Magnetism in Transition Metal Hydrides

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Magnetism in Transition Metal Hydrides.

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Abstract. – Using lattice parameters determined by total energy calculations we have performed calculations of the band structure for all the $3d$, $4d$ and $5d$ monohydrides in the NaCl structure. The results of these calculations are used to evaluate the Stoner criterion for ferromagnetism. We predict one strong candidate for ferromagnetism, *i.e.* CoH which exceeds by far the Stoner limit and two other hydrides, *i.e.* FeH and RhH which come close to the limit. In agreement with our results recent Mössbauer studies have shown that an f.c.c. γ-CoH$_x$ with $x > 0.9$ becomes ferromagnetic at hydrogen pressures near 9 GPa. Similar experiments demonstrate ferromagnetism in the h.c.p. phase of FeH. We offer these results as another example of success of the local density theory in predicting properties of materials.

It is now widely accepted that the density functional theory [1, 2] in the local density approximation for exchange and correlation [2] describes very accurately the ground-state properties of solids. Moruzzi *et al.* [3] first showed that the lattice parameter and the bulk modulus can be determined to within 1% and 10% accuracy, respectively. Recently, similar accuracy was claimed [4] in predicting the shear modulus and indeed all the elastic constants C_{ij}. Also, the McMillan-Hopfield parameter η that controls the electron-phonon interaction in superconductors has been calculated from first principles [5] and used to determine, at least semi-quantitatively, the superconducting transition temperature. Finally, the delicate tendency towards magnetism has been predicted [6] from first principles. Using the theory of Vosko and Perdew [7], a decade ago Janak [6] was able to compute the Stoner criterion for 32 metallic elements. His results clearly demonstrated magnetism for Fe and Ni with Stoner values for $N(E_F)I$ of 1.42 and 2.04, respectively. For Co he found $N(E_F)I = 0.97$ just short of satisfying the Stoner condition, probably because his calculations were done for f.c.c. and not h.c.p. Co. For the rest of the elements he showed that the Stoner criterion is not satisfied in agreement with experiment.

In this work we applied the Vosko-Perdew [7] theory to search for magnetism in transition metal hydrides. We considered all the $3d$, $4d$ and $5d$ monohydrides in the NaCl structure. For the $3d$ and $4d$ hydrides we used lattice parameters determined from total energy calculations by Moruzzi [8], while for the $5d$ hydrides we performed our own total energy calculations. Using these calculated lattice constants we carried out scalar-relativistic band structure calculations by the augmented plane-wave (APW) method, from which we obtained the densities of states (DOS). The APW calculations were performed self-

consistently in the muffin-tin approximation on a grid of 20 k-points in the irreducible Brillouin zone (BZ), and using the Hedin-Lundqvist formalism for exchange and correlation. The DOS were determined by the tetrahedron method from a set of 89 k-points in the 1/48th of the BZ and subsequent Fourier series interpolation. We estimate that the approximations made (muffin-tin and number of k-points) introduce an error in our results not exceeding 5% which would not affect our predictions.

The Vosko-Perdew [7] formalism requires the following input that is generated by the APW calculations, i.e. the self-consistent charge density and crystal potential as well as the values of the total $N(E_F)$ and angular momentum decomposed DOS $N_l(E_F)$. The relevant equations are given below:

$$I(r) = \int dr \, \gamma^2(r) |K(r)|, \qquad \gamma = \frac{1}{N(E_F)} \sum_l N_l(E_F) R_l^2(E_F),$$

where $R_l(E_F)$ is the Fermi level value of the radial wave function and $K(r)$ is a kernel giving the exchange and correlation enhancement of the external field due to the magnetization [7].

Our results are given in fig. 1-3 for the $3d$, $4d$ and $5d$ monohydrides, respectively. In fig. 1 (solid line) we note that CoH easily exceeds the Stoner criterion with a value of 1.98. The rest of the $3d$-element hydrides have values well below 1.0. At a recent conference Schneider et al. [9] presented Mössbauer studies which indeed confirm ferromagnetism in the Co-H system. They have identified two phases of CoH_x, both exhibiting ferromagnetism. In the composition $0 < x < 0.65$ the material is h.c.p. and forms for hydrogen pressures between 2 and 7 GPa and for $x \geqslant 0.9$ an f.c.c. γ phase is obtained at hydrogen pressures of 9 GPa. In the range $0.65 < x < 0.9$ the h.c.p. and f.c.c. phases coexist. Also in fig. 1 it is noted that FeH comes close to the Stoner limit with a value of 0.91 suggesting
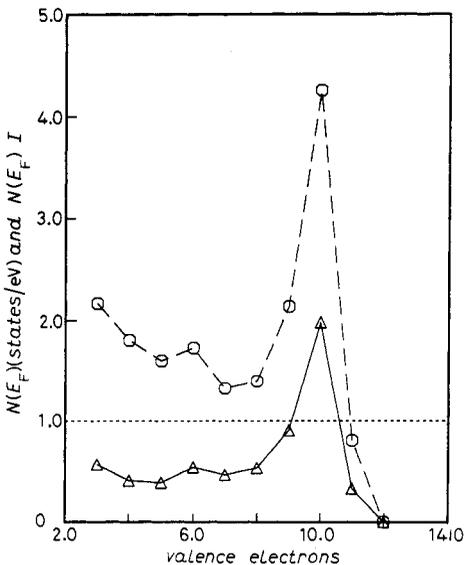

Fig. 1.   Fig. 2.

Fig. 1. – $N(E_F)$ (broken line) and $N(E_F)I$ (solid line) as a function of valence electrons in the $3d$ hydrides from CaH to CuH. The dotted line indicates the Stoner limit.
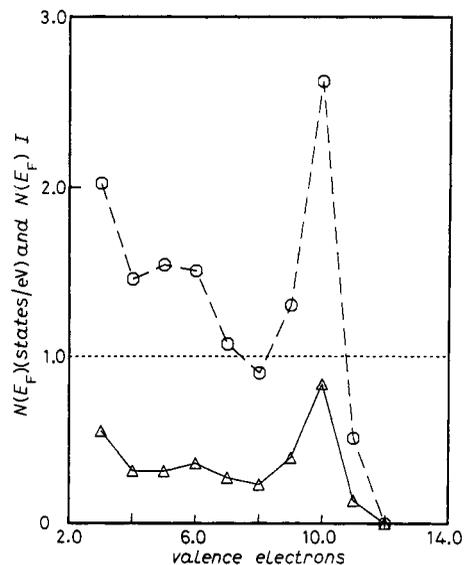
Fig. 2. – $N(E_F)$ (broken line) and $N(E_F)I$ (solid line) as a function of valence electrons in the $4d$ hydrides from SrH to AgH. The dotted line indicates the Stoner limit.
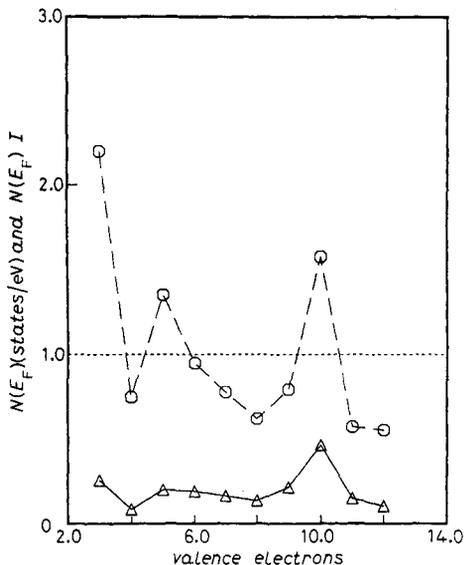
Fig. 3.   Fig. 4.

Fig. 3. – $N(E_F)$ (broken line) and $N(E_F)I$ (solid line) as a function of valence electrons in the $5d$ hydrides from BaH to AuH. The dotted line indicates the Stoner limit.
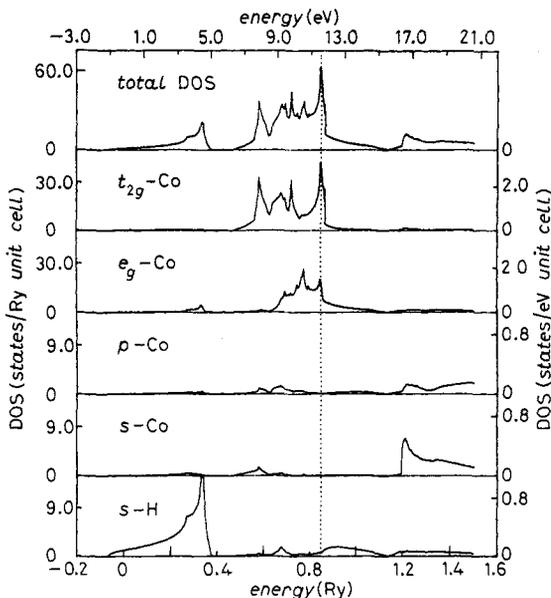
Fig. 4. – Densities of states functions for CoH broken down by symmetry. Note the differing scales of the panels.

magnetic instability, perhaps, in a related crystal structure. This seems to be consistent with the findings of Schneider *et al.* [9] who report ferromagnetism in a close-packed d.h.c.p. structure of FeH.

In fig. 2 we note that RhH has a Stoner value of 0.84 close to the required value for ferromagnetism. The rest of the $4d$ hydrides have low values of $N(E_F)I$ and therefore we do not expect magnetic instabilities there. While for RhH we are not aware of any experimental data, there have been reports of a magnetic moment observed in Pd-Ru-H alloys [10]. We note that for pure Pd the Stoner factor found by Janak is 0.775.

In fig. 3 $N(E_F)$ and $N(E_F)I$ are shown for the $5d$ hydrides. We note that all the $5d$ hydrides have $N(E_F)I$ values that are clearly less than 1.0 by at least a factor of two. For IrH, $N(E_F)I = 0.46$ is notably higher than the others, while BaH and HfH, despite their large $N(E_F)$, do not have a similarly large $N(E_F)I$. In fig. 1-3 together with the quantity $N(E_F)I$ we show (broken line) the density of states at E_F. It is clear that the two graphs are similar, which indicates that I varies slowly with the number of valence electrons but certainly cannot be taken as a constant.

An interesting observation is that the maximum $N(E_F)$ is found at 10 electrons for all the three transition metal d series; and this is also consistent with the pure metals where the highest $N(E_F)$ in the f.c.c. structure corresponds to the magnetic material Ni which also has 10 valence electrons.

We now return to CoH which is predicted to be ferromagnetic. In fig. 4 we show the DOS for $CoH_{1.0}$. We note that E_F falls on a sharp peak of the DOS which, as the angular-momentum decomposition indicates, comes from the d-like DOS with a dominant contribution from the t_{2g} symmetry. We also find a substantial contribution from the e_g symmetry, while the s-like hydrogen contribution is very small at E_F. Most of the hydrogen-induced

states appear at the bottom of the bands but, of course, they are crucial in determining the position of E_F. In addition to the CoH calculation, we performed the same kind of calculation for h.c.p. Co and found $N(E_F)I = 1.27$ in agreement with experiment. It should be noted here that Janak found the value of 0.97 for f.c.c. Co.

Now we address the question of stoichiometry in CoH_x. Our results shown in fig. 1 and fig. 4 correspond to fully stoichiometric monohydrides which are probably difficult to synthesize. The experiment suggests that magnetism occurs close to $x = 0.9$ for $C\mathring{o}H_x$. To make our results more realistic we performed a calculation on CoH_x by the coherent potential approximation (CPA) that takes properly into account nonstoichiometry effects. We have used the tight-binding (TB) form of the CPA, with the TB parameters determined by a very accurate least-squares fit to the APW eigenvalues. The value of $N(E_F)$ goes from 4.26 states/eV/cell in $CoH_{1.0}$ to 3.44 states/eV/cell in $CoH_{0.9}$ which, assuming a constant value for I, lowers the value of $N(E_F)I$ to ~ 1.7, but still well above the Stoner criterion.

In summary, we have applied the Vosko-Perdew [7] theory to calculate the Stoner criterion for magnetism in all transition element monohydrides. Our results show clearly that $B1$ structure CoH is ferromagnetic in agreement with recent measurements. It appears that the density functional theory within the local density approximation provides a reliable input to the Vosko-Perdew theory, which in turn is successful in predicting magnetic properties.

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