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Ab initio studies of structure and magnetic structure in YCo_3H_2

X.Y. Cui[a,b], J. Liu[a,c], I. Morrison[a,*], D.K. Ross[a]

[a] *Institute for Materials Research, University of Salford, Salford M5 4WT, UK*
[b] *School of Physics, The University of Sydney, Sydney, NSW 2006, Australia*
[c] *Department of Engineering Science, University of Oxford, Oxford OX1 3PJ, UK*

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Abstract

We present an ab initio density functional study of magnetic phase transitions in the YCo_3H_2 system. The augmented plane wave and local orbital method as employed in the WIEN2K code is used to predict the structure and electronic structure of this compound. Comparison is made with recent X-ray diffraction and magnetization studies. The calculations suggest that the YCo_3H_2 system is ferrimagnetic in character. Further, fixed spin moment calculations are used to predict and interpret magnetic phase transitions observed in externally applied magnetic fields.

Keywords: Intermetallics; Hydrogen storage materials; Electronic band structure; Magnetically ordered materials

1. Introduction

The Y–Co family of intermetallic compounds and their associated hydrides exhibit a wide range of interesting and variable magnetic properties. In the parent compounds the magnetic moment per cobalt atom increases from zero in YCo_2 to 1.64 in Y_2Co_{17}. Of particular interest is the intermediate compound YCo_3 and its related hydrides which exhibit a dramatic dependence of magnetic properties upon increasing hydrogenation. YCo_3 is a ferromagnet or ferrimagnet [1–4], some recent experimental and theoretical work suggests it is in fact ferromagnetic [5]. Experimentally, the β_1 phase, YCo_3H_x, $1.0 < x < 1.5$, is paramagnetic (or possibly antiferromagnetic with a Neel temperature of 273 K). The β_2 phase, with $1.5 < x < 2.0$, is ferromagnetic (our calculated results here suggest it is in fact ferrimagnetic), with a Curie temperature of 237 K. The γ phase, $3.5 < x < 4.0$, is antiferromagnetic (or paramagnetic) with a Neel temperature of 200 K [6]. These novel magnetic properties may be important for application purposes, for example the hydrogen driven metal-insulator transition on YH_x is being explored for novel display technologies [7]. Studies of these compounds under ultrahigh magnetic fields [8] also reveal multiple magnetic transitions as a function of field. In this paper we present the results of ab initio electronic structure calculations of the structure and magnetic structure in YCo_3H_2. In addition the fixed spin moment method is used to understand magnetic field induced transitions in the electronic structure.

2. Computational methodology

Calculations are performed with spin polarized density functional theory. We use the full-potential, scalar relativistic approach as employed in the WIEN2k code [9]. For the exchange and correlation potentials, we used the Perdew and Wang 91 implementation of the GGA. To improve the convergence behavior and computational efficiency, the augmented plane wave and local orbital (APW + lo) basis is employed. The initial basis set includes 5s, 5p and 4d valence and 4s, 4p for semicore functions for Y sites, 4s, 4p, and 3d valence and 3s and 3p semicore functions for Co sites and 1s states for H. The muffin tin radii used are 2.75 a.u. for Y, 2.0 a.u. for Co and 0.9 a.u. for H atoms. $R_{\min}K_{\max} = 4.5$

* Corresponding author. Tel.: +44 161 2955303; fax: +44 161 2955060.
E-mail address: i.morrison@salford.ac.uk (I. Morrison).

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and $G_{max} = 22$, $k = 400$ corresponding 44k points in the irreducible BZ, tests showed that properties had converged at this level of BZ integration. Spin orbit coupling is also included in the calculation (in the parent YCo_3 compound inclusion of spin orbit coupling is important for predicting the ferrimagnetic ground state as observed in recent experiments [5]) using the second variational approach, here a basis is calculated within spin polarized DFT and then used to diagonalise the Hamiltonian including the SO term. For the calculation including spin–orbital coupling, we assume that both the magnetization and field are parallel to the *c*-axis based on the fact that the easy direction of magnetization is along the *c*-axis [10]. Including the spin–orbital coupling decrease the symmetry, for YCo_3, the number of symmetry operations drops from 12 to 4. The fixed spin moment (FSM) method is used understand changes in the magnetic state of the system as a function of external field. In this approach a self-consistent calculation is performed subject to a requirement that the system possesses a particular total magnetic moment, this is achieved by separately varying the Fermi energy of majority and minority electrons. Investigation of the total energy as a function of magnetic moment can then reveal both local and global minima corresponding to different magnetic phases observed in an external magnetic field.

3. YCo_3H_2 structure

The parent compound, YCo_3 has the rhombohedral *R*-3*m* crystal structure, usually presented in hexagonal coordinates, and conveniently described in terms of the alternate stacking of YCo_5 cells of the $CaCu_5$ type and YCo_2 cells of the $MgCu_2$ type structure. It is isomorphous to $PuNi_3$ with two different sites for Y atoms (Y1 in 3a sites and Y2 in 6c sites) and three for Co atoms (Co1 in 3b sites, Co2 in 6c sites and Co3 in 18h sites). For the β_2 phase YCo_3H_x ($x = 1.5$–2.0), X-ray measurements show that the *R*-3*m* symmetry is retained throughout the region $0 < x < 2$ [11]. Neutron diffraction reveals that the hydrogen atoms occupy the 36i type interstitials in the YCo_2 block. This conclusion has been recently confirmed by synchrotron X-ray [5]. This structure is shown in Fig. 1, both the conventional hexagonal unit cell and the rhombohedral primitive cell used in calculations are shown. An important feature associated with the YCo_3H_2 crystal structure is that the Co1 atom is located at the center of a cluster of six hydrogen atoms, see Fig. 1. The distance between Co1 and H is 1.70 Å. The nearest neighbour of each H atom is a Co3 atom, at a distance 1.60 Å. But each H is neighbour to only one Co3 atom. The experimental and calculated geometry data are listed in Table 1 together with the data for the parent compound. The calculated data result from a full structural relaxation. An interesting effect on the parent structure on hydrogenation to the β_2 phase is the fact that the only an expansion of the host lattice along the *c*-axis occurs to accommodate the hydrogen.

4. Ground state electronic and magnetic structure

The electronic ground state of YCo_3H_2 was found to be ferrimagnetic with the Co1 atom having an anti-parallel alignment of local magnetic moment. The predicted total magnetic moment is $8.02\mu_B$, corresponding $0.89\mu_B$/Co, compared with experimental value $0.72\mu_B$/Co. One possible reason for this slight discrepancy is due to the impurities in the experimental sample reducing the magnetism. The calculated magnetic moments of the three distinct Co atoms are $-0.98\mu_B$ (Co1), $1.61\mu_B$ (Co2) and $1.21\mu_B$ (Co3). Note, these calculated local moments are simply the net spin mo-

Table 1
Calculated crystallographic data of (a) YCo_3 and (b) YCo_3H_2, compared with synchrotron X-ray diffraction (XRD) results [5]

	Experimental (synchrotron XRD)	Calculated
(a) YCo_3		
a (Å)	5.0159	5.020
c (Å)	24.273	24.25
Y_1 (3*a*)	0, 0, 0	0, 0, 0
Y_2 (6*c*)	0, 0, 0.1411	0, 0, 0.1399
Co_1 (3*b*)	0, 0, 0.5	0, 0, 0.5
Co_2 (6*c*)	0, 0, 0.3337	0, 0, 0.3346
Co_3 (18*h*, *x*, −*x*, *z*)	0.5006, 0.4994, 0.0815	0.5034, 0.4966, 0.0803
(b) YCo_3H_2		
a (Å)	5.0017	5.259
c (Å)	26.980	25.57
Y_1 (3*a*)	0, 0, 0	0, 0, 0
Y_2 (6*c*)	0, 0, 0.1308	0, 0, 0.1399
Co_1 (3*b*)	0, 0, 0.5	0, 0, 0.5
Co_2 (6*c*)	0, 0, 0.3346	0, 0, 0.3329
Co_3 (18*h*, *x*, −*x*, *z*)	0.4985, 0.5015, 0.0746	0.5008, 0.4992, 0.0705
H (36*i*, *x* −*x*, *z*)	0.4955, 0.5045, 0.1337	0.4945, 0.5055, 0.1332

The XRD results are for a stiochiometry of $YCo_3H_{1.9}$.

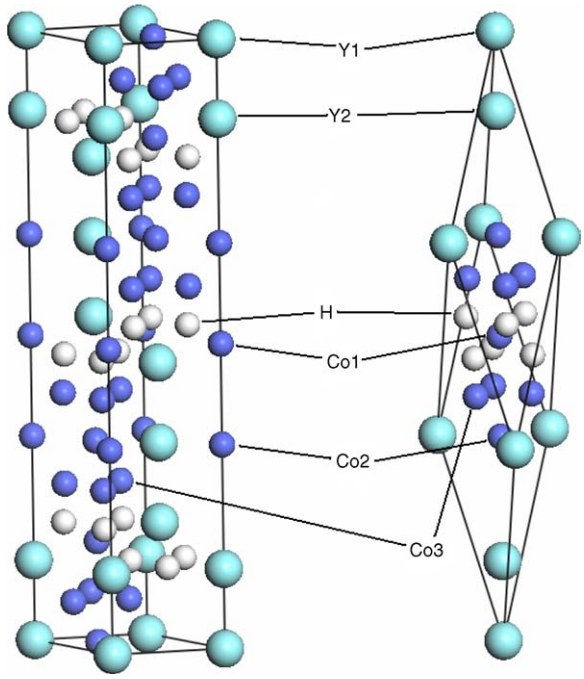

Fig. 1. The structure of YCo_3H_2. Both the conventional hexagonal unit cell and primitive rhombohedral unit cells are shown. Large spheres represent Y, small dark spheres Co and small light spheres H. Also indicated are the symmetry inequivalent atoms Co1, Co2, Co3, Y and H.

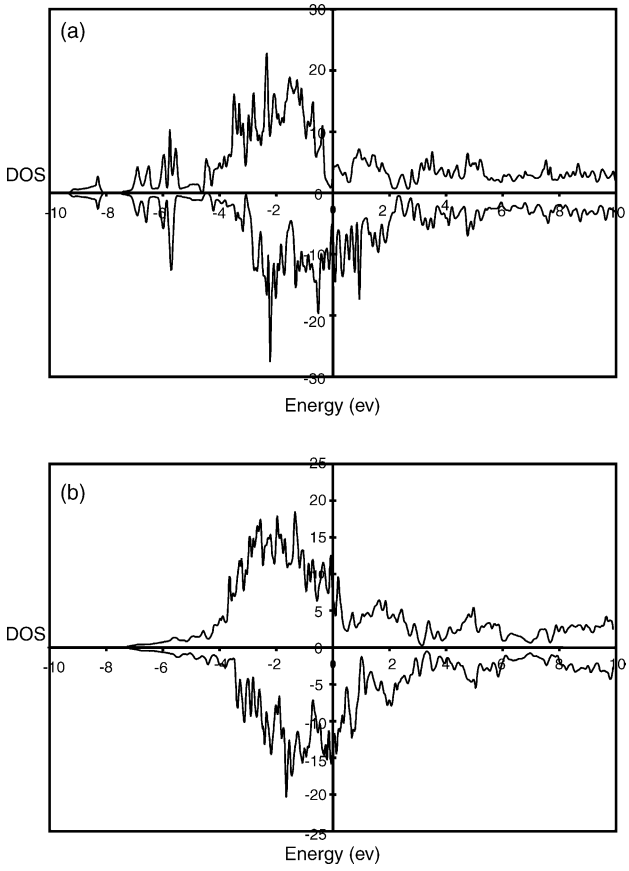

Fig. 2. The electronic density of states (DOS) for majority spin and minority spin electrons for both (a) YCo_3H_2 and (b) the parent compound YCo_3. The zero of the energy axis is the Fermi energy in each case. In each case the DOS is associated with the predicted ferrimagnetic ground states as discussed in the text.

ment inside each muffin tin sphere. In this structure the final self-consistent magnetic structure was independent of the choice of starting configuration, e.g. an initial ferromagnetic configuration converges to the above ferromagnetic configuration. It is interesting to compare these results to similar calculations performed for the parent compound [5], here again a ferrimagnetic solution is obtained but in YCo_3 it is the Co2 atoms have the anti-parallel magnetic moment, while in YCo_3H_2, it is Co1 atom. Furthermore, for YCo_3, to get a ferrimagnetic solution, an initial ferrimagnetic configuration is necessary. A ferromagnetic initial configuration leads to a meta-stable ferromagnetic state. However, for YCo_3H_2, no stable ferromagnetic state was found, although experimental results suggest β_2 phase is ferromagnetic. Our calculated results give a clear motivation for more careful and more extensive magnetization studies. In fact only recently have we determined that YCo_3 is ferrimagnetic compared to previous experimental and theoretical results suggesting it was ferromagnetic.

The electronic density of states (DOS) for YCo_3H_2, and also for YCo_3 for comparison, are presented in Fig. 2. A comparison of the DOS show the presence of the H 1s band strongly hydridised with the Co bands about 8 eV below the Fermi energy. The general effect that magnetization is increased on going from YCo_3 to YCo_3H_2 is explained by a combination of a relative lowering of the Fermi energy into a region of the DOS which favours a stronger splitting and a structural effect changing Co–Co distances with an associated sharpening of features in the Co related DOS.

5. Fixed spin moment results

To attempt to understand the magnetic transition in YCo_3H_2 under externally applied magnetic fields [12] we have performed a series of fixed spin moment (FSM) calculations. The calculated total energy in Rydbergs and the local Co sites magnetic moment (MM) as function of the total MM are presented in Fig. 3. For low values of total MM ranging from MM = 4–10μ_B a ferrimagnetic solution is obtained. From MM = 10μ_B a ferromagnetic solution is obtained. The transition from ferri to ferro can be understood as a field-induced spin-flip process under a high external magnetic field. Two energy minima are observed. One corresponds to the ferrimagnetic ground state located at MM = 8μ_B. The other one minima corresponds to a ferromagnetic state with total MM = 10.5μ_B. Furthermore, the ferrimagnetic solution, corresponding 0.89μ_B/Co, is consistent with the experimental value (0.67–0.78μ_B/Co) in zero field. The minimum for the ferromagnetic solution,

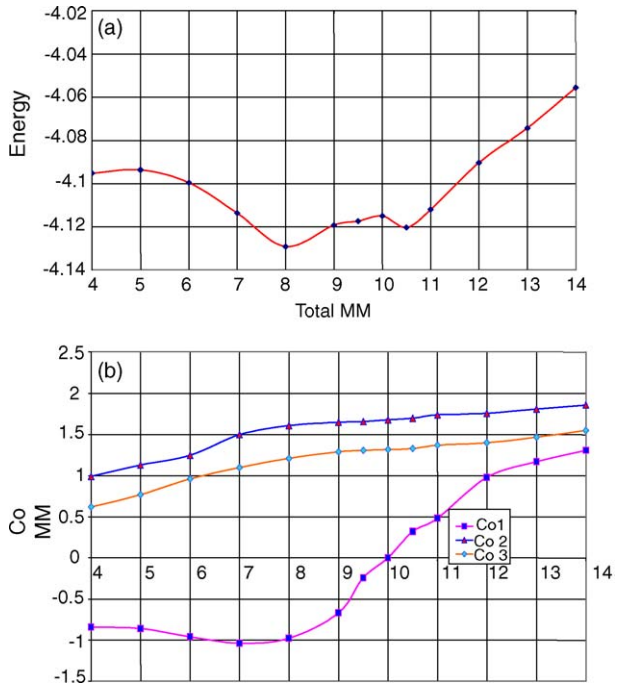

Fig. 3. (a) The total energy and (b) the local Co magnetic moments as a function of total magnetic moment associated with the FSM calculations described in the text. Magnetic moments are in units of μ_B. Note in (a) the two energy minima corresponding to the ferri and ferromagnetic states.

corresponding $1.15\mu_B$/Co, is consistent with the terminal point ($1.03\mu_B$/Co) in the magnetic transition under applied field. Based on our FSM results, we predict that the magnetic transition is a process that YCo_3H_2 changes from the ground state ferrimagnetic state and terminates as the ferromagnetic state.

6. Conclusions

The first principles calculations presented here are in agreement with recent structural determination in YCo_3H_2. Interestingly, the calculations predict a ferrimagnetic ground state compared to the, conventionally accepted, experimental ferromagnetic structure. This suggests that further experimental studies are necessary to completely understand the magnetic structure or that a higher level of theory and computation than is presented here is necessary. Note that the overall magnetic moments predicted here are in good agreement with experiment. Further, FSM calculations predict a ferri to ferromagnetic transition under application of an external field, again the total moments predicted are in good agreement with observation.

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