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Structural, electronic, and magnetic properties of Co: Evidence for magnetism-stabilizing structure

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Total-energy local-spin-density energy-band calculations are employed to study the different structural phases (hcp, fcc, and bcc) and magnetic states of Co metal as a function of volume. In the paramagnetic state, the fcc phase is lowest in energy with magnetic order stabilizing the hcp phase as the (observed) ground state. Unlike the case of Mn, Cr, and Fe which have stable antiferromagnetic states in the fcc phase, the ferromagnetic state is the most stable for all three phases of Co.

The ability to make novel artificial structures on the nanometer scale using sophisticated thin-film techniques has raised the prospect of inducing metastable structures having new, perhaps exotic, properties. Considerable interest has been centered recently on magnetic properties and their relation to crystal structure. Thus, Walmsley *et al.*[1] were able to stabilize Co in a "forced" bcc structure of polycrystalline modulated films of cobalt and chromium. Recently, Prinz[2] succeeded in stabilizing metastable bcc Co via epitaxial growth on GaAs. A variety of experiments indicated that a ferromagnetic material was obtained which is very similar to α-Fe both electronically and magnetically.

Prinz's work addressed, and so served to focus attention on, a longstanding problem—namely, the contribution of magnetism to structural phase stability. Co metal has a stable hcp structure which is strongly ferromagnetic at ambient pressure. This structure and property is in contrast to that of the $4d$ and $5d$ transition elements in the same column: Rh is a paramagnetic metal and Ir is a superconductor and both have a stable fcc structure. These differences raise questions regarding the possible existence of a strong correlation between magnetism and structure. In an attempt to obtain some answers to this question, we report on a total-energy local-spin-density[3] energy-band study of the structural, electronic, and magnetic properties of bulk Co metal in its hcp, fcc, and bcc phases.

Many self-consistent electronic band-structure calculations[4] have been performed for cubic and hcp Co using various energy-band approaches. Recently, Moruzzi, Marcus, Schwarz, and Mohn[5] investigated the structural and magnetic stabilities of Co in its bcc and fcc structures by employing the augmented spherical wave-band method.[6]

In this work, we study the ground-state cohesive properties and the pressure-induced magnetic properties of bulk Co using a total-energy approach: We have employed the local-spin-density approximation (LSDA) and calculated the total energy as a function of volume by means of the linear-muffin-tin-orbital (LMTO)[7] band method. This method has been demonstrated to work well for the close packed structures considered here. The von Barth-Hedin[8] exchange correlation potential, a semirelativistic approximation[9] for the valence electrons and a fully relativistic treatment of the core electrons are utilized. The precision in the resulting total energy (less than 1 mRy) is sufficient for determining the relative energetics of the phases considered.

We first performed self-consistent paramagnetic total energy band structure calculation on Co in its hcp, fcc, and bcc phases. Some results summarized in Table I include the equilibrium lattice constant r_{WS}^0 (r_{WS}: the Wigner-Seitz radius in a.u.), the total energy at r_{WS}^0 (in Ry), the bulk modulus (in Mbar) and the cohesive energy (in eV). In all phases, the calculated r_{WS}^0 are within 0.01 a.u. of each other. As seen, we find that the fcc phase is lowest in energy in the paramagnetic state—similar to observations for the $4d$ (Rh) and $5d$ (Ir) elements in the same column. The fcc phase is only slightly lower in energy (~ 1 mRy) than the hcp phase and the bcc phase is highest near the equilibrium lattice constant (by 8 mRy). As we will show, this structural order changes, however, when we introduce magnetism.

The results of the spin-polarized LSDA calculations for ferromagnetic Co are given in Table II. This shows that the hcp phase becomes more stable than the fcc by about 2 mRy and the total energy of bcc Co becomes close to that of the fcc phase. If one comparaes the energetics of the paramagnetic structures with those of the ferromagnetic structures, one sees that the hcp phase is lowered in energy as a result of magnetic ordering by ~ 15 mRy with respect to the stable paramagnetic fcc phase. A comparison of the theoretical total energies versus r_{WS} is shown in Fig. 1. Also given in Table II are the calculated magnetic moments. From this it is clear that the larger magnetic moment of the bcc phase causes the large exchange energy gain by about 20 mRy. As is seen in Table II, the calculated equilibrium lattice constants again are the same (to 0.01 a.u.) for each structure and for hcp agree closely with experiment. However, the bulk moduli and cohesive energies are a little bit overestimated, which is the usual case for the $3d$ transition metals.[4] (Since the cohesive energy is the difference in total energy of the solid and the free atom, a correct description

TABLE I. Total energy E_{tot}, equilibrium Wigner-Seitz radius r_{WS}^0, bulk modulus B, and cohesive energy E_{coh} from the paramagnetic band results of Co.

	E_{tot} (Ry)	r_{WS}^0 (a.u.)	B (Mbar)	E_{coh} (eV)
fcc	−2782.174	2.57	2.64	6.61
bcc	−2782.165	2.58	2.69	6.50
hcp	−2782.173	2.57	2.76	6.60

TABLE II. The same parameters as Table I and the total-spin magnetic moments from the ferromagnetic-band results of Co. The other theoretical and experimental values are also given for comparison.

	E_{tot} (Ry)	r_{WS}^0 (a.u.)	B (Mbar)	E_{coh} (eV)	m (μ_B)
fcc	−2782.186	2.61	2.35	6.36	1.64
bcc	−2782.185	2.62	2.45	6.35	1.73
hcp	−2782.188	2.61	2.49	6.39	1.63
Theory[a] (fcc)	−2760.768	2.56	2.40	6.48	1.56
Theory[b] (bcc)		2.61			1.68
Theory[c] (bcc)					1.72
Theory[c] (hcp)					1.59
Expt.[d] (fcc)		2.61			1.61
Expt.[e] (bcc)		2.63			1.41
Expt.[f] (hcp)		2.62	1.91	4.40	1.58

[a]Nonrelativistic self-consistent KKR (Korringa-Kohn-Rostoker) results by Moruzzi *et al.* in Ref. 4.
[b]Reference 5.
[c]Herman *et al.* in Ref. 4.
[d]Reference 10.
[e]Reference 2.
[f]Reference 11.

of the electronic structure of the free atom is a prerequisite. Unfortunately, errors in the LSDA approach for atoms are sizeable, in that multiplet structure and other factors are not included. As a reference atomic energy, we use $E_{tot} = -2781.7182$ Ry assuming the electronic configuration as $3d_{\uparrow}^{5}\,3d_{\downarrow}^{3}\,4s^{1}$.) Results of other theoretical calculations and experimental values of the magnetic moment are also given in Table II for comparison. The calculated magnetic moments for hcp and fcc phases are in reasonable agreement with experiment. However, the calculated magnetic moments for bcc phase [$(1.68-1.73)\mu_B$] seem much larger than the measured value ($1.41\mu_B$).[1,2] Since the calculated values are consistent among the results using different band methods, this disagreement may originate from defects in the sample, as pointed out by Marcus and Moruzzi.[4]

The angular momentum decomposed density of states at E_F and the partial charge occupations for hcp Co near experimental lattice constant are given in Table III. The s and p electrons are negatively polarized compared with the d electrons as is also seen in Fe and Ni and the total spin magnetic moment, $1.64\mu_B$, is larger ($\sim 4\%$) than the experimental value[11] of $1.58\mu_B$.

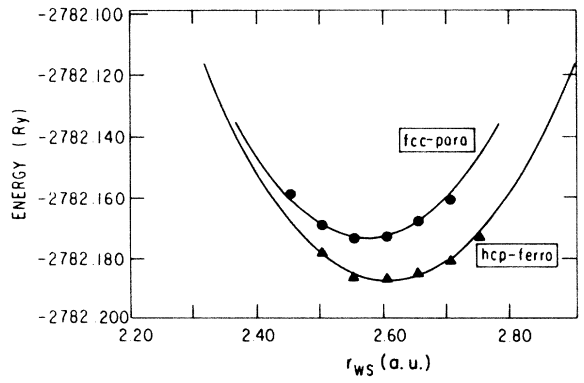

FIG. 1. Total-energy curve of Co for the paramagnetic fcc phase and the ferromagnetic hcp phase vs Wigner-Seitz radius r_{WS}.

It is expected that magnetism disappears with decreasing lattice constant (increasing pressure). We investigate this property by calculating the Stoner exchange correlation parameter, $\bar{S} = N(E_F)I_{xc}$ for the paramagnetic states. Near their equilibrium lattice constants, the calculated $\bar{S}$'s are 1.57 (hcp), 1.27 (fcc), and 1.85 (bcc), respectively. These $\bar{S}$ values are found to decrease with decreasing lattice constant and finally to become less than one at the magnetic instability points. These occur at the lattice constants (we use Wigner-Seitz radius r_{WS} in a.u. here) of 2.34 (hcp), 2.48 (fcc), and 2.23 (bcc). Thus the hcp and bcc phases maintain magnetic states at much higher pressures than does the fcc phase. This result is consistent with that of Moruzzi *et al.*,[5] who obtained a stable paramagnetic fcc phase at a 4% reduced latticed constant compared with a reduction of ours by 5.3%.

We have also examined the possible occurrence of an antiferromagnetic state in these structures. Interestingly, we find that the stable magnetic state of Co is ferromagnetic for all crystal structures although a metastable antiferromagnetic state exists. This is in contrast with other transition metals Mn, Cr, and Fe which have a stable antiferromagnetic structure in their fcc phases.[12] In the case of fcc Co, the antiferromagnetic phase is higher in energy (by 9 mRy) than the ferromagnetic phase, which implies that the relation between structure and magnetism is very delicate, and dependent upon the electronic configuration. These properties of magnetic transition metals will be discussed in more detail elsewhere.[13]

In this study, we considered only the static structural properties. Phonon effects[14] which might play an important role in determining the stable magnetic phase as well as the stable crystal structure, have not been included. Nevertheless, this work provides theoretical evidence that the bcc Co can be stabilized in artificial materials under the condition of negative pressure. Our work also indicates a strong cor-

TABLE III. The angular momentum decomposed density of states at E_F, N_l, and the occupied charges Q_l, at $r_{WS}=2.62$ a.u. of hcp Co.

	N_s	N_p	N_d	N_{tot} (E_F)	Q_s	Q_p	Q_d	Q_{tot}
↑	0.21	0.49	2.10	2.80	0.32	0.36	4.64	5.32
↓	0.05	0.58	10.18	10.81	0.34	0.42	2.92	3.68
m (μ_B)					−0.02	−0.06	1.72	1.64

relation between the stable structure and magnetism, in that the stability of both the hcp and bcc phases originates from the magnetic order.

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