Band theory of induced magnetic moments in CoM (M=Rh, Ru) alloys

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Experimentally observed induced magnetism on Rh and Ru when alloyed with Co is studied within a tight binding linear muffin-tin orbital (TB-LMTO) method in atomic sphere approximation (ASA). Different possible crystal structures of Co_3M (M=Rh,Ru) are considered and it is shown that the hexagonal close packed (hcp) structure is the most stable with induced magnetic moments on Rh and Ru. Some other off-stoichiometric structures such as $Co_{71}M_{29}$ and $Co_{67}M_{33}$ are also considered. The band theory explains quite well the observed induced magnetism in different cases.

I. INTRODUCTION

One of the most active researches pursued these days is the induced magnetism in otherwise nonmagnetic transition metals (NTM's) alloyed with $3d$ ferromagnetic transition metals (FTM's). The magnetism induced in a nonmagnetic spacer due to FTM overlayers is very interesting due to new phenomena observed in these systems. One of them is the exciting observation of spin wave oscillations as a function of spacer thickness between two succesive FTM layers.[1] Besides this sandwich technique, the induced magnetism in $4d$ elements is also studied through intermetallic alloying with FTM. One of the classical systems is the FeRh alloy which was first studied by Fallot in 1938 (Ref. 2) and still facinates many research workers.[3] In earlier studies, these intermetallic alloys contained mainly Fe FTM or in a few cases Ni. Recently, Harp *et al.*[4] have grown Co/$4d$ (Rh, Ru) alloy samples as 500–1000 Å thick films on fused quartz wafers by codeposition using magneton sputtering with the substrate held at 500 °C. They have thus obtained alloys of $Co_{77}Rh_{23}$, $Co_{71}Ru_{29}$, and $Co_{49}Rh_{51}$. The induced magnetic moments in these alloys were investigated through x-ray magnetic circular dichroism (XMCD). The interesting results are that in the Co_xRh_{100-x} (x=77, 49) alloy, the induced magnetic moment on Rh is about 1/3 the Co moment whereas in $Co_{71}Ru_{29}$ the induced moment on Ru is $<$1/14 the Co moment. So far the origin of these induced magnetic moments have not been explained on the basis of the band theory. In the present work we undertake a self-consistent energy band calculation by the tight binding linear muffin-tin orbital (TB-LMTO) method in the atomic sphere approximation (ASA).[5] In the next section we give some details of an energy band calculation of these alloys and present the results obtained. Then, these results are discussed and compared with experimental data. Finally, a short conclusion is drawn.

II. CALCULATION AND RESULTS

The Co_3M (or Co_6M_2) alloys are of the same structure as Co_3Pt which were grown earlier by Harp *et al.*[6] and also by Maret *et al.*[7] It is a hexagonal close packed (hcp) structure composed of two alternating planes A and B. In one case each plane has one atom of M and three atoms of Co which is the usual Ni_3Sn type DO_{19}. Another possibility is that plane A contains two atoms of M and two of Co while B has only Co atoms. This structure we call *modified* DO_{19} or DO'_{19} Besides hcp structure these alloys may also exist in a cubic structure $L1_2$ where three simple cubic sublattices of a face centred cube are occupied by Co and the remaining one is occupied by M.[8,9] According to phase diagram Co_3Ru does not exist in the $L1_2$ phase.[10] Hence, for Co_3Ru the energy band calculations have been done only for hcp structure. The Co_3M chemical formula approaches $Co_{77}Rh_{23}$ quite well but only approximately to $Co_{71}Ru_{29}$, the alloys studied by Harp *et al.*[4] To approach $Co_{71}M_{29}$ closer, we have studied Co_5M_2 and Co_4M_2 by replacing the lacking Co sites (in Co_6M_2) by empty spheres. These empty spheres are denoted by E_n (n=1,2) so the general chemical formula for off-stoichiometric alloys becomes stoichiometric in the form of $Co_{6-n}M_2E_n$ (n=1,2). Furthermore, to obtain magnetic moments with a higher concentration of M in CoM alloys without empty spheres, we have also considered the system $Co_{6-n}M_{2+n}$ (n=1,2) where missing Co_n are replaced by M_n. These above systems are only studied in hcp structure.

The electronic structure calculations are performed by the TB-LMTO method[5] with an atomic sphere approximation (ASA). Thus, the charge transfer is the measure of the charge variation in a given atomic sphere as compared to the neutral configuration. The valence electrons in neutral configuration are $3d^74s^24p^0$ for Co, $4d^65s^25p^0$ for Ru, and $4d^75s^25p^0$ for Rh. The rest of the occupied levels are considered frozen. The Brillouin zone (BZ) integration is performed by the usual tetrahedron technique.[11] We use about 200 k points in the irreducible BZ to construct the tetrahedrons. These points are found sufficient to obtain a converged result for these structures.[9]

Since the lattice parameters for these alloys are not yet known precisely, we have performed the calculations of the electronic structure in each case as a function of the lattice parameter to obtain the lowest energy lattice constant. For a given alloy structure this lowest energy lattice parameter is found to be the same in para (P) and ferro (F)-magnetic phases. Around the lowest energy lattice parameter, the total energy increases parabolically for decreasing or increasing

TABLE I. For different alloy CoM (M=Rh, Ru) structures the nearest neighbor distance d_{NN} (a.u.), energy of magnetization ΔE (mRy), density of states/unit cell, $n(\epsilon_F)$ at the Fermi level, magnetic moment μ_α (α=Co,M) (in μ_B), and charge variation ΔQ_α in a given α atomic sphere are presented.

Alloy structure	d_{NN}	ΔE	$n(\epsilon_F)$	μ_{Co}	μ_α	ΔQ_{Co}	ΔQ_α	ΔQ_E
$Co_6Rh_2-L1_2$	4.72	− 0.030	225.19	1.23	0.34	0.0325	−0.0975	
$Co_6Rh_2-DO_{19}$	4.78	−0.049	271.48	1.50	0.51	0.0365	−0.1095	
$Co_6Rh_2-DO'_{19}$	4.80	−0.038	248.81	1.52	0.39	0.065	−0.195	
$Co_6Ru_2-DO_{19}$	4.75	−0.030	283.00	0.74	0.15	0.085	−0.255	
$Co_6Ru_2-DO'_{19}$	4.78	−0.015	189.68	1.10	−0.01	0.115	−0.345	
$Co_5Rh_2E_1$–hcp	4.74	−0.020	282.14	1.42	0.53	−0.092	−0.305	1.07
$Co_4Rh_2E_2$–hcp	4.65	−0.014	233.17	1.07	0.37	−0.310	−0.537	1.157
$Co_5Ru_2E_1$–hcp	4.65	0.000	166.74	0.00	0.00	−0.062	−0.411	1.132
$Co_4Ru_2E_2$–hcp	4.61	0.000	136.65	0.00	0.00	−0.317	−0.556	1.19
Co_5Rh_3–hcp	4.86	−0.048	322.61	1.54	0.40	0.071	−0.118	
Co_5Ru_3–hcp	4.82	−0.005	203.88	0.87	0.05	0.446	−0.743	
Co_4Rh_4–hcp	4.83	−0.008	232.11	1.01	0.16	0.252	−0.252	
Co_4Ru_4–hcp	4.85	−0.001	173.27	0.43	0.02	0.367	−0.367	

lattice parameter. The curvature of the parabola is quite large and the minimum energy point can be determined without any ambiguity. When the magnetic moments in the F phase are studied as a function of lattice parameters, one obtains transition from the P to F phase at a critical point, then the magnetic moment increases monotonically as the lattice parameter increases. All three phases ($L1_2$, DO_{19}, and DO'_{19}) of Co_3Rh are found to be more stable in the F phase.

For $Co_{6-n}M_2E_n$ and $Co_{6-n}M_{2+n}$ we have studied only hcp structures since we know that Co_3M (M=Rh, Ru) have the lowest energies in the DO_{19} phase. According to the present calculation $Co_{6-n}M_2E_n$ is found to be magnetic when M=Rh, whereas, when M=Ru the self-consistency always converges to a nonmagnetic phase. Lastly, $Co_{6-n}M_{n+2}$ (n=1, 2) are found to be stable in the F phase even when M=Ru, which is not true for $Co_{6-n}M_2E_n$. In Table I we present the magnetic moments μ_α (α=Co,Rh,Ru)/atom, energy of magnetization ΔE/unit cell and some other physical quantities. The energy of magnetization ΔE is defined as the difference of energies $E(F)-E(P)$ in the F and P phases.

III. DISCUSSION

The nearest neighbor distance d_{NN} which gives the lowest total energy for a given structure indicated in the second column of Table I shows that the the lattice parameters are not the same for the different cases considered here. This type of fully self-consistent calculation deemed necessary due to the absence of any measured value of the lattice parameters.

In the third column of Table I we give the energy of magnetization as defined earlier. The alloy Co_6Rh_2 has the lowest energy in the DO_{19} structure in its magnetic phase. The same is true for Co_6Ru_2 as well. For this alloy only DO_{19} and DO'_{19} crystal structures are considered since $L1_2$ according to the phase diagram[10] does not exist. The magnitude of energies of magnetization for $Co_{6-n}M_2E_n$ (n=1,2) are smaller than the corresponding Co_6M_2. In the case of $Co_{6-n}Ru_2E_n$ the ΔE is strictly zero since the self-consistent calculation always converges to paramagnetic phase. For the alloy of type $Co_{6-n}M_{2+n}$ (n=1,2) where there is no empty sphere we again obtain a small energy of magnetization even when M=Ru. These results show that $Co_{6-n}Ru_{2+n}$ is magnetic as opposed to $Co_{6-n}Ru_2E_n$. When we compare the density of states $n(\epsilon_F)$ at the Fermi level ϵ_F, given in column 4 of Table I, for different compositions and structures, it is noticed that the presence of empty space in $Co_{6-n}Rh_2E_n$ does not change much $n(\epsilon_F)$ as compared to Co_6Rh_2. On the contrary, in the case of $Co_{6-n}Ru_2E_n$, the $n(\epsilon_F)$ is reduced dramatically as compared to Co_6Ru_2. This fact is in favor of the absence of magnetism in $Co_{6-n}Ru_2E_n$.

The magnetic moments on Co and M are given in columns 5 and 6, respectively. The magnetic moments on Co (μ_{Co}) and Rh (μ_{Rh}) in the $L1_2$ structure in Co_6Rh_2 are smaller than the corresponding values in DO_{19} and DO'_{19} The μ_{Co} in DO_{19} and DO'_{19} are the same whereas μ_{Rh} in DO'_{19} is somewhat smaller than in DO_{19}. For comparison with experimental values we will consider DO_{19} since this has the lowest total energy. The experimental values for $Co_{77}Rh_{23}$ given by Harp *et al.*[4] are $\mu_{Co}=1.34\mu_B$ and $\mu_{Rh}=0.64\mu_B$. According to these authors the x-ray magnetic circular dichroism (XMCD) measurements may have an error of 20 and 30 % in μ_{Co} and μ_{Rh}, respectively. The theoretical values $\mu_{Co}=1.50\mu_B$ and $\mu_{Rh}=0.51\mu_B$ are in quite good agreement with experimental measurements.

In the case of Co_6Ru_2, again the ferromagnetic DO_{19} phase is the most stable. In DO'_{19} the Co atom has an important magnetic moment $1.10\mu_B$ whereas Ru has a small ($-0.01\mu_B$) magnetic moment antiparallel to the Co atom. In the stable phase (DO_{19}) the magnetic moments ($\mu_{Co}=0.74\mu_B$, $\mu_{Ru}=0.15\mu_B$) are much stronger, particularly μ_{Ru}, than the experimental values $\mu_{Co}=0.42$ and $_{Ru}<0.03$ μ_B measured on alloy $Co_{71}Ru_{29}$. This alloy has a somewhat higher concentration of Ru than $Co_{75}Ru_{25}$ that we have treated theoretically. Thus, to check the effect of the concentration we have studied $Co_{6-n}M_{2+n}$ (n=1,2) and $Co_{6-n}M_2E_n$. The first chemical formula is compact

whereas the second contains empty spheres. The empty spheres E_n simply replace the missing Co_n lattice sites. For these cases we consider the usual hcp of the DO_{19} structure of Co_6M_2 and replace missing Co_n lattice sites by M_n or by E_n, respectively, for $Co_{6-n}M_{2+n}$ and $Co_{6-n}M_2E_n$. The nonstoichiometric alloy $Co_{6-n}M_2$ thus becomes stoichiometric due to the presence of E_n. The results are certainly very surprising. The presence of empty spheres in the case of $Co_{6-n}Rh_2E_n$ varies slightly the magnetic moments μ_{Co} ($1.42\mu_B$) and μ_{Rh} ($0.58\mu_B$) when $n=1$, but it does decrease to $1.07\mu_B$ (μ_{Co}) and $0.37\mu_B$ (μ_{Rh}) when $n=2$. On the other hand for $Co_{6-n}Ru_2E_n$ the magnetization disappears even with a single vacant site. These observations exclude the possibility of the presence of high vacancies in the experimental samples where in $Co_{71}Ru_{29}$ a magnetic moment of the order of $0.42\mu_B$ on Co is obtained. This chemical formula is represented by Co_5Ru_2 with empty spheres in place of missing Co.

When we consider concentrated alloys of the type $Co_{6-n}M_{2+n}$ we obtain a stable ferromagnetic state for M=Rh as well as Ru and also when $n=1$ and 2. The measured magnetic moments in $Co_{49}Rh_{51}$ ($\mu_{Co}=0.45\mu_B$, $\mu_{Rh}=0.11\mu_B$) (Ref. 4) are smaller than the values $\mu_{Co}=1.01\mu_B$ and $\mu_{Rh}=0.16\mu_B$ that we obtain for Co_4Rh_4 (Table I). It should be noted that their measured values of the magnetic moments on $Fe_{77}Rh_{23}$ are also much smaller than a perfectly ordered bulk alloy.[12] But the tendency that the μ_{Co}/μ_{Rh} ratio increases almost two times when we go from $Co_{77}Rh_{23}$ to $Co_{49}Rh_{51}$ as observed by Harp *et al.*[4] is confirmed by the present band theory (see Co_6Rh_2 and Co_4Rh_4 in Table I). The satisfactory results are also obtained for $Co_{6-n}Ru_{2+n}$ as far as the respective magnetic moments are concerned. The magnetic moments on Co and Ru decrease as we increase the Ru concentration but that on Ru decreases more rapidly than that on Co. The magnetic moments (μ_{Co}; μ_{Ru}) are (0.87;0.05) and (0.43;0.02), respectively, for Co_5Ru_3 and Co_4Ru_4. The experimental observation[4] $\mu_{Co}=0.42$, $\mu_{Ru}<0.03$ and $(\mu_{Co}/\mu_{Ru})>14$ for $Co_{71}Ru_{29}$ agrees quite well with our results for Co_4Ru_4. But keeping in mind that, usually, the values of magnetic moments by XMCD (Ref. 4) are much smaller than the corresponding bulk calculations, our results for Co_5Ru_3 (i.e., $Co_{67}Ru_{33}$) could be considered comparable with experimental values, particulary, when we compare μ_{Co}/μ_{Ru}.

IV. CONCLUSION

From the present energy band calculation we reach the same conclusion as earlier[4] that Rh and Ru behave and polarize much differently when alloyed with Co. The surprising observation that $(\mu_{Co}/\mu_{Ru})>14$ is confirmed by this *ab initio* study. The vacancies (empty spheres) do not produce the same effect in Co-Rh and Co-Ru alloys. In the case of Co-Ru even a single vacancy (i.e., Co_5Ru_2E) destroys the magnetism. Accordingly, we exclude the presence of any appreciable vacancies in the experimental sample of the Co-Ru alloy used by Harp *et al.*[4] It should be noted that the experimentally prepared samples are real alloys whereas our theoretical samples are compounds with three-dimensional periodicity (bulk). In spite of this difference our results are very close to the experimental measurements.

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