASA were constructed in such a way that the ratio is kept equal to the ideal value of the touching spheres.

3. Calculated results

In the upper and lower parts of figure 1 the calculated results of the total energy and local moments of Y atom and Co atoms on the 3g and 2c sites in YCo_5 are shown, respectively, as a function of the volume of the unit cell V. The calculated minimum energy is achieved at $V = 75$ Å^3, which is 11% smaller than the observed $V(= 84$ Å$^3)$. The discrepancy comes probably from the ASA used in this paper. The local moments of Co atoms on the 3g and 2c sites are 1.47 and 1.52 μ_B/atom, respectively, at the observed V. Moreover, the moment 0.30 μ_B/atom on Y atoms is found to be induced in the opposite direction to the Co moments, which is due to the different hybridizations between 4d states of Y and 3d states of Co in the majority- and minority-spin bands [2, 16]. These results are almost the same as those calculated by Malik *et al* [4] and Nordström *et al* [5].

The calculated spin moment 7.15 μ_B per formula unit (f.u.) is smaller than the observed moment 7.99 μ_B/f.u. [3]. The difference between the calculated and observed results is attributed to the orbital moment of Co atoms. The observed value of the orbital moment for YCo_5 by polarized neutrons is 1.76 μ_B/f.u. [3]. On the other hand, Nordström *et al* [5, 6] calculated the orbital moments of Co in YCo_5 and got a value smaller than the observed one. As shown in figure 1 the Co moments decrease rapidly near $V = 75$ Å^3. A transition from a high-moment state to a low-moment one occurs at this critical V. The change in Co moments on the 3g site is found to be larger than that on the 2c site.

The calculated results of the total energy and local moments of Y atom and Ni atoms on the 3g and 2c sites in YNi_5 are shown in figure 2. At the top of the figure, the total energies E_{para} and E_{ferro} in the paramagnetic and ferromagnetic states, respectively, are shown as a function of V. The difference between the two is too small to be distinguished on this scale.

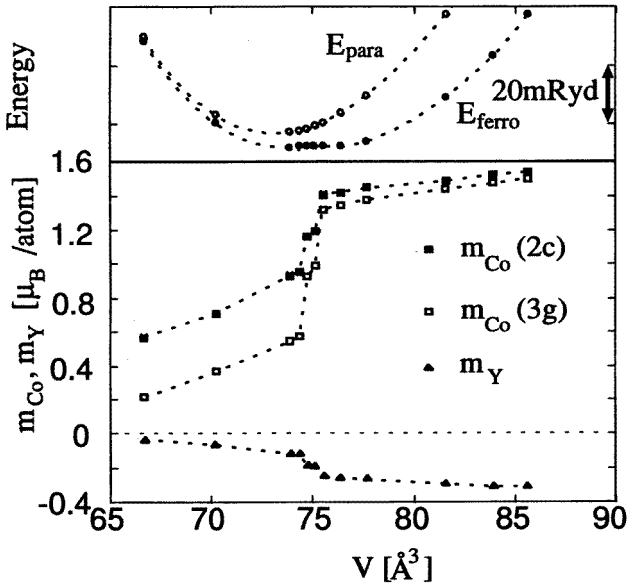

Figure 1. Calculated results of the total energy and local moments for YCo_5 as a function of V. In the upper part the total energies per unit cell in the non-magnetic and magnetic states are shown by E_{para} (open circles) and E_{ferro} (closed circles), respectively. In the lower part, the local moments m_{Co} on the 2c (closed squares) and 3g sites (open squares) and m_{Y} (closed triangles) are shown.

In the middle, the difference ΔE between E_{para} and E_{ferro} is shown. At the bottom, the local moments of Y and Ni atoms are shown. The calculated minimum energy is achieved at $V = 76.4$ Å^3, which is smaller than the observed V ($= 81.5$ Å^3).

At the observed V, YNi_5 is paramagnetic. At $V = 87$ Å^3, Ni atoms have moments about 0.25 and 0.40 μ_{B}/atom on the 2c and 3g sites, respectively. In this case the moment 0.1 μ_{B}/atom is induced on the Y atom, which is in the opposite direction to the Ni moments. Gignoux *et al* [12] have observed that the moment induced on the Ni atom by Gd moments in $GdNi_5$ is 0.16 μ_{B}/atom, which is rather smaller than our estimated value. The critical lattice constant for the onset of the magnetic moment is a little larger than the observed one. Then the Ni atoms in YNi_5 may become magnetic with extremely high magnetic field or by substituting the magnetic rare-earth atoms for Y.

It is said that Co and Ni atoms in $Y(Co, Ni)_5$ occupy predominantly the 3g and 2c sites, respectively. The present authors [13] calculated the density-of-states curve for YCo_5 by the self-consistent LMTO-ASA and showed that the local DOS of Co on the 2c site at the Fermi level is rather higher than that on the 3g site. That is, the gain of the band energy is less when the Co atom in YCo_5 is replaced by Ni and the extra electrons of Ni occupy the larger local DOS of Co on the 2c sites rather than 3g sites. This fact suggests that the preferred site of Ni is the 2c site. The calculations are carried out for the hypothetically ordered compound YCo_3Ni_2 where Co and Ni atoms occupy the 3g and 2c sites, respectively.

The calculated results of the total energy and local moments of the Y atom and Co and Ni atoms on the 3g and 2c sites are shown in the upper and lower parts of figure 3, respectively, as a function of V. The magnetic moments on Co and Ni atoms at the observed

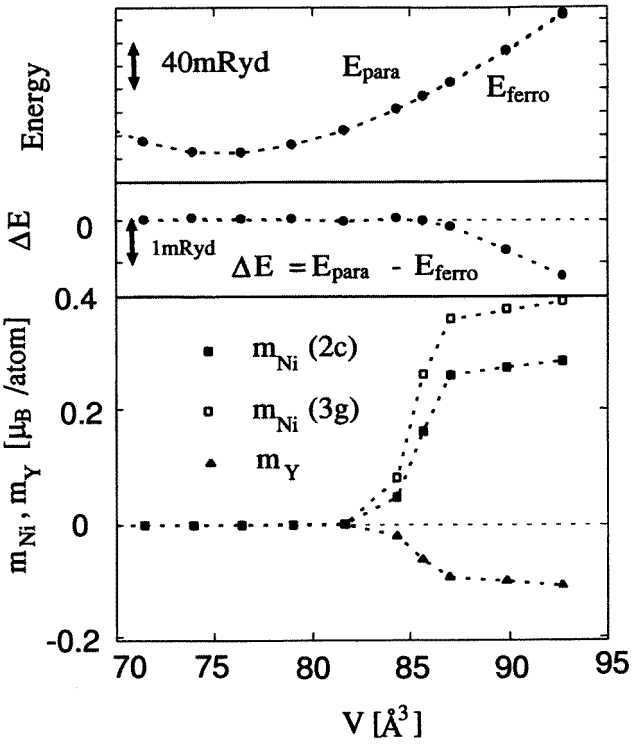

Figure 2. Calculated results of the total energy and local moments for YNi_5 as a function of V. At the top of the figure, the total energies E_{para} and E_{ferro} in the non-magnetic and magnetic states are shown. In the middle, the difference $\Delta E = E_{\text{para}} - E_{\text{ferro}}$ is shown. At the bottom, the local moments m_{Ni} on the 2c (closed squares) and 3g sites (open squares) and m_{Y} (closed triangles) are shown.

V (= 82.6 Å^3) are estimated as 1.41 and 0.36 μ_B/atom, respectively. The induced spin moment on Y atoms is estimated as 0.27 μ_B/atom, which is in the opposite direction to the Co and Ni moments. The calculated total spin moment is 4.68 μ_B/f.u., which is smaller than the observed bulk moment 5.2 μ_B/f.u. for $Y(Co_{0.6}Ni_{0.4})_5$ [7, 8]. The difference is attributed again to the orbital moments of Co atoms. The critical lattice constant for the onset of the magnetic moment is a little smaller than the observed V.

4. Two magnetic states of the Co atom on the 3g site

As shown in figures 1 and 3, calculated values of the magnetic moments for YCo_5 and YCo_3Ni_2 decrease abruptly at a critical volume V_0. The change in the Co moment on the 3g site for YCo_5 is found to be larger than that on the 2c site. For YCo_3Ni_2, on the other hand, the Co atom on the 3g site loses its moment at V_0. These facts mean that the Co atom on the 3g site in these compounds has two magnetic states, i.e., a high-moment state and a low-moment or non-magnetic state, depending on the volume.

In figures 4(a), (b) and (c), the total and local DOSs for YCo_5, YCo_3Ni_2 and YNi_5 calculated in the non-magnetic state at the observed volume are shown, respectively. E_F

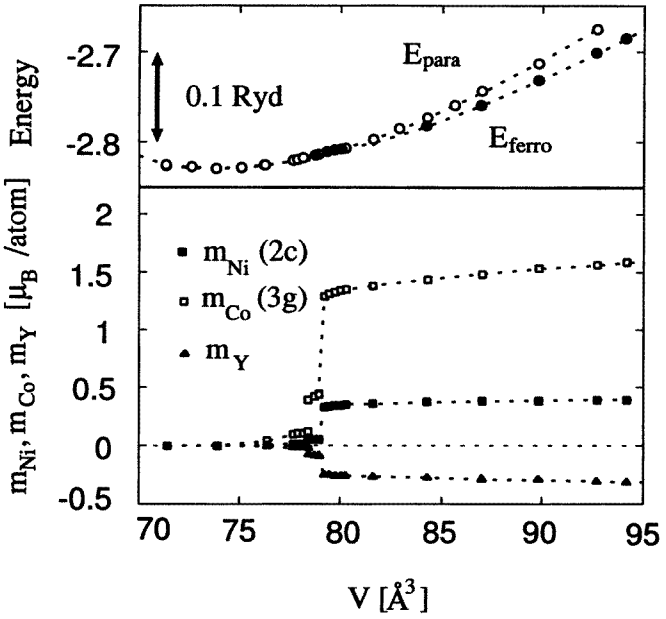

Figure 3. Calculated results of the total energy and local moments for YCo_3Ni_2 as a function of V. In the upper part the total energies per unit cell in the non-magnetic and magnetic states are shown by E_{para} (open circles) and E_{ferro} (closed circles), respectively. In the lower part, the local moments m_{Co} on the 3g site (open squares), m_{Ni} on the 2c site (closed squares) and m_{Y} (closed triangles) are shown.

denotes the Fermi level. The local DOSs of Co on the 3g site for YCo_5 and YCo_3Ni_2 are very similar to each other near E_F. The shape of the local DOS of Ni on the 2c site in YCo_3Ni_2 is also similar to that of Co on the 2c site in YCo_5, but the position of E_F is different. It is noted that E_F in both compounds comes to the position of the positive curvature of the local DOS of Co atom on the 3g site. In this case, two magnetic states with large moment and without moment may coexist, just like the Co atom in YCo_2 with the cubic Laves phase structure [16].

At larger volume than V_0, the Co atom on the 3g site in YCo_5 is magnetic, while it is non-magnetic at $V < V_0$ as the band-width increases and then the height of the DOS decreases with decreasing V. As shown in figure 4(a), E_F lies near the peak of the local DOS of the Co atom on the 2c site, so the Co on this site is magnetic even at $V < V_0$. Therefore, the 3g-site-Co moment at $V < V_0$ is induced by the 2c-site-Co moment. At $V > V_0$ the 3g-site-Co atom has a large moment and then the 2c-site-Co moment will increase a little from the value at $V < V_0$, as shown in figure 1. On the other hand, for YCo_3Ni_2, E_F is far from the peak of the local DOS of Ni atom on the 2c site and the Ni atom is non-magnetic. Therefore, the 3g-site-Co moment in this compound cannot be induced at $V < V_0$. In this way, it can to be understood that the Co atom on the 3g site in YCo_5 and YCo_3Ni_2 has two magnetic states with large moment and without moment.

For YNi_5 a small number of d holes seems to exist both on 2c and 3g site-Ni atoms, as shown in figure 4(c). Therefore, small magnetic moments appear on the Ni atoms at $V > V_0$.

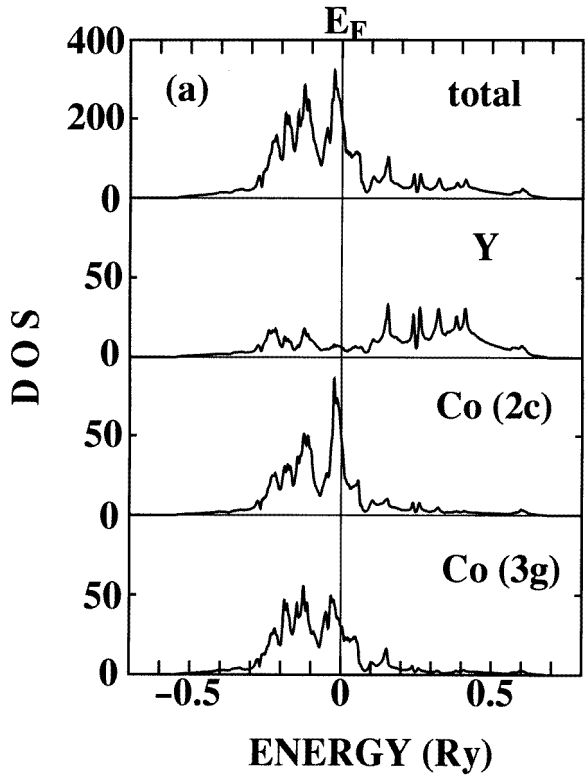

Figure 4. Total and local DOSs in the units of states/Ry. f.u. and states/Ry. atom for YCo_5 (a), for YCo_3Ni_2 (b) and for YNi_5 (c) calculated at the observed volume. E_F denotes the Fermi level.

5. Conclusions and discussion

In this paper, the electronic structures of $Y(Co, Ni)_5$ compounds with the hexagonal $CaCu_5$-type structure have been calculated by the self-consistent LMTO-ASA. The calculated total energy gives a systematically smaller lattice constant than the observed one. However, the magnetic moments calculated at the observed lattice constants agree well with the experimental data if small orbital contributions to the bulk moments are taken into account. It has been found that Co moments in YCo_5 decrease abruptly at a critical lattice constant. At this lattice constant, the change in Co moment on the 3g site is found to be larger than that on the 2c site. A similar result is also obtained for $ThCo_5$ [17], where Co atoms exhibit a metamagnetic transition from a low-moment state to a high-moment state with applied magnetic fields as observed in [18]. These two moment states of Co are obtained not only in $ThCo_5$ but also in YCo_5, as shown in section 4.

At the observed lattice constant, however, the high-moment state of Co is stable in YCo_5, being different from that in $ThCo_5$. This is because Y is a trivalent atom, while Th is a tetravalent one. The hybridization between d states of Y and Co in YCo_5 is weaker than that of Th and Co in $ThCo_5$ [16]. Then, the local DOS of 3d electrons in YCo_5 becomes higher than that in $ThCo_5$. In this way, the high-moment state of Co in YCo_5 is stabilized and, then, the critical lattice constant of YCo_5 becomes small.

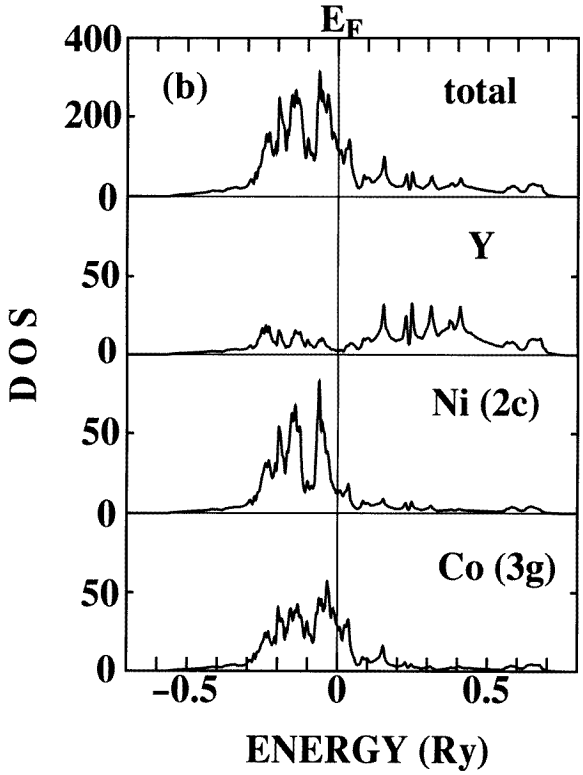

Figure 4. (Continued)

The critical lattice constant has also been found to exist in YNi_5 and YCo_3Ni_2. The calculated value of the critical volume for YNi_5 is a little larger than the observed one. The Ni atoms in YNi_5 are paramagnetic at the observed V. However, the ferromagnetic state is stabilized at a V a little larger than the observed one. Therefore, YNi_5 may become magnetic with extremely high magnetic field, i.e., a metamagnetic transition, and by substituting the magnetic rare-earth atoms for Y as observed in (Gd,Y)Ni_5 [12]. On the other hand, the calculated critical lattice constant for YCo_3Ni_2 is a little smaller than the observed one. This result shows that Co and Ni atoms may lose their moments under the high pressure.

The critical volumes for the onset of magnetic moment in YCo_5, YCo_3Ni_2 and YNi_5 were obtained to be about 75, 80 and 87 Å^3, respectively, as shown in figures 1, 2 and 3. This fact suggests that the critical lattice constant increases with increasing Ni concentration. On the other hand, the observed lattice constant decreases with increasing Ni concentration and, subsequently, crosses the critical lattice constant for the onset of the moment. Therefore, Co and Ni moments in $Y(Co_{1-x}Ni_x)_5$ may decrease abruptly at a value of x a little larger than 0.4. The observed bulk moments for $Y(Co_{1-x}Ni_x)_5$ [7, 8, 9] and $La(Co_{1-x}Ni_x)_5$ [8, 10, 11] decrease rapidly between $x = 0.4$ and 0.6, which is consistent with our result.

Crisan *et al* [19] have recently calculated the concentration dependence of the bulk moment in $Y(Co, Ni)_5$, by using the recursion method. However, they did not get a rapid decrease of the moment. It is concluded that the rapid decrease of the moment in $Y(Co_{1-x}Ni_x)_5$ and $La(Co_{1-x}Ni_x)_5$ between $x = 0.4$ and 0.6 is due to the instability of the 3g-site-Co moment as a reflection of the detailed electronic structures.

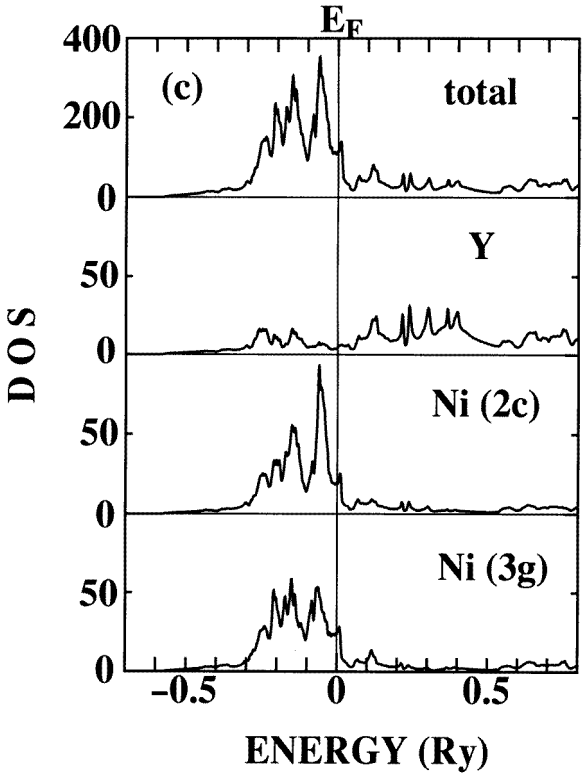

Figure 4. (Continued)

Acknowledgments

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