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BRIEF REPORTS

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Total energy of trigonal and tetragonal cobalt

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The electronic structures of bulk trigonal, tetragonal, and hcp cobalt are calculated from first principles using density-functional theory. The results are used to predict lattice spacings, magnetic moments, and elastic properties. Attention is focused on the bcc and fcc structures, which are special cases of both the trigonal and tetragonal structures. An energy minimum is found around the fcc structure with properties in agreement with previous calculations and experiments. The bcc structure does not correspond to an energy minimum, and is therefore not a stable structure, with respect to tetragonal distortions. Our extensive calculations confirm the results of previous, more limited, density-functional calculations and are in contrast with experimental results that found metastable bcc cobalt thin films. [S0163-1829(99)01931-1]

I. INTRODUCTION

Electronic structure calculations of ideal bulk crystalline materials are a powerful tool for gaining insight into the properties of experimentally observable systems. For example, one can compare the magnetic moments predicted by such a calculation to experimental measures of the corresponding physical system. Calculations of the total energy for a range of different crystal structures can be turned to a variety of uses. The overall variation in energy among the structures can point directly to the overall stability of particular crystal configurations. One can also look closely at the variation in total energy for slight geometric variations around a particular structure of interest, such as a known stable configuration of the system. One can extrapolate from this variation the energetics of stress and strain on the stable structure and from this its elastic constants.

Electronic structure calculations for bulk materials can also provide insight when looking at thin films grown on substrates. In the first monolayer or two the interface between the film and substrate dominates the energetics of the system. The layers of the film beyond the initial growth layer, however, are often characterized by energetics similar to that of the bulk material. The significant difference between this film structure and the bulk structure is that the underlying substrate will impose a lattice constant on the film that is often different from that of the bulk.[1] By judicious choice of substrates pseudomorphic films can be grown with a variety of geometries normally not stable in the corresponding bulk material. Since electronic structure calculations can be performed for any crystal structure it is possible, and often useful, to compare the results of such a calculation for a bulk material to the observed properties of a thin film of corresponding geometry, which can be expected to show largely similar characteristics.

Cobalt is one such system that has received significant attention. Various approaches have been taken to using *ab initio* electronic structure calculations to shed light on several questions about cobalt both in bulk and as grown in thin films. In particular there is the question of the stability of cobalt films grown in a body-centered cubic structure.[2] Previous results have shown that total-energy electronic structure calculations do not seem to support the stability of bulk bcc cobalt.[3] In this paper, we give the results of electronic structure calculations for ferromagnetic bulk cobalt over a wide range of geometries. We look at a range of structures for the hcp, bct, and trigonal crystal configurations. Our calculations are performed using the full-potential linearized augmented plane-wave method with Janak's parametrization of von Barth and Hedin's local-density approximation to the exchange and correlation potential.[4,5]

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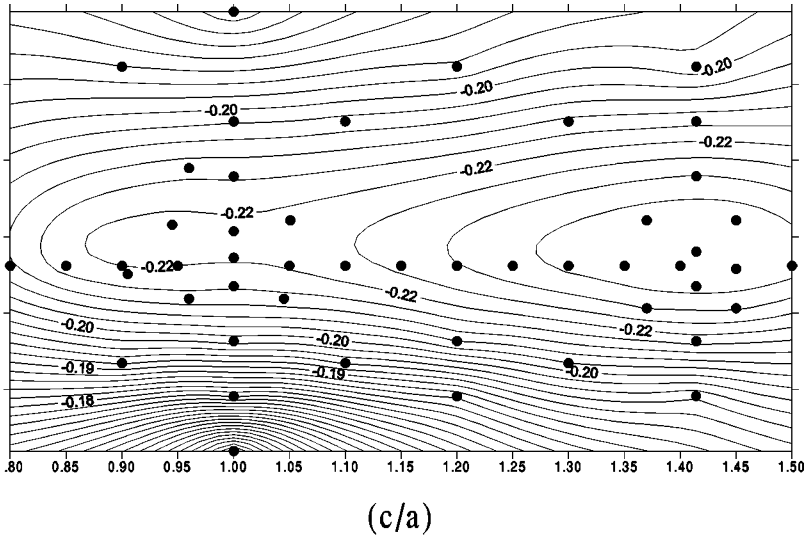

FIG. 1. Contours of constant energy (mRyd/atom) of ferromagnetic tetragonal cobalt as a function of volume and c/a ratio. Dots indicate geometries at which electronic structure calculations were performed. All energies are offset by 2782 mRyd.

II. BULK RESULTS

The tetragonal and trigonal crystal structures are ideal for investigating the bulk properties of materials. They each contain, as special cases, both the face-centered and body-centered cubic structures. By performing total-energy calculations for a variety of configurations under each of these crystal structures one can extract a great deal of information about the bulk material. In the case of cobalt, it is also important to look at the hexagonal close-packed structure since this is the stable structure found for bulk cobalt around room temperature.

Tetragonal and trigonal crystals allow two degrees of variational freedom. Tetragonal structures vary in overall unit-cell volume (as can the bcc and fcc structures) but also in the ratio (c/a) of the length of its two unit vectors. At particular ratios the tetragonal structure becomes identical to the bcc or fcc structure. In Fig. 1 we show the points (in a space defined by the unit-cell volume and c/a) at which electronic structure calculations were performed for tetragonal structures. At each of these points total energy and magnetic moments for ferromagnetic bulk cobalt were obtained. A standard mathematical technique (Kriging) was used to interpolate contours of constant energy from the energy values at the calculated points. These contours provide only a rough guide to the true energy surface for the complete range of tetragonal structures. Calculational points were concentrated in areas of particular interest. More points would be needed in outlying areas if a more precise map of the entire energy surface were required. Of particular note is the minima that occurs at the c/a ratio corresponding to an fcc structure. Figure 2 shows corresponding contours of constant magnetic moment extrapolated from the structures where calculations were performed.

Similarly, Fig. 3 shows the calculated points and interpolated constant-energy contours for ferromagnetic bulk cobalt in the trigonal structure. Trigonal structures can be defined in terms of three equal-length vectors and the equal angle between then, with a single atom at the origin and terminus of each vector. The length and angle can be cast in terms of a unit-cell volume and a ratio of lengths (c/a), where c is the length of one of the unit vectors and a is such that the bcc and fcc structures have c/a ratios of 0.5 and 2.0, respectively. Note that for clarity we present the data as a function of the logarithm of c/a. Again, a minima near the c/a values corresponding to the fcc structure is prominent in the contour plot. In addition we see a second minima corresponding to the bcc structure. Finally, Fig. 4 shows the contours of constant magnetic moment for this range of trigonal structures.

These data combined with similar calculations for ferromagnetic bulk hcp cobalt over a range of volumes allow us

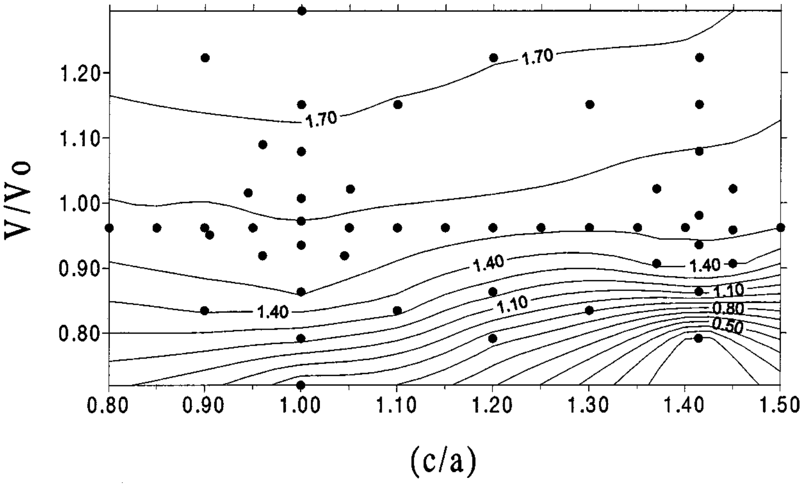

FIG. 2. Contours of constant magnetic moment (μB/atom) of ferromagnetic tetragonal cobalt as a function of volume and c/a ratio. Dots indicate geometries at which electronic structure calculations were performed.

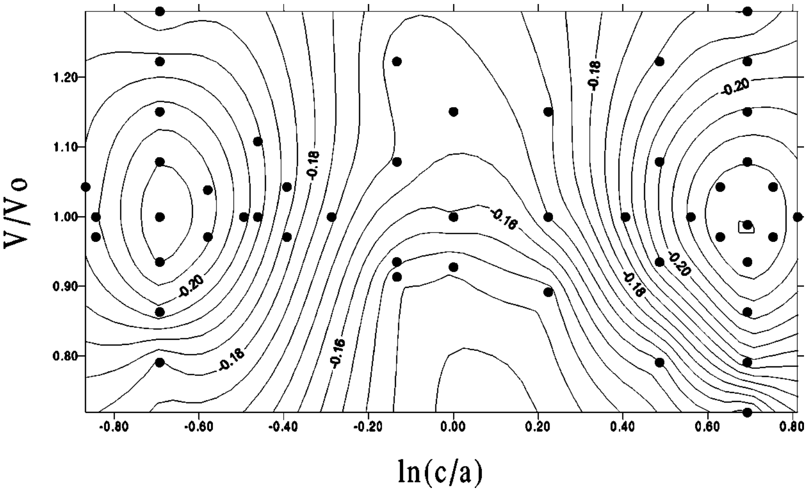

FIG. 3. Contours of constant energy (mRyd/atom) of ferromagnetic trigonal cobalt as a function of volume and c/a ratio. Dots indicate geometries at which electronic structure calculations were performed. All energies are offset by 2782 mRyd.

to predict the range of properties for bulk ferromagnetic cobalt in bcc, fcc, and hcp structures (Table I). As we did with similar calculations for ferromagnetic iron,[6] we arrive at these numbers by combining results from a number of different fits to our data. Ideally, we would perform a number of calculations at points near enough to the local energy minima to map out the region over which the energy varies in a largely quadratic fashion. The energy variation in this region, however, is smaller than the accuracy of this calculational technique. Hence, to obtain a meaningful range of energy variations we are forced to look at crystal structures outside the region where the total energy can be modeled quadratically. Therefore, we performed fits with quadratic models in three dimensions (volume, c/a, energy) and with various models in two dimensions (volume and energy with c/a fixed at the ideal bcc or fcc structure). Our results in Table I represent the synthesis of all these results with the variation among fitting models giving a best guess at accuracy of the results. Also, in Table I are results from other similar calculations as well as experimental results from the corresponding physical systems. The results are largely consistent with previous results. The lattice constants are consistently a few percent lower than the corresponding experimental results, which is a recognized characteristic of this sort of local density approximation calculation. This small unit cell volume leads naturally to a value for the bulk modulus that is a few tens of percent too high. In Table II, we present further elastic constants for fcc cobalt which could be extrapolated because of the strong fcc minima that occurs in both the trigonal and tetragonal calculations.

III. BODY CENTERED CUBIC COBALT

There has been considerable discussion of the stability, or metastability, of bcc cobalt as grown in a thin-film. In several cases the growth of a stable bcc cobalt film has been reported.[7,8] Preliminary total-energy calculations similar to those performed here have pointed toward an inherent instability in such a structure.[3] In particular, those calculations indicated that no significant energy barrier existed for a distortion along a constant volume path from a bcc to a fcc structure. We have performed a number of calculations in this region of structures and have found similar results. As is clear in comparing Figs. 1 and 3, the calculations for the bct structures lack the strong local minima near the bcc structure, which is present in the corresponding plot of trigonal structures. This lack of a strong minima points to energy instability in bcc cobalt against tetragonal distortion. If we look closer at a line of constant volume points near the bcc structure in Fig. 1 we find only a small (0.05 mRy) energy dip around $c/a = 0.92$, similar to that found previously. This slight dip (and a lack of any deeper minima) is the only noticeable feature near the bcc structure in the energy surface shown in Fig. 1. Since this shallow minimum is to the left of

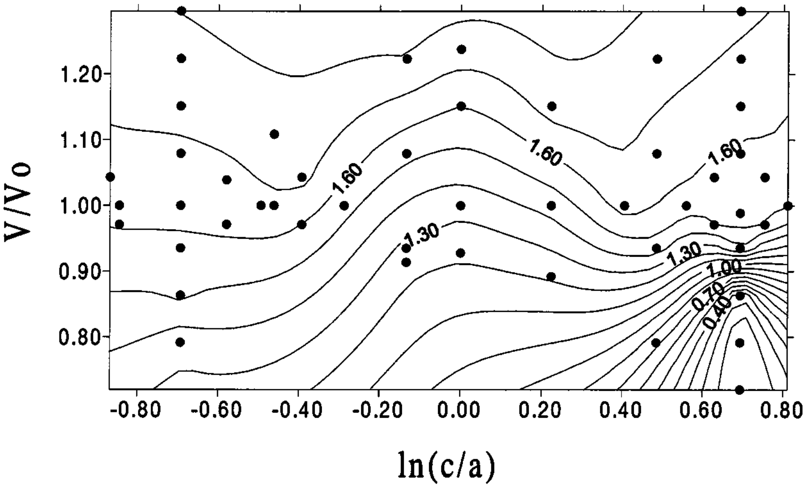

FIG. 4. Contours of constant magnetic moment (μB/atom) of ferromagnetic trigonal cobalt as a function of volume and c/a ratio. Dots indicate geometries at which electronic structure calculations were performed.

TABLE I. Properties of hcp, bcc, and fcc cobalt. Results from this study and other density-functional calculations, as well as experimental results. All elastic properties are in Mbar.

	Lattice constant (a.u.)	Moment (μB)	Bulk modulus
hcp			
Theory	4.59±0.1	1.45±0.1	2.70±0.15
Theory [a]	4.74	1.63	2.49
Expt. [b]	4.75	1.58	1.91
Fcc			
Theory	6.49±0.1	1.51±0.05	2.37±0.08
Theory [c]	6.68	1.64	2.35
Theory [d]	6.48		2.69
Expt.	6.69 [e]	1.61 [f]	1.98 [g]
bcc			
Theory	5.18±0.1	1.62±0.05	2.51±0.06
Theory [h]	5.32	1.73	2.45
Theory [i]	5.18		2.54
Expt.	5.33 [j]	1.53 [k]	

[a] From Ref. 9.
[b] From Ref. 10.
[c] From Ref. 9.
[d] From Ref. 3.
[e] From Ref. 11.
[f] From Ref. 12.
[g] From Ref. 13.
[h] From Ref. 9.
[i] Reference 3.
[j] Reference 8.
[k] Reference 7.

the bcc line, it follows that there is a saddle point in the total energy surface at a bcc structure. Symmetry dictates that the total energy at constant volume as a function of c/a has to be an extremum for both fcc and bcc. Because we have a saddle point for the bcc structure there is no extremal point in between fcc and bcc. The instability of the bcc structure has been analyzed in terms of features in the density of states before.[3]

When we attempt to fit a quadratic to this region in order to extract the elastic constants we get results that (not surprisingly) are very sensitive to the particular points chosen for the fit. Of particular note we see that the values for c_{11} range from 3.0 to 1.9, while the values of c_{12} range from 2.0 to 2.8. Since $c_{11}-c_{12}>0$ is one condition for elastic stability these numbers would indicate, and reinforce what it already obvious from the graphs, that there isn't a strongly stable structure in this region.

TABLE II. Elastic properties off fcc cobalt.

	c_{11}	c_{12}	c_{44}
Theory	4.9±1.0	1.1±0.4	1.7±0.5
Expt. [a]	2.23	1.86	1.1

[a] From Ref. 13.

In contrast, it is clear from Fig. 2 that with respect to a strain via a trigonal distortion bcc cobalt is energetically stable. This indicates that it should be possible to grow bcc cobalt on a 111 surface of an appropriate substrate.

IV. CONCLUSIONS

In this paper, we looked at cobalt in a range of tetragonal, trigonal, and hcp crystal structures. The general crystal properties extracted from our calculations are in agreement with previous experiment and calculations. In addition a close look at the stability of bcc cobalt show that such a structure is unstable with respect to tetragonal distortions toward an fcc structure. This also is in agreement with previous theoretical studies and leaves open the question of the nature of previously report cobalt films that appear to have been grown in a stable (or metastable) bcc structure.

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