

Ferromagnetism in hexagonal-close-packed elements

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(Received 25 July 1988)

The Stoner theory of ferromagnetism has been applied to 3*d* transition metals in the hexagonal-close-packed (hcp) phase. The elements Co and Ni (and possibly Cr) are found to be ferromagnetic. A self-consistent calculation of the band structure of paramagnetic hcp Ni revealed the highest-known density of states at the Fermi level of any transition metal in any structure, providing strong evidence for ferromagnetism. A first-principles, spin-polarized band-structure calculation for hcp Ni yielded a stable magnetic moment of 0.76 μ_B per atom and an average spin splitting of 0.1 Ry.

I. INTRODUCTION

Molecular-beam epitaxy (MBE) has made possible the stabilization of metastable phases of elements not previously found to occur naturally. The first new ferromagnetic elemental structure was obtained by Prinz,¹ for body-centered-cubic (bcc) Co. Other metastable phases of elements have also been obtained by MBE, and an unlimited number of new alloys or compounds may be realized. The prospect for new and important man-made magnetic materials is excellent.²⁻⁴

Some theoretical work to help sort out possible magnetic phases has been completed. Janak⁵ applied a local-density approximation of electronic exchange and correlation in a parameter-free generalization of the Stoner⁶ theory of ferromagnetism to explain successfully the magnetic structure of 32 cubic metallic elements in the periodic table. More recent studies extended this treatment to 3*d* and 4*d* transition elements in possible metastable cubic phases.^{7,8}

Total-energy studies of ferromagnetic elements in various cubic phases have also been remarkable in their ability to predict or explain magnetic structure,^{9,10} although at this time some controversy exists about certain elements.¹¹ Since differences in total energy per atom from one magnetic phase of an element to another may be as small as 1 mRy/atom, approximations such as shape of potential, choice of zone integration grids, inclusion of relativistic effects, type of exchange, and correlation treatment of the many-body problem must all be examined carefully.

II. STONER THEORY FOR hcp 3*d* TRANSITION METALS

The purpose of this research was to extend the search for new magnetic materials to 3*d* transition elements in the hcp phase. The generalized Stoner theory⁵⁻⁷ has

been applied with the following procedure: (1) Existing paramagnetic hcp band structures were used where possible.¹² (2) The rigid-band approximation was made to obtain hcp band structures not already available. (3) It was assumed that the Stoner parameters computed by Janak⁵ are independent of crystal structure and lattice constants to the first approximation.¹³

The condition for magnetism is expressed in terms of the many-body enhanced magnetic susceptibility $\chi(q)$ which measures the response of a paramagnetic phase to an arbitrary small applied magnetic field $H(q)$ with wave vector q :

$$\chi(q) = \frac{\chi_0(q)}{1 - I\chi_0(q)}, \quad (1)$$

where $\chi_0(q)$ is the unenhanced susceptibility and I is the Stoner parameter. Poles of Eq. (1) give the magnetic instabilities, $q=0$ corresponding to a uniform field (ferromagnetism) and $q \neq 0$ corresponding to an alternating field (antiferromagnetism). For $q=0$, $\chi_0(0)$ is just the density of states at the Fermi energy $D(E_F)$ and the Stoner condition for ferromagnetism is

$$ID(E_F) \geq 1. \quad (2)$$

This condition is not sufficient, since poles of Eq. (1) at finite q may correspond to a more stable antiferromagnetic than ferromagnetic state.

Predictions of Eq. (2) for the 3*d* hcp transition metals are summarized in Table I using tabulated⁵ values of I . The two-centered, orthogonal Slater-Koster fits of Ref. 12 were used to obtain rigid-band approximations to estimate $D(E_F)$ for structures not already computed from first principles. $D(E_F)$ for 3*d* hcp transition metals based upon Sc, Ti, and Co band structures are compared with the Stoner values $D_s(E_F) = 1/I$, the minimum value necessary for a magnetic instability. As may be seen from Table I, accuracy of the rigid-band approximation is

TABLE I. Density of states at the Fermi energy for hcp 3d transition metals from rigid-band approximations. The first column lists the number of valence electrons per atom, and the second column gives the chemical symbol of the element. The third through fifth columns list $D(E_F)$ for each element as obtained from the band structures of Sc, Ti, and Co (Ref. 12). The column labeled Stoner is the minimum density of states necessary for a magnetic instability of the paramagnetic state. $D(E_F)$ is given in states/Ry atom in the last four columns. Numbers in square brackets are first-principles results. The first-principles result for Ni is 74 states/Ry atom (see text).

Electrons	Element	Sc	Ti	Co	Stoner
3	Sc	[28]	24	26	40
4	Ti	15	[14]	22	40
5	V	40	31	35	38
6	Cr	30	33	45	36
7	Mn	16	15	24	33
8	Fe	21	17	23	29
9	Co	40	36	[43]	28
10	Ni	66	47	55	27

good for adjacent elements in the periodic table, except where $D(E_F)$ falls close to a sharp peak in $D(E)$. The hcp elements Co and Ni easily satisfy the Stoner condition [Eq. (2)], while predictions for V and Cr depend upon the rigid-band source. Since V is closest to Ti, $D(E_F)=31$ states/Ry atom should be a more accurate prediction and hcp V fails the ferromagnetism test. The case for Cr is not so clear since it falls between Ti and Co, and a first-principles calculation is needed to make an unequivocal prediction.

III. BAND STRUCTURE OF hcp NICKEL

The Stoner predictions of the preceding section suggest that there should be at least two ferromagnetic hcp 3d transition elements. Experimentally, the ground state of Co is hcp and ferromagnetic. Ni in the hcp phase is certain to be magnetic if it can be produced. $D(E_F)$ for hcp Ni in Table I (from all three rigid-band calculations) is predicted to be higher than for Co.

To verify this last result a self-consistent augmented-plane-wave (APW) calculation was performed for hcp Ni. The lattice constants were determined by assuming equal volume per atom as in the stable face-centered-cubic (fcc) phase of Ni and a c/a ratio of 1.62, the same as hcp Co. This yields $a=4.718$ a.u. and $c=7.643$ a.u. The APW calculation was scalar relativistic and was performed in the muffin-tin approximation. Exchange and correlation were treated using the von Barth-Hedin local-density theory.¹⁴

The APW results were then fitted to a nonorthogonal Slater-Koster Hamiltonian containing 67 parameters as described in Ref. 12. The rms deviation from the APW bands was 3 mRy for the top 12 bands, and about 1 mRy at E_F . This tight-binding Hamiltonian was used to generate the density of states (DOS).

Figure 1 shows the total DOS together with its angular momentum components for paramagnetic hcp Ni. Aside from a very slight narrowing of the d bands, it is very similar to the density of states of paramagnetic hcp Co,¹²

justifying the rigid-band approximation from Co to Ni. An accurate calculation of $D(E_F)$ for hcp Ni yielded 74 states/Ry atom, the highest $D(E_F)$ for any transition element in any structure known to these authors. This is a consequence of the very sharp peak in the density of both t_{2g} and e_g d -electron states, which are coincident in the hcp structure. In all of the hcp band structures, the integrated density of states reaches the center of this peak at ten, the number of valence electrons for Ni, producing a large $D(E_F)$. This confirms and strengthens the Stoner conclusions for hcp Ni: The product $ID(E_F)$ in Eq. (2) is the largest found to date for transition metals.

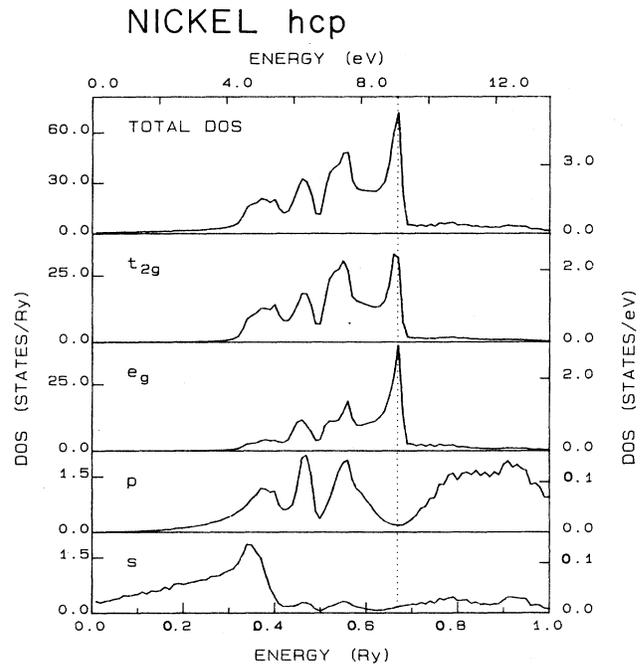


FIG. 1. Total and angular momentum decomposed densities of states for paramagnetic hcp Ni. Note the different scale in the s - and p -like DOS.

In order to verify this prediction of ferromagnetism for hcp Ni, a spin-polarized calculation at the same lattice constants was also performed. The energy bands from this calculation for spin up and spin down are shown in Fig. 2. Again the similarities with the spin-polarized bands of Co found in Ref. 12 are striking. E_F is now higher to accommodate the two extra electrons per unit cell. We have evaluated the spin splittings and found for the d -like states an average splitting of 0.1 Ry. The s - and p -like states have a much smaller splitting of the order of 0.002 Ry. The spin splitting of the d states in hcp Ni is approximately double that of fcc Ni.¹⁵ We have also calculated the DOS from the spin-polarized calculation and, as one might predict from the bands of Fig. 2, found a large $D(E_F)$ for spin down and small $D(E_F)$ for spin up. From the integrated DOS we found a magnetic moment of $0.76\mu_B$, which is almost 50% higher than that found in fcc Ni.

IV. CONCLUSION

While it is hoped that metastable hcp phases of transition metals can be stabilized by MBE on an appropriate substrate, the predictions made here apply to bulk properties (perhaps ten or more atomic monolayers). The instability of hcp phases toward formation of more complex hexagonal structure on a substrate and the possibility of more complex magnetic structures in the hcp phase itself have not been explored. The theory was done at zero temperature, but should be useful up to the Curie temperature, which is unknown. With these limitations and the specific assumptions listed in Sec. II, conclusions of the Stoner theory and additional findings stimulated by it are the following.

- (1) hcp Co and Ni are ferromagnetic.
- (2) hcp Cr requires more careful analysis.
- (3) Paramagnetic hcp Ni has a band structure very close to that of paramagnetic hcp Co and displays the highest-known $D(E_F)$ of any transition metal.
- (4) Ferromagnetic hcp Ni is similar to ferromagnetic hcp Co and has a magnetic moment of $0.76\mu_B$ per atom and spin splitting of 0.1 Ry.

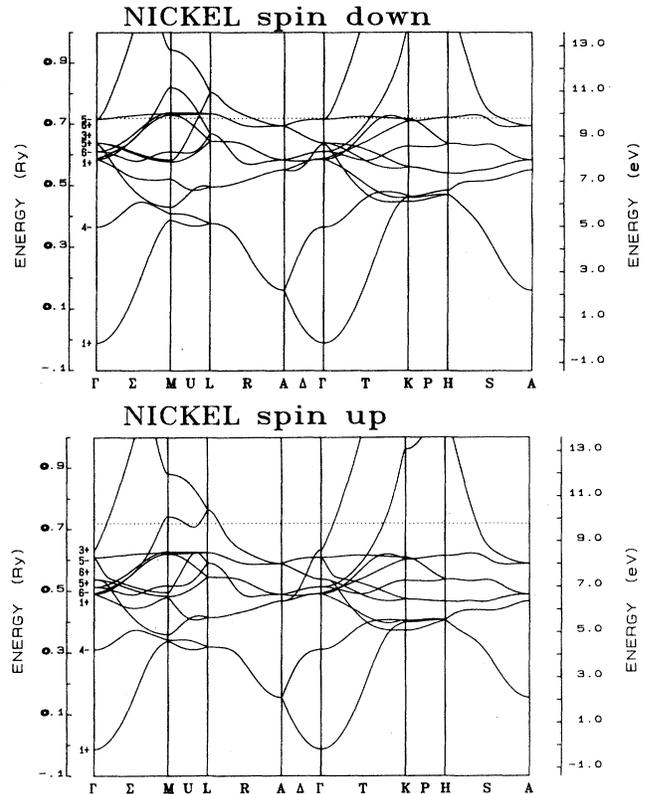


FIG. 2. Spin-polarized energy bands of hcp Ni.

- (5) The prospect for new magnetic materials produced by MBE in hcp (and other) phases appears to be excellent.

ACKNOWLEDGMENTS

Discussions with Dr. G. A. Prinz are gratefully acknowledged. This work was supported in part by the U. S. Office of Naval Research and The Robert A. Welch Foundation.

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