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Elastic instability of bcc cobalt

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General-potential linearized-augmented-plane-wave calculations of the elastic properties of body-centered cubic Co are presented. The bcc structural phase of Co, which is not found in nature, is calculated to be unstable with respect to a volume-conserving tetragonal distortion. The total energy of body-centered tetragonal Co decreases monotonically as the c/a ratio is varied from 1, which corresponds to the bcc structure, to $\sqrt{2}$, which corresponds to the face-centered-cubic structure. This means that bcc Co is not a true metastable phase of bulk Co and suggests that the existing samples of bcc Co that have been grown in the laboratory are stabilized by interactions with the substrate and/or defects.

I. INTRODUCTION

At room temperature Co is found in the hexagonal close-packed structure, and above 700 K it undergoes a Martensitic transformation into the face-centered-cubic structure. Prinz[1] has demonstrated that it is possible to synthesize in the laboratory the body-centered-cubic phase of Co, which is not found in nature. Noting that an extrapolation of data for $B2$ $Fe_{1-x}Co_x$ alloys to $x = 1$ yields a lattice parameter for a postulated bcc phase of Co that is nearly equal to half the GaAs lattice parameter, Prinz grew metallic Co films on GaAs substrates using molecular-beam epitaxy (MBE). Structure-determination studies on the thickest single-crystal sample (357 Å) grown in this manner indicate a bcc structure.[1–3] The existence of such a thick sample has been taken as evidence that bcc Co is a true metastable phase of bulk Co rather than a forced structure stabilized by the interaction with the substrate.[1,3] However, it should be noted that despite repeated efforts to synthesize thicker samples, the 357-Å film reported in Ref. 1 remains the thickest bcc Co film grown. In attempts to fabricate thick Co films using MBE, the bcc structure usually collapses around 50 Å, and hexagonal diffraction peaks appear.[2] The reason for the difficulty in growing thick samples remains an open question.

The synthesis of bcc Co films in the laboratory has motivated several theoretical studies of the various structural phases of Co. Total-energy calculations have found that all three structural phases of Co lie close in energy, and that near the equilibrium volume the ferromagnetic state is the most stable in each case.[4,5] Like hcp and fcc Co, bcc Co is calculated to be a strong magnet, and local-spin-density-approximation (LSDA) calculations yield magnetic moments in the range of (1.6–1.7)μ_B for all three phases.[4–7] For fcc and hcp Co, the calculated moments are in good agreement with the measured values, but various measurements[1,2,8,9] of the moment in bcc Co yield significantly smaller values. It has been suggested that the discrepancy between the measured and calculated moments may be due to imperfections in the Co films.[4]

The existence of a critical thickness beyond which it becomes difficult to grow bcc Co films, together with the suggestion that defects are responsible for the reduced moment measured in existing samples, suggests that pure bcc Co may not be a true metastable phase of bulk Co. In this work, we investigate the elastic properties of bcc Co to see whether the bcc phase lies at a local minimum on the total-energy surface. The general-potential linearized-augmented-plane-wave (LAPW) method is used to calculate the total energy of bcc Co as a function of various strains. We find that bcc Co is elastically unstable with respect to the Bain strain,[10] which is a volume-conserving tetragonal distortion that continuously transforms the bcc structure into the fcc structure. Thus bulk bcc Co is not properly termed metastable. It is likely that the presence of the GaAs substrate is important for stabilizing many of the bcc Co films that have been synthesized. For the thicker samples, however, it is unlikely that the interfacial energy gained by forcing registry with the substrate is sufficient to overcome the bulk energy costs of maintaining the bcc structure. This suggests that impurities or structural defects in these films may play a role not only in suppressing the magnetic moment, as has been suggested previously,[4] but also in stabilizing the bcc structure.

II. METHOD

The general potential LAPW method has been described in detail elsewhere,[11] and so only the details particular to this work are given here. The core states are fully relativistic, while the valence states are treated scalar relativistically. The exchange correlation interaction is represented by the von Barth–Hedin function parametrized to reproduce the Hedin-Lundqvist function for non-spin-polarized systems.[12] A sphere radius of $R = 2.15$ a.u. is used for Co, and the wave-vector cutoff for the basis functions is given by $K = 9.5/R$. This leads to a highly converged set of approximately 120 LAPW basis functions per atom. Local orbitals are used to remove any linearization errors that may be associated with the d bands.[13]

A cubic crystal has three independent elastic moduli. These can be taken to be the bulk modulus (B) and two shear moduli ($C_{11} - C_{12}$, C_{44}). The condition for elastic stability is that B, $C_{11} - C_{12}$, and C_{44} are greater than zero. As discussed in Ref. 14, the bulk modulus is determined by calculating the total energy as a function of hydrostatic strain, and the shear moduli are determined by calculating the total energy as a function of volume-conserving strains that break the cubic symmetry. For example, to calculate $C_{11} - C_{12}$, we apply a tetragonal strain that transforms the lattice vectors according to

$$\overleftrightarrow{a}' = \begin{pmatrix} 1+e_1 & 0 & 0 \\ 0 & 1+e_1 & 0 \\ 0 & 0 & \frac{1}{(1+e_1)^2} \end{pmatrix} \overleftrightarrow{a}, \qquad (1)$$

where $\overleftrightarrow{a}'$ and $\overleftrightarrow{a}$ are the new and old lattice vectors, respectively. The associated energy change per cell is given by

$$\Delta E = 3V(C_{11} - C_{12})e_1^2 + O(e_1^3), \qquad (2)$$

where V is the cell volume. Similarly, to calculate C_{44}, a volume-conserving monoclinic strain given by

$$\overleftrightarrow{a}' = \begin{pmatrix} 1 & \frac{1}{2}e_6 & 0 \\ \frac{1}{2}e_6 & 1 & 0 \\ 0 & 0 & \frac{4}{(4-e_6^2)} \end{pmatrix} \overleftrightarrow{a} \qquad (3)$$

is applied. In this case, the energy change is even in the strain parameter and is given by

$$\Delta E = \tfrac{1}{2}VC_{44}e_6^2 + O(e_6^4). \qquad (4)$$

To ensure consistency, energy differences are taken with respect to the total energy of the unstrained lattice calculated with the reduced symmetry of the strained cells.

Sampling grids of 240 and 408 special k points[15] in the irreducible wedge of the Brillouin zone are used for the bcc and fcc structures, respectively. Equivalent grids of 344 (tetragonal) and 612 (monoclinic) points are used for the strained bcc lattices. We have also carried out calculations using denser k-point meshes for several tetragonally strained structures. When the number of points is increased from 344 to 635, the energy differences between the strained and unstrained structures change by less than 0.1 mRy. Hence our results for the total energy as a function of strain are well converged with respect to k-point sampling.

III. RESULTS AND DISCUSSION

We start by comparing the static structural properties of ferromagnetic bcc and fcc Co (Table I). The equilibrium volume of fcc Co is approximately 2% smaller than that of bcc Co, and the bulk moduli of the two phases are similar. Compared to the experimental values, the calculated lattice constants are approximately 2.8% too small, which is typical for general potential LSDA calculations for $3d$ transition-metal systems.[16,17] The underestimation of the lattice constants indicates that the elastic moduli calculated in this work are probably overestimates. As expected, fcc Co is found to be more stable than bcc Co, with an energy difference between the phases of 8.9 mRy/atom. Furthermore, we find that the hcp phase lies at least 2 mRy/atom lower in energy than the fcc phase.[18] While earlier calculations that employed various spherical approximations to the potential found the same ordering of the phases, the energy range spanned by the phases was calculated to be significantly smaller than what is found in the present general potential calculation. For example, a linearized muffin-tin orbital (LMTO) calculation found all three phases to lie within an energy range of 3 mRy, with a bcc-fcc difference of only 1 mRy,[5] while an augmented spherical wave (ASW) calculation for the cubic phases yielded a bcc-fcc energy difference of about 5 mRy.[4]

When the cubic symmetry of bcc Co is broken by the volume-conserving monoclinic distortion described by Eq. (3), the total energy of the system increases. A fit to Eq. (4) of the total energy as a function of the monoclinic strain in the range of $0.0 \leq e_6 \leq 0.08$ yields a shear modulus of $C_{44} = 152$ GPa. This is similar to the corresponding values calculated for bcc Fe and $B2$ FeCo.[17] In contrast, as shown in Fig. 1, bcc Co sits at a maximum in energy as a function of tetragonal strain.

TABLE I. Structural properties of bcc and fcc Co. Here a is the lattice constant in Å, B is the bulk modulus in GPa, and $E_{\text{bcc}} - E_{\text{fcc}}$ is the difference in total energy between the two phases in mRy/atom.

		bcc		fcc		
		a	B	a	B	$E_{\text{bcc}} - E_{\text{fcc}}$
Calc.	LAPW[a]	2.74	254	3.43	269	8.9
	LMTO[b]	2.82	245	3.53	235	1
	ASW[c]	2.80		3.50		5
Expt.		2.82[d]		3.54[e]		

[a] This work.

[b] Reference 5.

[c] Reference 4.

[d] Reference 3, grown on a GaAs (110) substrate.

[e] J. Donohue, *The Structures of the Elements* (Wiley, New York, 1974).

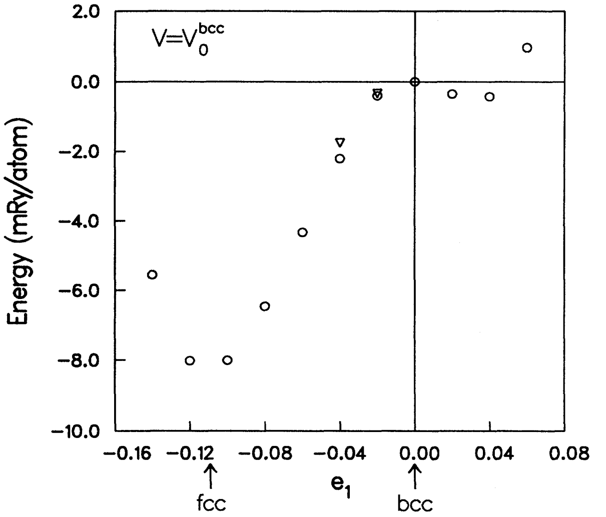

FIG. 1. Total energy vs tetragonal strain for bcc Co. The volume is fixed at the calculated equilibrium value for bcc Co, and the energies are measured with respect to the total energy of bcc Co. The circles are calculated energies for pure Co, while the triangles are calculated energies for Co_7As supercells.

As may be expected, the energy is not symmetric about the unstrained structure, and local minima are found at strains of approximately $e_1 = -0.11$ and 0.03. A fit of the total energy near $e_1 = 0$ to the functional form of Eq. (2) yields $C_{11} - C_{12} = -73$ GPa. This instability of bcc Co with respect to tetragonal distortions is found not only at the calculated equilibrium bcc volume, but also at the calculated fcc equilibrium volume, and at the measured bcc volume as well.

The deeper of the two local minima seen in Fig. 1 coincides with the fcc structure. This can be seen as follows: A bcc lattice that has been tetragonally strained according to Eq. (1) can be described as a body-centered-tetragonal lattice with $c/a = (1+e_1)^{-3}$. When $c/a = \sqrt{2}$, the separation between atoms along the [110] direction is equal to that along the [001] direction. This corresponds to an fcc lattice, where the fcc [100] axis is parallel to the bct [110] direction.[10] Hence the monotonic decrease in total energy from the local maximum at $e_1 = 0$ to the minimum at $e_1 \approx -0.11$ indicates that bcc Co is elastically unstable with respect to a continuous homogeneous transformation to the fcc phase.

Although the other local minimum at $e_1 \approx 0.03$ does not coincide with a high-symmetry structure, we note that it is possible to continuously transform the bcc lattice into the hcp lattice if the tetragonal strain is combined with additional degrees of freedom. For example, one path that relates the two structures involves a tetragonal strain that compresses the bct cell along the [001] direction until $c/a = \sqrt{2/3}$, coupled with a shear of the bct (110) planes.[19] Since the shallow minimum at $e_1 \approx 0.03$ corresponds to a bct lattice in which c/a is about 0.91, we speculate that if additional degrees of freedom are allowed, there may be an unstable strain from bcc to hcp Co as well.

One factor that contributes to the instability of bcc Co is its high electronic density of states (DOS) at the Fermi level (E_f). The DOS as a function of energy for bcc Co is plotted in Fig. 2(a). Because the majority-spin d states are fully occupied in bcc Co, we concentrate on the minority-spin DOS. In the minority-spin DOS, the Fermi level lies on the side of a broad peak composed primarily of d states with t_{2g} character. As shown in Fig. 2(b), the DOS is relatively insensitive to the application of a monoclinic distortion. On the other hand, the tetragonal distortion leads to significant changes in the DOS [Figs. 2(c) and 2(d)]. As the structure is distorted away from bcc towards fcc, the t_{2g} peak near E_f in the minority-spin DOS broadens and flattens. The result is a decrease in the DOS at E_f, which helps to destabilize the bcc structure with respect to the tetragonal distortion.

It is interesting to compare these results to a similar investigation of Fe.[20] In the case of ferromagnetic bct Fe, LSDA calculations yield local minima as a function of tetragonal strain at both the fcc and bcc structures. While the overall shape of the minority-spin DOS is similar in bcc Fe and bcc Co, the difference in the number of valence electrons causes the Fermi level in Fe to lie in the valley just below the t_{2g} peak. Hence, unlike the situation in Co, a tetragonal distortion of bcc Fe tends to increase the DOS at E_f.[21] This may account for the

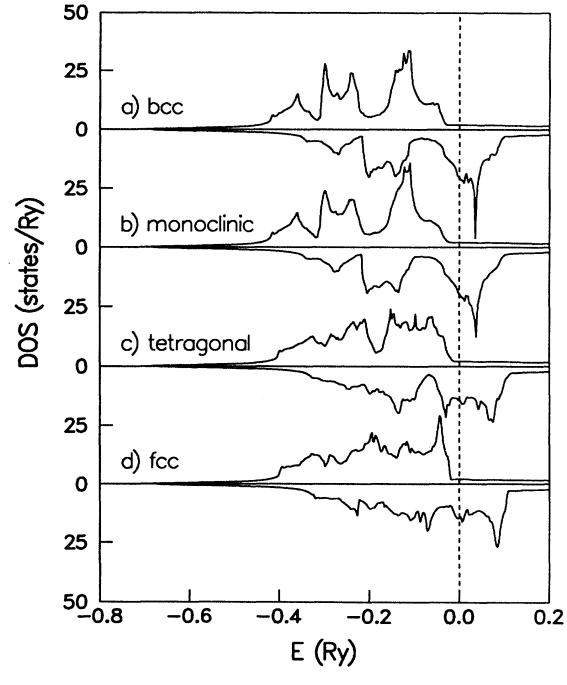

FIG. 2. Electronic density of states (DOS) calculated for (a) bcc Co, (b) monoclinically strained bcc Co ($e_6 = 0.06$), (c) tetragonally strained bcc Co ($e_1 = -0.06$), and (d) tetragonally strained bcc Co ($e_1 = 2^{\frac{1}{6}} - 1 \approx -0.11$). As described in the text, the last structure corresponds to the fcc phase. In each panel, the upper curve represents the majority-spin states and the lower curve corresponds to the minority-spin states. Energies are measured relative to the Fermi level, which is indicated by the dashed line.

different behavior of bcc Fe and bcc Co with respect to the Bain transformation.

It should be emphasized that the predicted elastic instability of bcc Co applies to the bulk. The existing samples of bcc Co have been grown epitaxially, and at least for thin films, the substrate provides a constraint on the in-plane lattice constant. The estimated lattice mismatch between GaAs and bcc Co is only 0.2% if data for the lattice parameter of $B2$ $Fe_{1-x}Co_x$ alloys are extrapolated to $x = 1$, and so it is expected that there is very little strain in coherent bcc Co films on GaAs.[1] On the other hand, as shown in Table I, the lattice parameter of fcc Co is about 25% larger than that of bcc Co.[22] On GaAs substrates, a coherent epitaxial fcc Co lattice would be highly strained and energetically unfavorable. Therefore, we expect that for thin samples, the interfacial energy dominates and stabilizes the bcc phase. With increasing thickness, the interfacial interaction should at some point become insufficient to maintain coherency, leading to a collapse of the bcc structure.

For the most part, this picture is consistent with what is observed in attempts to grow thick bcc Co films on GaAs.[1,2] Beyond thicknesses in the range of 40–80 Å, polycrystalline samples consisting of close-packed phases usually form. Nevertheless, a few thick bcc Co films of up to 357 Å have been synthesized, and in light of the calculated elastic instability of bcc Co, it remains an open question as to why the thick samples are stable. We speculate that these films may be stabilized by defects because, in general, the thicker films have been grown with fast growth rates and under less well-controlled conditions.[23] As mentioned, the possibility of imperfect films has already been raised in connection with the anomalously low magnetic moment measured in bcc Co films.[4] It has been suggested that the 0.2–0.3 discrepancy between the measured and calculated moments in bcc Co may be due to the presence of As impurities in the films.[8] There is some experimental evidence for the migration of small amounts of As into the Co region,[24] and LSDA calculations have shown that substitutional As acts as a moderately effective poisoning agent of magnetism in bcc Co.[25]

We have performed supercell calculations to test whether As impurities might be responsible for stabilizing Co in the bcc structure. Because the atomic size of As is relatively large, it is reasonable to assume that the As impurities occupy substitutional rather than interstitial sites. An eight-atom supercell of Co_7As was used. As described in Ref. 25, the undistorted supercell has a bcc Bravais lattice, and there are no internal structural parameters to relax when the symmetry is lowered by the tetragonal distortion. As shown in Fig. 1, tetragonal strains of $e_1 = -0.02$ and -0.04 lower the total energy per atom in Co_7As by amounts similar to what is found for pure bcc Co, indicating that the presence of 12.5% substitutional As impurities is not effective in stabilizing bcc Co against the Bain distortion. Since the actual As concentration in the Co films is significantly smaller, it appears unlikely that As impurities are the stabilizing agents in the existing bcc Co samples.

IV. CONCLUSION

The elastic properties of bcc Co have been calculated using the general potential LAPW method. Rather than lying in a local minimum on the total-energy surface, which is the condition for metastability, bcc Co sits at a saddle point: It is stable against isotropic and monoclinic strains, but it is unstable with respect to the tetragonal Bain strain. This result is consistent with the observation that there is a critical thickness of several tens of Å beyond which it becomes difficult to grow bcc Co. It is likely that the interaction with the lattice-matched GaAs substrate stabilizes the bcc structure in many of the existing films. We speculate that imperfections in the samples are responsible for stabilizing the few thick films that have been synthesized. The exact nature of the imperfection remains unknown, but we have ruled out one of the more obvious candidates, namely, that of substitutional As impurities.

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[21] Unlike Co, bcc Fe does not exhibit strong magnetism, and so both the majority- and minority-spin DOS must be considered. However, our calculations indicate that the majority-spin DOS at E_f is relatively insensitive to small tetragonal distortions.

[22] Alternatively, if bct lattice vectors are used to describe the fcc lattice, the lattice vectors in the (001) plane are reduced in length from the cubic vectors by a factor of $1/\sqrt{2}$. This is about 11% smaller than the bcc Co lattice parameter.

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