Magnetic and electronic structure of CoH

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Local-spin-density-approximation calculations of the magnetic and electronic properties of CoH are reported. In its ground state CoH is found to be a strong ferromagnet with a moment of approximately $1.16\mu_B$ and a magnetic energy of 10.1 mRy/f.u. The magnetic properties and their relationship to those of Co are discussed in terms of the electronic structure. The large moment in CoH is explained in terms of proton-induced hybridization of the electronic states.

I. INTRODUCTION

Two phases have been identified in the CoH_x system.[1,2] These are the hcp ε phase (related to hcp Co), which exists for $x < 0.65$ and a fcc NaCl structure γ phase with $x > 0.9$. Like pure Co, both γ and ε phase CoH_x are ferromagnetic metals, with a magnetic moment that decreases monotonically with H concentration.[1] Local-density-approximation (LDA) band-structure calculations[3–5] have established the basic features of the electronic structure and bonding of the transition metal monohydrides. The introduction of protons into interstitial sites of the transition-metal lattice lowers the interstitial crystal potential. Since the wave functions of the s-like states at the bottom of the transition-metal valence bands have substantially more weight in the interstitial region than the more localized d bands, they are pulled down in energy, typically forming a split-off band. It is this lowering of energy that provides the basic bonding mechanism. However, at the same time, each H atom introduces an additional electron into the crystal lattice. This electron, which enters at the Fermi energy, also makes a significant contribution to the binding, as emphasized by Switendick[3] and Williams, Kubler, and Gelatt[4] who were able to explain the anomalously high tendency towards hydride formation of Ni and Pd in terms of this contribution.

This picture leads to certain expectations regarding the properties of CoH. Co metal in its usual hcp structure as well as in the fcc and bcc structures is a strong ferromagnet in the sense that its majority spin d bands are fully occupied.[6–8] As a result the spin moment of Co is relatively insensitive to crystal structure. The extra electron introduced by the addition of H is then expected to enter predominantly the unoccupied minority spin d bands at the Fermi energy leading to a strong reduction in the moment of approximately $1\mu_B$ at $x = 1$. In this picture, the effect on the magnetism of adding H to Co to form CoH is analogous to going across the $3d$ series from Co to Ni, which leads to a reduction in the spin moment of about $1\mu_B$ due to the addition of an electron to the minority spin bands. One may anticipate that the reduction in the moment from Co to CoH could be larger. This is because as H is added, the exchange splitting of the d bands may

decrease. If this decrease is large enough, then the majority spin d bands may become partially unoccupied leading to a further reduction in the spin moment. These expectations are, however, at odds with experimental studies of CoH,[1] which find a moment of more than $1.3\mu_B$ for polycrystalline samples, i.e., the reduction in spin moment from Co is less than half that expected from the above considerations. Previous LDA calculations are, however, consistent with this experimental finding; a ferromagnetic instability is found[9,10] and in the self-consistent local-spin-density-approximation (LSDA) calculations of Alouani, Demangeat, and Kulikov a spin moment of $1.4\mu_B$ is found at a calculated lattice parameter of 7.16 a.u. In fact, Stoner calculations[9] based on the theory of Vosko and Perdew[11] indicate that of the NaCl structure hydrides only CoH is ferromagnetic: FeH, for which magnetism is observed for a hexagonal structure and RhH are predicted to be close to but below the Stoner limit in the NaCl structure. It should be noted, however, that the calculated lattice parameter in the self-consistent calculations of Ref. 9 is more than 1.5% larger than the experimental lattice parameter of 7.05 a.u. for γ CoH, and that LDA pattice parameters larger than experiment are anomalous.

Here we reexamine the electronic and magnetic structure of γ CoH using well-converged LSDA calculations performed using an extension[12] of the general potential linearized-augmented-plane-wave (LAPW) method.[13–15]

II. COMPUTATIONAL METHOD

The general potential LAPW method has been reviewed in considerable detail elsewhere.[13–15] Accordingly, only details specific to the present calculation are discussed here. Both the core and valence states were calculated self-consistently, the valence states in the full crystal potential with a scalar relativistic approximation and the core states fully relativistically in a spherical approximation. A well-converged set of approximately 130 LAPW basis functions was used with sphere radii of 2.05 a.u. and 1.40 a.u. for the Co and H, respectively. In addition, local orbitals were used to relax the linearization of the d bands. Comparably converged total-energy calculations with reduced sphere radii of 1.95 and 1.35 a.u. for Co and H were performed in order to determine the

equation of state. The Brillouin-zone averages needed in the self-consistent calculations were performed using a set of 408 special points[16] in the irreducible 1/48 wedge. The Hedin-Lundqvist[17] exchange correlation functional was used with the spin scaling of von Barth and Hedin.[18] Parallel calculations for fcc Co were performed in order to facilitate comparison of the electronic structures of CoH and fcc Co.

III. RESULTS AND DISCUSSION

A Birch[19] fit of total energies calculated for several lattice parameters in the range from 6.70 to 6.99 a.u. was used to determine the equilibrium lattice parameter of CoH. In this way an LSDA lattice parameter $a = 6.84$ a.u. was obtained. This is approximately 3% smaller than the experimentally determined value at room temperature of $a = 7.05$ a.u. This discrepancy is consistent with known LSDA errors for other $3d$ magnetic systems. The variation of the spin magnetic moment with lattice parameter is shown in Fig. 1. The variation is weak and nearly linear over the range shown, consistent with the electronic structure, which shows that CoH is a strong ferromagnet (see below). The spin moment at the experimental lattice parameter is $1.16\mu_B$ per Co atom, as compared to $1.62\mu_B$ per Co atom obtained in parallel LSDA calculations for fcc Co at 6.68 a.u. (the experimental volume). The calculated magnetic energy (the difference in energy between a non-spin-polarized calculation and a ferromagnetic calculation at fixed lattice parameter) is 10.1 mRy/Co atom at $a = 7.05$ a.u. This is only slightly reduced from the magnetic energy of fcc Co, which we calculate to be 12.5 mRy/atom, implying that the ferromagnetism of CoH is quite robust. Our calculated spin moment for CoH is 11% smaller than the experimental moment, which contains an orbital component. Although we have not calculated the orbital moment for
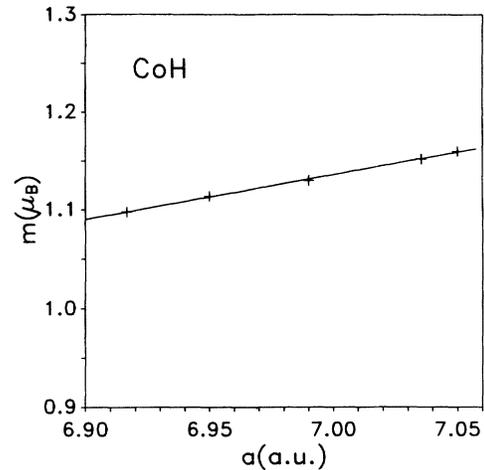

FIG. 1. Calculated spin moment of CoH as a function of the lattice parameter. The + symbols denote the calculated points. The solid line is a linear fit.

CoH, nor as far as we know has it been determined experimentally, it seems reasonable to speculate that it accounts for the above difference. In any case, consistent with experimental measurements and the calculations of Ref. 9, we find a moment for CoH that is much larger than that of fcc Ni, corresponding to a smaller than expected reduction in the moment of Co metal. This may be understood in terms of the electronic structure.

The calculated band structures of CoH, and for comparison, fcc Co are shown in Fig. 2. The corresponding electronic densities of states (DOS) are given in Fig. 3. From these figures it is apparent that the majority spin d bands are completely occupied in both CoH and fcc Co. Thus, like Co, CoH is a strong ferromagnet. One notable difference between the DOS and CoH and that of fcc Co is the considerably enhanced DOS in the tail above the
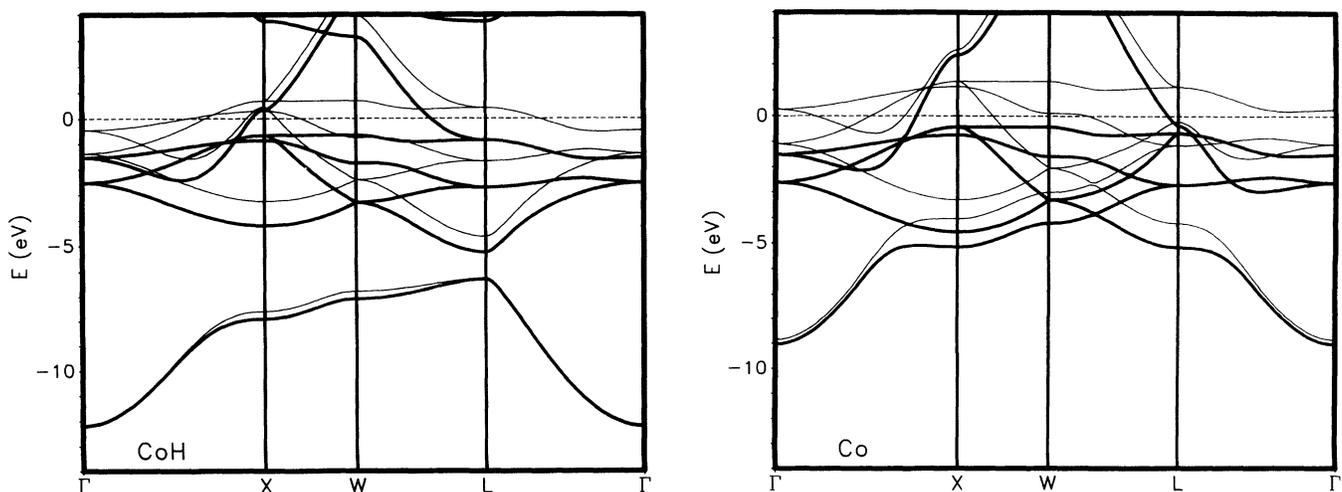

FIG. 2. Calculated band structures of CoH (left) and fcc Co (right) at $a = 7.05$ and 6.68 a.u., respectively. The heavy lines denote majority spin bands, while the light lines denote minority spin bands. The dashed horiziontal lines denote the Fermi energy.
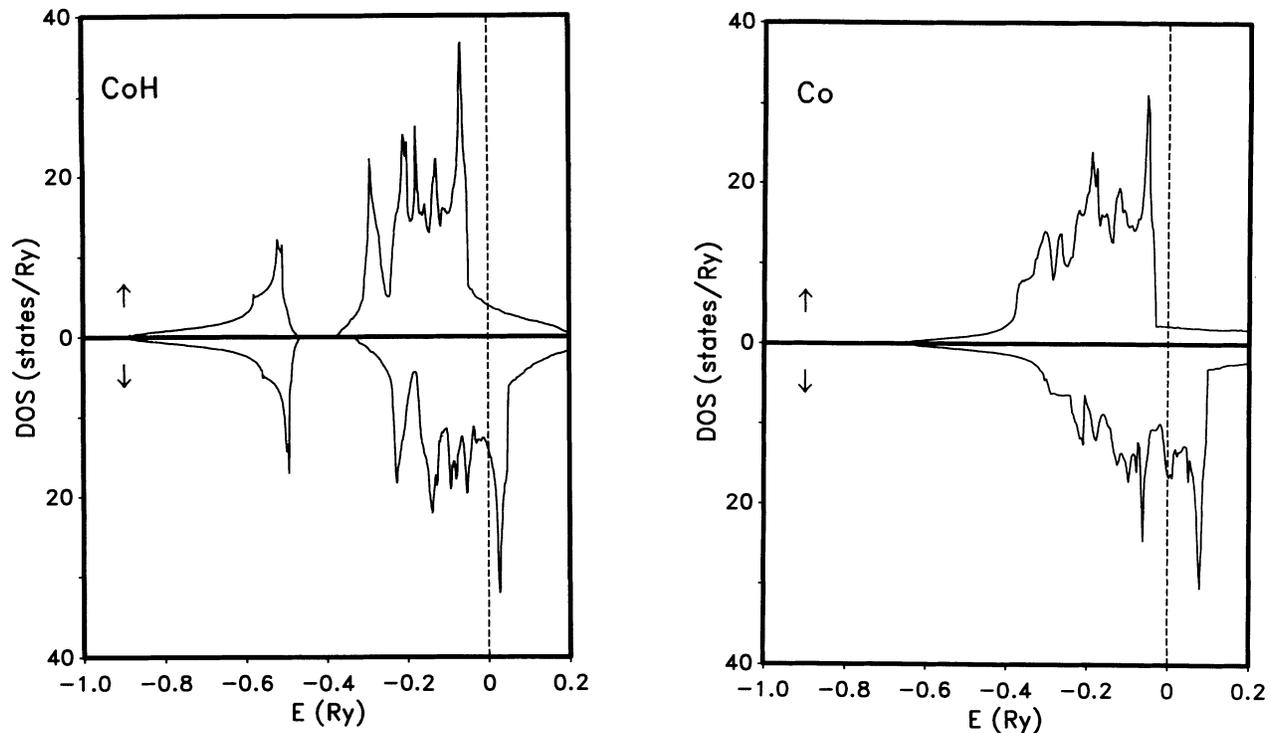
FIG. 3. Electronic density of states of CoH (left) and Co (right). Majority (minority) spin contributions are shown above (below) the axis. The dashed vertical line denotes the Fermi energy.

main d bands; this enhancement occurs in both the majority and minority spin channels and arises from a Co $3d$ component; this implies increased hybridization of the Co $3d$ derived states with Co $4s$- and $4p$-like states in CoH (it is convenient to regard the Co $4s$ and $4p$ states as breathing in the crystal potential and thereby neglect the H $1s$ states; the breathing could also be viewed as hybridization of the $4s$ and $4p$ states with the H states). The value of the DOS at E_F, $N(E_F)$ for CoH is 18.0 Ry^{-1} of which 3.9 Ry^{-1} derives from the majority spin bands. fcc Co at its experimental lattice parameter has a similar $N(E_F)$ of 18.5 Ry^{-1} but a smaller majority spin contribution of 2.2 Ry^{-1} and a larger minority spin contribution.

As expected the DOS of CoH shows a split-off peak below the d bands relative to fcc Co. These are the split-off s-like states characteristic of the hydrides as discussed in Refs. 3–5. In CoH the band giving rise to this peak is separated from the higher-lying bands by a direct gap of 1.04 eV, which occurs between majority spin states at the L point. Although no additional bands occur in the valence region due to the addition of H to Co, other substantial differences between the band structures of CoH and fcc Co may be noted. However, the band characters provide a more clear understanding of why the moment in CoH is larger than expected.

At the Γ point there are six valence bands for each spin. These are, in order of increasing energy, a split off Γ_1 s-like state, and threefold degenerate Γ_{25}, and twofold degenerate Γ_{12} states, which are derived from Co d states. The weight of the Γ_1 state inside the Co sphere is reduced

by approximately $\frac{1}{3}$ relative to fcc Co reflecting the attractive H potential, while the weights of the d-derived states at Γ are nearly unchanged. If this picture held throughout the Brillouin zone, one would expect a large reduction in moment close to $1\mu_B$ in going from Co to CoH as discussed above. However, away from the zone center, symmetry restrictions are relaxed allowing hybridization between the Co s, p, and d channels. Significant changes in these hybriziations occur between CoH and fcc Co, and these provide the explanation for the larger than expected moment. In particular, we find that occupied bands, which have both Co $3d$ and Co $4s$ character in fcc Co, have much weaker Co $3d$ character in CoH. For example, the L_1 band (the lowest-lying valence band in fcc Co and the second-lowest-lying valence band in CoH) has 60% Co $3d$ character[20] in Co but only 50% Co $3d$ character in CoH. This $3d$ weight is shifted above the Fermi energy, mainly to a conduction band occurring at 3.7 eV in CoH. Even larger changes are found at the X point. For example, the lowest-lying band has 69% Co d character in fcc Co and only 38% Co d character in CoH. This transfer of Co $3d$ weight to bands above the Fermi energy occurs throughout the zone, with the exception of the Γ point where it is prevented by symmetry. It is caused by the attractive interstitial potential due to the proton in CoH. This energetically favors the extended Co $4s$- and $4p$-like states over the Co $3d$ states, which are more strongly localized near the Co atom. Thus Co d weight is transferred, relative to fcc Co, from the hybridized bands near the bottom

of the valence region, which are occupied in both spin channels to the tail in the DOS above the main d bands. As mentioned, this effect is due primarily to the attractive proton potential in CoH. The additional electron due to the H enters at the Fermi energy, leading both to an increased occupation of the minority spin-d bands as well as the enhanced majority spin tail in the DOS. This tail accounts for approximately $\frac{1}{4}$ of the total DOS in the region near E_F. Thus we are led to the expectation that each added electron (i.e., H atom) should lead to a reduction in the Co moment of only $0.5\mu_B$ (0.75 minority-0.25 majority). On this basis a spin moment of roughly $1.1\mu_B$ per Co atom would be expected for CoH, consistent with the detailed calculations presented above and experimental measurements.

IV. CONCLUSIONS

LSDA calculations of the magnetic and electronic structure of CoH have been presented. A spin moment of $1.16\mu_B$ at the experimental lattice parameter is obtained. This moment is much larger than that of isoelectronic fcc Ni. This difference is understood in terms of the attractive interstitial potential due to the protons in CoH.

ACKNOWLEDGMENTS

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