Formation of a weak ferromagnetic state in $Y(Co_{1-x}Al_x)_2$ compounds: a coherent potential approximation study

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Abstract
The band structure of substitutionally disordered $Y(Co_{1-x}Al_x)_2$ has been calculated for various concentrations in the range $0 \leqslant x \leqslant 0.25$ employing the coherent potential approximation embodied in an all-electron tight-binding linear muffin-tin orbital method. On the basis of the results, we provide a new explanation for the formation of weak ferromagnetic moments in these compounds. The discussion of the non-spin-polarized calculated densities of states is supported by direct evidence of the weak ferromagnetic states for certain lattice constants and Al concentrations. The roles of the disorder and the volume effects are discussed.

1. Weak itinerant ferromagnetism in $Y(Co_{1-x}Al_x)_2$

The cubic Laves phase compound YCo_2 is a strongly enhanced Pauli paramagnet which shows a pronounced maximum in the temperature dependence of the susceptibility $\chi(T)$ [1]. It also exhibits a metamagnetic transition to a ferromagnetic state at an applied magnetic field of about 70 T [2]. It has been found that the substitution of small amounts of non-magnetic Al for Co reduces the value of the critical field for $Y(Co_{1-x}Al_x)_2$ and the metamagnetic transition can be observed for fields less than 42 T for $x > 0.05$ [3, 4]. For increasing Al concentration the critical field decreases further [5] and for an Al concentration range between $x \simeq 0.12$ and 0.20 a small ($\approx 0.1~\mu_B/Co$) spontaneous magnetic moment appears and $Y(Co_{1-x}Al_x)_2$ becomes a ferromagnet with a low Curie temperature [6] $T_c^{max} \simeq 26$ K. In this concentration range under an applied field, a transition to a high-moment state with a magnetic moment of ≈ 0.6–$0.7~\mu_B/Co$ takes place as can be seen from the inflection point appearing in the corresponding Arrott plot [7]. The complete phase diagram of $Y(Co_{1-x}Al_x)_2$ in the concentration range $x \leqslant 0.2$ is given by Duc *et al* [7]. For a detailed review of the theoretical and experimental state of the art on the magnetism of RCo_2 compounds (R = rare earth) we refer the reader to Duc and Brommer [12] and Duc and Goto [11].

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From the very beginning, this complex magnetic behaviour of $Y(Co_{1-x}Al_x)_2$ has been given various and quite different interpretations. It is generally accepted that $Y(Co_{1-x}Al_x)_2$ ($x \approx 0.13$–0.20) is a weak itinerant ferromagnet and it is obvious that the value of the density of states at the Fermi level $N(\varepsilon_f)$ plays a major role in the explanation of the formation of the weakly magnetic ground state in these compounds. Originally, Yoshimura and Nakamura [6] proposed that the increase of $N(\varepsilon_f)$ as aluminium substitutes for cobalt is due to an increase of the lattice parameters which in turn causes a narrowing of the d bandwidth. Aleksandryan *et al* [3] suggested that the onset of magnetic order is caused by a shift of the Fermi level towards a higher value of the DOS due to the decrease of the 3d-electron concentration. The motivation for this idea is drawn from the well known structure of the density of states near the Fermi level ε_f in pure YCo_2 (figure 1). In YCo_2, ε_f lies on a sharply falling portion of the density-of-states curve near a narrow peak just below of the Fermi level. If the concentration of the 3d electrons is reduced due to Al substitution, the value of $N(\varepsilon_f)$ should increase because ε_f must shift downwards towards the narrow peak. As will be shown in section 3, neither of these intuitive explanations is completely valid. The assumption that effects of alloying do
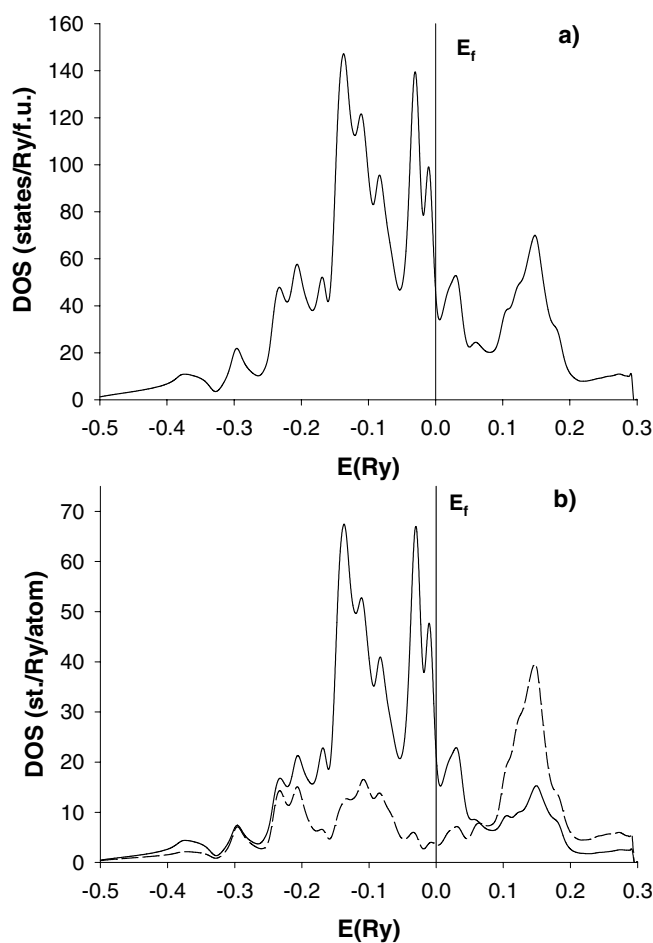

Figure 1. (a) The total DOS of YCo_2 given per formula unit (f.u.). (b) The atom-resolved DOS of YCo_2: Co: full line; Y: dashed line.

not cause a major change of the structure of the DOS curve (the rigid-band picture) implies that the substituted Al atoms provide contributions to the total DOS which are similar to the Co contribution. Such a picture is approximately valid only if another 3d metal is substituted for Co. For example, the DOS of YCo$_2$ and YFe$_2$ [9] look very similar and only differ in the position of the Fermi level due to the different numbers of d electrons of Fe and Co. In the case of the Y(Co$_{1-x}$Al$_x$)$_2$ compounds the 3d metal (Co) is replaced by an sp metal (Al). The number of d electrons per unit volume is reduced, but simultaneously the weight (height) of the total Co DOS per unit volume is also reduced by the same amount whereas the Al atoms provide only a very broad sp band around ε_f. Consequently it is very hard to say *a priori* what happens to the position of the Fermi level as the Al concentration increases.

Aoki and Yamada [9] have performed self-consistent band-structure calculations for the fictitious ordered Y(Co$_{0.75}$Al$_{0.25}$)$_2$ compound employing the APW method. On the basis of their results they pointed out that the effect of the narrowing of the 3d band due to the lattice expansion does not play an essential role in the onset of the magnetic moment in Y(Co$_{1-x}$Al$_x$)$_2$. In addition, they reported that the sharp double peak near the Fermi energy vanishes upon Al substitution at $x = 25\%$; however, a single sharp peak and a small broad peak have been shown to remain near ε_f. The value of the total DOS at ε_f in Y(Co$_{0.75}$Al$_{0.25}$)$_2$ has been found to be lower than in pure YCo$_2$. In order to explain the appearance of a small spontaneous magnetic moment at intermediate concentrations, these authors [9] proposed that the Fermi level shifts towards lower energies with increasing Al concentration and that ε_f crosses a small broad peak. However, as we mentioned earlier, in the case of an Al substitution the evolution of the DOS with increasing Al concentration is not so obvious. Additionally, it should be noted that the effects of disorder must be taken into account in order to obtain a correct description of the problem.

To explore the situation more carefully, we performed an *ab initio* band-structure calculation for Y(Co$_{1-x}$Al$_x$)$_2$ compounds within density functional theory and the local density approximation (DFT-LDA) for various concentrations of Al up to $x = 0.25$. The effects of alloying were treated within the coherent potential approximation (CPA). We separate the effects of alloying from those of the lattice expansion due to Al substitution by performing the calculations for each concentration at two lattice constants:

 (i) we pin the calculation to the experimental lattice constant of pure YCo$_2$;
(ii) the calculations are performed at the experimental lattice constant values for a given concentration of Al.

Although the main conclusion is drawn from the analysis of non-spin-polarized densities of states, spin-polarized calculations have been carried out in order to search for the weak ferromagnetic moment *ab initio*.

It should be clear that local environment effects are treated in an averaged manner via the 'coherent potential' used. Nevertheless, in a highly itinerant ferromagnet like Y(Co$_{1-x}$Al$_x$)$_2$ these effects should be small anyway. From investigations into other Co-containing alloys and compounds, one usually finds that the magnetic moment of Co is much less sensitive to local environment or lattice relaxation effects than e.g. the respective Fe moments. After all, there are no hints in the literature that local environment effects should play a major role in the quite intensively [11] studied Y(Co$_{1-x}$Al$_x$)$_2$ compounds.

Leaving the detailed discussion to a later section of this article, we note here that the main result of the present work is the conclusion that the mechanism of formation of weak magnetic moments in the Y(Co$_{1-x}$Al$_x$)$_2$ is a subtle effect of the electronic structure which is connected neither with the shifting of the Fermi level to lower energies nor with volume effects, but originates from changes of the DOS around ε_f due to the alloying.

2. Calculational details

The intermetallic compound YCo_2 crystallizes in the C15 cubic Laves phase ($MgCu_2$ type, $Fd3m$). In $Y(Co_{1-x}Al_x)_2$ the Al and Co atoms randomly occupy Cu (Co) positions. The electronic structure of the substitutionally disordered $Y(Co_{1-x}Al_x)_2$ systems was calculated by the all-electron self-consistent tight-binding linear muffin-tin orbital (TB-LMTO) method in the atomic-sphere approximation (ASA) [15] combined with the coherent potential approximation (CPA) [16]. The valence bands were treated with an angular momentum cut-off $\ell_{max} = 2$; the integrations over the Brillouin zone (BZ) were performed using a uniform mesh corresponding to 8000 k-points in the full BZ. The energy integrations in the self-consistency loop were carried out using 14 nodes along a semicircular contour in the complex-energy plane. The densities of states were obtained from the self-consistent one-electron potentials using the Green function quantities calculated at energies with a small imaginary part ($\sim$10 mRyd) followed by numerical analytic continuation to the real axis [17]. Effects of exchange and correlation were treated within non-relativistic density functional theory with an exchange potential using the Perdew–Zunger [18] parametrization. The ratio of the Wigner–Seitz radii ascribed to the inequivalent sites of the C15 Laves phase was chosen as 1.25 au, according with previous studies for the ordered system [13]. The radii of the Co and Al atomic spheres were assumed to be equal over the whole concentration range ($0 \leqslant x \leqslant 0.25$).

To study the influence of the lattice expansion, our calculations were performed for two different values of the lattice constant for each compound—one being the lattice constant of the parent phase YCo_2 (7.215 Å), which will be called the 'fixed lattice constant', and the second being the experimental lattice constant for the given concentration as given in table 1, called the 'experimental lattice constant'.

Table 1. Experimental values of the lattice constant as given by Yoshimura and Nakamura [6]. The lattice constant for $x = 0.25$ is derived by extrapolation as in reference [9].

x, $Y(Co_{1-x}Al_x)_2$	0.00	0.05	0.10	0.15	0.20	0.25
a, lattice constant (Å)	7.215	7.244	7.275	7.312	7.342	7.380

3. The mechanism of the weak-itinerant-moment formation

The density of states of pure YCo_2 is presented in figure 1. The atom-resolved DOS (figure 1) shows that the sharp double peak just below ε_f and the small broad peak above appearing in the total DOS originate mainly from the d bands of Co. It does not make much difference which one—the total or the partial Co-resolved non-spin-polarized DOS—is used in the qualitative discussion of the magnetic properties of the pure YCo_2 compound. A discussion of the magnetic instability in $Y(Co_{1-x}Al_x)_2$ compounds implies an application of pure Stoner theory in a certain sense. As mentioned in the introduction, the quantity of central interest in this case is the density of states at the Fermi energy $N(\varepsilon_f)$, since in the Stoner theory the magnetic stability depends on the sign of the Stoner factor $1 - IN(\varepsilon_f)$ where the constant I is defined as the intra-atomic exchange integral which thus remains essentially unaffected under alloying. We have found for various Al concentrations and various volumes that the changes of $N(\varepsilon_f)$ of the total as well as the Co partial DOS are rather small, but different. In view of that, we have to specify more precisely in which sense we understand a Stoner instability in this section. The major contribution to the total moment comes from the Co site, but it has been shown earlier, from spin-polarized calculations for the pure YCo_2 compound [13], that there

exists a small but sizable contribution from the Y site which even has the opposite sign. This Y moment appears as a result of the polarization effect due to the magnetically active 3d band of Co rather than as a genuine Y moment.

When Al is substituted for Co, it provides a partly filled broad s–p band to the total density of states and a fully empty 3d band far above the Fermi energy (neglecting small hybridization effects); consequently the magnetic polarization of Al is essentially zero. It follows that only the Co atoms are magnetically active in Y(Co$_{1-x}$Al$_x$)$_2$. The spontaneous magnetic moment which appears in Y(Co$_{1-x}$Al$_x$)$_2$ at an Al concentration of $x \simeq 0.12$ is thus due to the intra-atomic electron–electron interaction at the Co sites. In view of these arguments, we can assume that it is $N(\varepsilon_f)$ for the Co-projected DOS which is relevant for the moment formation in these compounds rather than the value of $N(\varepsilon_f)$ of the total DOS. Moreover, in the limit of small Co concentrations (which is beyond the scope of the present paper), it appears that a Stoner criterion based on the local Co DOS becomes equivalent to the Anderson condition [14] for the appearance of local moments for transition metals in the dilute-alloy limit.

In order to support the general discussion of weak-moment formation based on non-spin-polarized calculations, we tried to obtain the weak ferromagnetic moment directly from our spin-polarized *ab initio* calculation. For most of the Al concentrations ($x < 0.25$) this attempt encountered huge difficulties when trying to stabilize such a solution, since the energy differences between the low-moment and high-moment states are extremely small and favour the high-moment state. This problem arises from the well known tendency of the LDA interpolation formulae to favour solutions with high magnetic moments. The problem is thus similar to that in the case for YCo$_2$ where, at the experimental lattice constant, a high-moment state was also found to be lower in total energy than the paramagnetic state [13]. Also in Y(Co$_{1-x}$Al$_x$)$_2$ the high-moment state is experimentally only accessible by applying an external magnetic field (see section 1), which lowers the energy of the high-moment state to below that of the low-moment (or paramagnetic) state. Using the respective experimental lattice constants, the spin-polarized calculations always converge to the high-moment state (with a moment ≈ 0.5–0.7 μ_B/Co). Indeed, it is not a weak ferromagnetic state that we are looking for, because it was found throughout the concentration range $0 \leqslant x \leqslant 0.25$ for the experimental lattice constant and it has a rather high magnetic moment, ≈ 0.5–0.7 μ_B/Co. If we fix the lattice constant as that of YCo$_2$ for all Al concentrations, the high-moment states can no longer be observed in our calculations for $x \geqslant 0.15$. In this range we find a weakly ferromagnetic state for the concentrations $x = 0.18$ and $x = 0.19$ with a magnetic moment (table 2) very similar to the experimentally observed ones (≈ 0.1 μ_B/Co). For all other concentrations in the range $x \geqslant 0.15$, only a paramagnetic state is found (e.g. for $x = 0.17$ and $x = 0.20$ no stable weakly ferromagnetic state could be detected). These results are regarded as extremely important for the further discussion, since they demonstrate that the bare alloying effects (under a fixed volume) lead to the formation of a spontaneous moment in Y(Co$_{1-x}$Al$_x$)$_2$ compounds and allow a rough estimation of the critical value of the Co $N(\varepsilon_f)$ at which a magnetic instability will occur.

Table 2. The calculated energy difference ΔE between the paramagnetic and weak ferromagnetic states, the magnetic moment m per Co atom, and $N(\varepsilon_f)$, the Co-atom-projected DOS of the respective non-spin-polarized calculation. The lattice constant has been taken as that for YCo$_2$: 7.215 Å.

x, Y(Co$_{1-x}$Al$_x$)$_2$	ΔE (mRyd/f.u.)	m (μ_B/Co)	$N(\varepsilon_f)$ (states Ryd^{-1}/Co)
0.18	-0.027	0.125	24.3
0.19	-0.017	0.097	24.2

It should be noted that the results of the spin-polarized calculations for the high-moment states are important for the discussion of the metamagnetic transition in applied fields, in particular when it comes to the relative influence of volume and alloying effects on the value of the critical field for $Y(Co_{1-x}Al_x)_2$. The discussion of these results, however, is beyond the scope of the present paper and will be published elsewhere.

The total densities of states calculated for $x = 0.15$ for both the experimental and fixed lattice constants (figure 2) show that volume effects do indeed lead to a narrowing of the bands of the order of 0.1 eV, and cause a small increase of the DOS at the Fermi level $N(\varepsilon_f)$. This is also true for the Co-projected DOS. This effect supports the magnetic instability, but does not play a major role in the formation of the weak itinerant moment. The partial atom-resolved DOS (per atom) (lower panel of figure 2) shows that the contribution of the Al states to the total DOS is very small, as discussed earlier. If we compare the densities of states of YCo_2 (figure 1) and $Y(Co_{0.85}Al_{0.15})_2$ (figure 2), we immediately see that only a single peak remains

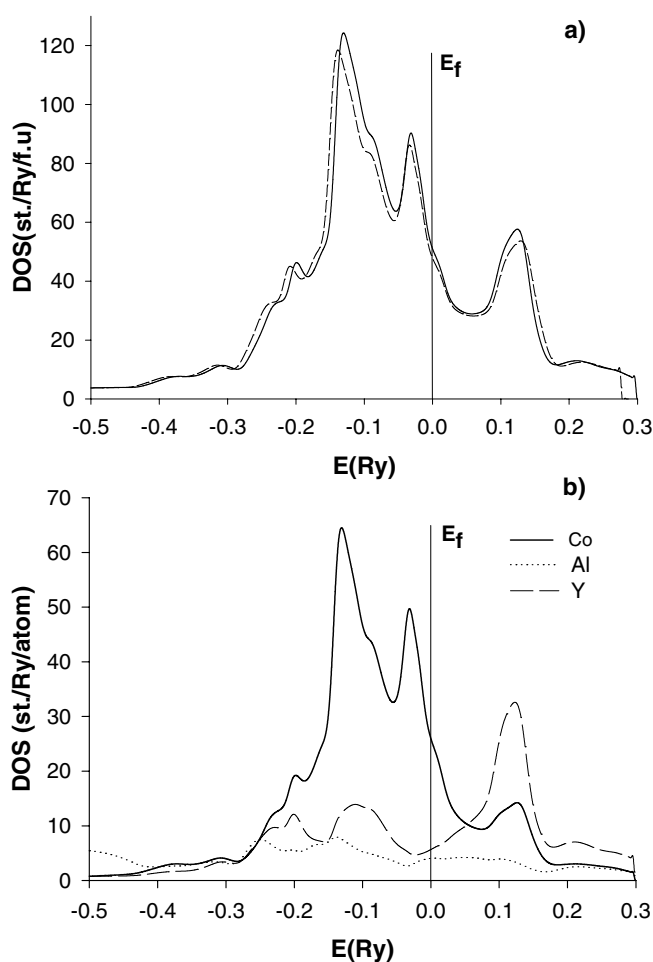**Figure 2.** (a) The total DOS of $Y(Co_{0.85}Al_{0.15})_2$. Full line: the DOS calculated at the experimental lattice constant; dashed line: the DOS calculated for a fixed lattice constant (see the text). (b) The atom-resolved DOS of $Y(Co_{0.85}Al_{0.15})_2$ given per atom calculated at the experimental lattice constant.

below the Fermi energy in $Y(Co_{0.85}Al_{0.15})_2$ rather than a double peak as for pure YCo_2, and the small broad peak just above the Fermi level also disappears. As a remaining trace of this latter broad peak we find a change of the slope of the DOS just above ε_f. Similar features have been seen by Aoki and Yamada [9] for ordered $Y(Co_{0.75}Al_{0.25})_2$, the only difference being that the DOS calculated remains less dispersed because the effects of disorder are not properly taken into account in their approach. As can be seen from our CPA calculation of the DOS for $x = 0.25$ (figure 3), only a single rather broad peak remains and there is no indication of other additional structures.

The evolution of the density of states with increasing Al concentration can be clearly understood from figure 3 where the Co-atom-resolved densities of states are presented for the fixed (for all concentrations) and experimental lattice constants. It is immediately obvious that all peaks of the density of states start to become broadened and reduced in height due to the alloying of Al. The Fermi level slightly shifts towards a higher value of the energy as the Al concentration increases, which is in contrast to the intuitive expectations discussed in the introductory section. However, although the overall height of the Co DOS decreases with increasing Al concentration, in the vicinity of the Fermi level the values of the DOS slightly increase due to a peculiar mechanism: in pure YCo_2 the Fermi energy is placed in the valley between two pronounced peaks close to a minimum of the DOS (figure 1). Upon alloying, these peaks below and above ε_f start to broaden and to overlap. This causes $N(\varepsilon)$ to actually increase in the energy range between these peaks (figure 3). This is exactly the energy region where one finds ε_f for $Y(Co_{1-x}Al_x)_2$ (figure 3).

We conclude that the increase of $N(\varepsilon_f)$ which leads to the magnetic instability is an electronic structure effect connected to the smoothing of the DOS due to disorder. It can be expected that supercell calculations for the virtual ordered structures of $Y(Co_{1-x}Al_x)_2$ in comparison to CPA calculations, which treat the alloy effect on a better footing, will lead to different results, since in supercell calculations the inevitable long-range order always produces rather sharp peaks in the DOS. Comparing our results with the calculation for the ordered Y_2Co_3Al compound as given by Aoki and Yamada [9], we note that they found an increasing Co partial DOS but a decreasing total DOS with respect to pure YCo_2, whereas we describe an increase for both the Co partial DOS and the total DOS if we compare the values for $x = 0.0$ and $x = 0.25$. The increase of the total DOS $N(\varepsilon_f)$ as derived from our CPA calculation can thus be clearly attributed to the effects of disorder.

The numerical values of $N(\varepsilon_f)$ for the partial Co-atom-resolved DOS and the total DOS are summarized in table 3.

Table 3. Calculated values of the densities of states at the Fermi level of $Y(Co_{1-x}Al_x)_2$. The 'fixed' lattice constant is equal to that of pure YCo_2. The 'experimental' lattice constants are those from table 1.

x, $Y(Co_{1-x}Al_x)_2$	0.00	0.05	0.10	0.15	0.20	0.25	Lattice constant
$N(\varepsilon_f)$, atom DOS (states Ryd^{-1}/Co)	21.4	21.0	23.3	24.2	24.1	23.5	Fixed
$N(\varepsilon_f)$, atom DOS (states Ryd^{-1}/Co)	21.4	21.4	24.3	25.9	26.4	26.4	Experimental
$N(\varepsilon_f)$, total DOS (states Ryd^{-1}/Co)	46.3	44.8	47.9	47.8	46.2	48.5	Fixed
$N(\varepsilon_f)$, total DOS (states Ryd^{-1}/Co)	46.3	45.7	49.8	50.8	50.2	48.7	Experimental

Comparison of the values of $N(\varepsilon_f)$ for the Co-resolved DOS from tables 2 and 3 clarifies the role of the increasing volume in these systems with respect to the formation of weak ferromagnetic order. Due to the volume increase, the concentration range of existence of the weak ferromagnetism is extended towards lower values. This can be seen from the third row in table 3 where $N(\varepsilon_f)$ for concentrations $x > 0.1$ is higher than $N(\varepsilon_f)$ calculated for a fixed
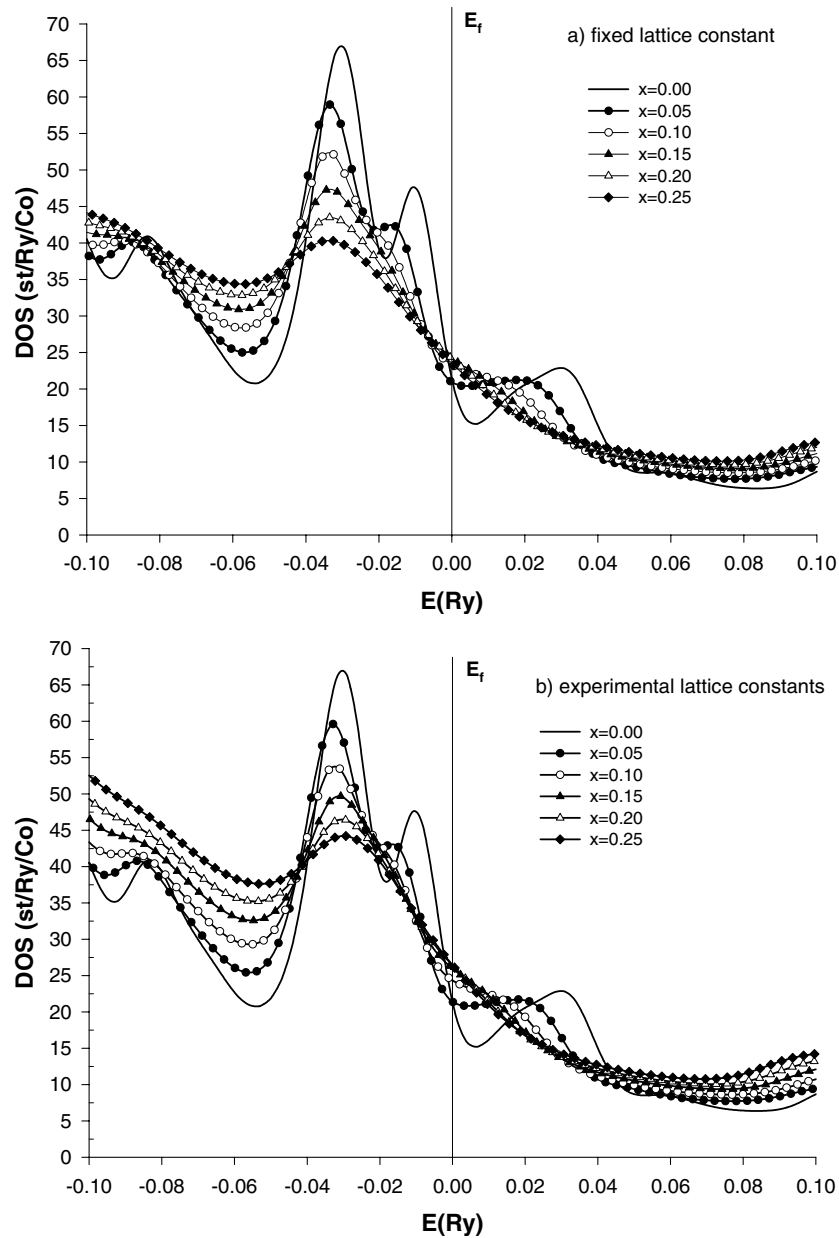
Figure 3. Details of the Co-projected DOS in the vicinity of the Fermi level of the $Y(Co_{1-x}Al_x)_2$ compound: (a) with the lattice constants of all of the compounds fixed to the values for YCo_2; (b) with the experimental lattice constants taken from table 1.

lattice constant (see e.g. the respective value for $x = 0.18$ as given in table 2). We wish to point out that our analysis of the results should be considered more qualitative than quantitative, because of the small changes of $N(\varepsilon_f)$ as a function of the concentration x, which nevertheless provide a new understanding of the moment formation in these systems. From our results we also find that the increase of $N(\varepsilon_f)$ is faster between $x = 0.1$ and $x = 0.15$ and thereafter

changes slowly for higher concentrations. This observation can be used to explain the almost constant pressure (in the range 8.9–11 kbar) that is required to suppress weak ferromagnetism in the concentration range $0.143 \leqslant x \leqslant 0.175$ as determined by Armitage *et al* [8].

To support our interpretation of the weak-moment formation due to density-of-states effects, fixed-spin-moment calculations, which are at present beyond our capabilities within the CPA code, would be desirable for future investigations.

4. Conclusions

The results of the all-electron CPA band-structure calculations presented clearly explain the mechanism of formation of the weak ferromagnetic moment for Y(Co$_{1-x}$Al$_x$)$_2$ compounds. Neither of the earlier-proposed intuitive explanations for this phenomenon is fully valid:

 (i) The volume effects alone are not sufficient to explain the spontaneous moment formation, but they help to extend the concentration range where weak ferromagnetism exists in these compounds.
 (ii) A rigid-band mechanism where the Fermi level is supposed to shift to lower energies with increasing Al content has been shown to be completely obsolete.

The increase of the DOS at the Fermi energy is found to be a direct consequence of smoothing of the DOS peaks due to alloying, so the effects of disorder play a primary role in the spontaneous ferromagnetic moment formation in these compounds. We conclude that the application of the CPA in this case is particularly important.

The description of the low-moment state (for the fixed lattice constant) at certain concentrations of Al obtained directly from *ab initio* spin-polarized calculations can be considered an important result that directly shows that the bare alloying effects in Y(Co$_{1-x}$Al$_x$)$_2$ can lead to a spontaneous magnetic moment on the Co sublattice.

Acknowledgments

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