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Magnetic phase transformations of face-centered cubic and hexagonal close-packed Co at zero Kelvin

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Abstract

The 0 K pressure-induced magnetic phase transformations of face-centered cubic (FCC) and hexagonal close packed (HCP) Co have been examined using first-principles calculations. Issues of fitting an equation of state to the first-principles energy versus volume data points containing a magnetic transformation and comparing to experimental phase equilibria are discussed. It is found that a fitting scheme employing only data where the magnetic moment decreases linearly with volume offers a physically meaningful behavior for the equation of state at metastable volumes. From this fitting, the ferromagnetic to nonmagnetic transformations with increasing pressure at 0 K are at 77 GPa and 123 GPa for FCC and HCP, respectively, and are first order and second order, respectively, on the basis of an unambiguous measure proposed in the paper. In addition to the HCP/FCC structure transformation at 99 GPa, another transformation at negative pressures is predicted, at −31 GPa. These results are shown to be consistent with the extrapolations of the experimental pressure–temperature phase diagram to 0 K.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

For the last 30 years, first-principles calculations based on density functional theory have revealed the behavior of Co at 0 K [1, 2]. Properties such as phase stability [3], electronic structure [4], and magnetic moment [2] have been accurately calculated as functions of volume, allowing the derivation of equations of state (EOS's) and elastic properties [5]. The choice of EOS fitting can have large effects on the resulting predictions, as shown recently for Ti [6]. However, important details regarding the EOS fitting for the magnetic states remain, particularly how to perform the fit near magnetic transformation [2]. In regards to phase stability with pressure, several investigations have reproduced the experimentally observed high pressure phase stability [2, 3], but these results have not explicitly been placed in the context of the experimental pressure–temperature (P–T) phase diagram. Since density functional theory calculations do not include thermal contributions to the free energy, such as vibrational or electronic entropy, the resulting predictions represent the 0 K phase stability of Co. If comparisons to experiments are made, it should be by extrapolating the experimental P–T diagram to 0 K. Even only at 0 K, crucial details of P–T phase diagrams can be revealed by first-principles calculations, such as metastable and magnetic phase transformations and the order of such transformations, as will be shown for Co in the present work.

Correctly predicting metastable phase transformations at 0 K is essential as they have the potential to become stable at higher temperatures (such as the Curie transformation of FCC Co) and can significantly affect the prediction of the P–T diagram, which is a key goal of first-principles calculations of the phase stability of the elements. The present paper begins by examining the order of the magnetic transformations for FCC and HCP Co from the ferromagnetic (FM) to the nonmagnetic (NM) state with an efficient application of Landau theory. Then

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the issue of fitting an EOS to the FM phases near the FM to NM transformation volume is discussed, where three fitting schemes are examined in detail. A physically meaningful EOS is necessary for the accurate prediction of the stable and metastable 0 K phase transformations, which are shown to be consistent with the experimental P–T diagram.

2. Method

FCC and HCP Co in the NM and FM states are considered in this work. First-principles calculations were performed using the Vienna *Ab initio* Simulation Package [7] (VASP). The projector augmented wave method [8] was used together with the generalized gradient approximation [9] exchange–correlation functional of Perdew *et al* [10] supplied with VASP. Calculations were performed for a series of volumes for HCP and FCC Co in the ferromagnetic and nonmagnetic states, where the atomic coordinates and lattice parameters were allowed to relax with the volumes kept fixed, followed by a final, static calculation. The results were fully converged with respect to the energy cutoff of 350 eV, the Monkhorst–Pack k-point mesh of 20 × 20 × 20 for the FCC structures, and the gamma-centered k-point mesh of 17 × 17 × 11 for the HCP structures. The total energy as a function of magnetic moment at fixed volume was calculated by stepping the total magnetic moment for the system. For EOS fitting to the energy versus volume curves, Shang *et al* [11] discussed various EOS formulae. In the present work, the four-parameter Birch–Murnaghan EOS [12] was used with its linear form [11] given by

$$E(V) = a + bV^{-2/3} + cV^{-4/3} + dV^{-2}. \qquad (1)$$

3. Results and discussion

3.1. Determining the order of magnetic transformations

The issue of whether a phase transformation is first or second order is an important one to consider in regards to 0 K phase stability as the order of the transformation will have a large impact on how it behaves with temperature. Structural transformations between HCP and FCC Co are expected to be first order since the volumes of the two states at the transformation pressures are different, as seen in the calculated pressure versus volume curves in figure 1. The high pressure transformation from HCP to FCC is experimentally observed at around 105 GPa [13], but no volume change is reported. This observation had been attributed to small energy differences between HCP and FCC and a lack of hydrostatic pressure in the sample [13].

For magnetic transformations, differences in volume are difficult to discern as the magnetic moment changes continuously with volume to varying degrees. In the case of cobalt, the magnetic moment in HCP–FM is sustained to smaller volumes and goes to zero more gradually than in FCC, as shown in figures 2 and 3, respectively. A more unambiguous measure of the order of this phase transformation is needed. In the present work, we propose to use the criterion whether the FM state maintains a magnetic moment at volumes where it

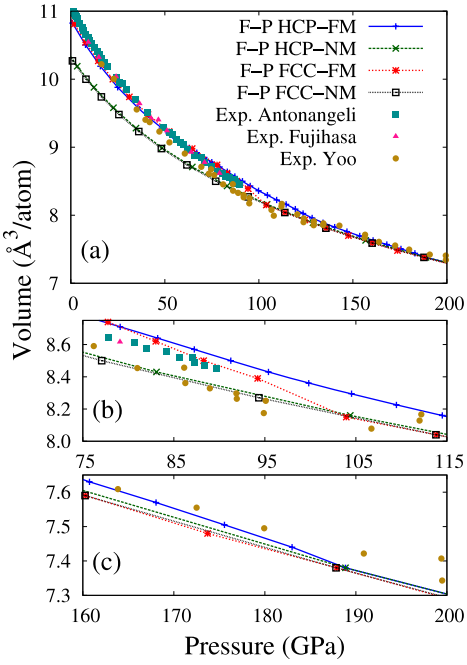

Figure 1. (a) Pressure versus volume for Co from first-principles calculations in comparison with experiments [13, 19, 20] with enlargements of the (b) FCC FM to NM and (c) HCP FM to NM transformations.

is metastable with respect to the NM state. If so, the volume will change discontinuously with pressure from FM to NM, and the transformation is first order. If the moment goes to zero at the same volume the energies become the same, the transformation is defined herein as second order since the volume changes continuously with pressure. Figures 2 and 3 illustrate this behavior for HCP and FCC Co by plotting the energy difference between the NM and FM states (the magnetic stabilization energy) [2, 14] alongside the magnetic moment of the FM state. In the case of HCP, the magnetic moment goes to zero at the same volume that the energy difference does. Therefore, the FM to NM transformation for HCP Co is second order. For FCC, the FM state is still magnetic when the energy difference is zero, so the transformation is first order. This is possible because FM continues into a metastable region where the energies are more positive than NM and still retain a magnetic moment. In fact, this would be required for any first-order magnetic transformation to occur as a consequence of Landau theory (further developed by Moruzzi) [15]. Results similar to the tops of figures 2 and 3 were published recently by Steinle-Neumann [2], but the metastable behavior of FCC–FM near the FM/NM transition volume was not reported.

The FCC–FM metastable region can be further explored by performing fixed magnetic moment calculations, predicting the energy of the system as a function of the total moment. Such calculations for a series of fixed volumes were performed for HCP and FCC cobalt, shown in figures 2 and 3, respectively. FCC Co has a local minimum near 1.1 μ_B when the volume is 8.5 Å^3, in the FM metastable region, with a NM ground state, confirming the prediction of the first-order transformation. For smaller volumes, this local minimum disappears. For larger volumes, the FM state becomes the

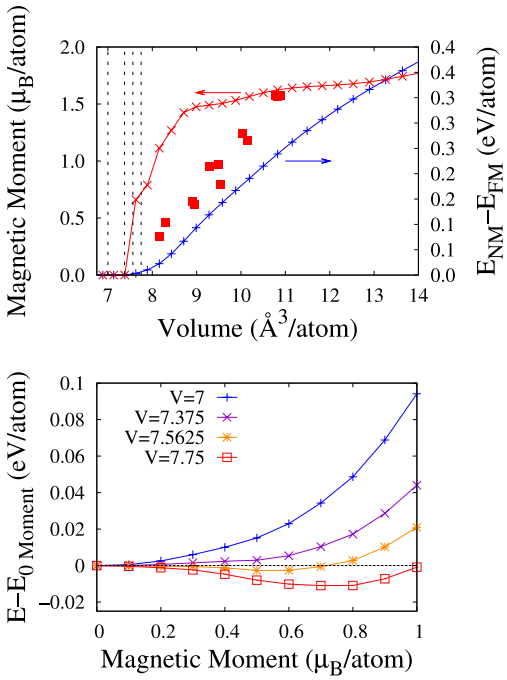

Figure 2. (Top) first-principles predictions of the magnetic moment of HCP Co plotted alongside the energy difference between the FM and NM states. The FM to NM transformation is second order for HCP Co since no metastable states are present. The dashed lines correspond to the volumes where magnetic moment calculations were performed. Filled squares refer to experimental measurements of the magnetic moment of the HCP phase at 298 K [27]. (Bottom) first-principles predictions of the energy of HCP Co as a function of magnetic moment at fixed volumes (in Å^3/atom) with respect to the energy at zero moment.

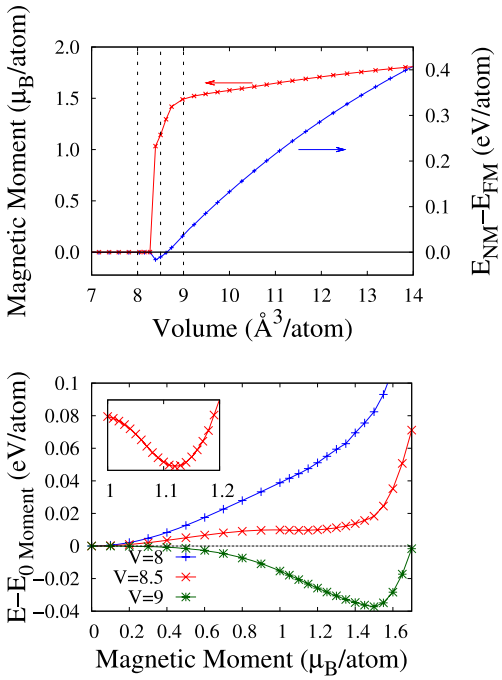

Figure 3. (Top) first-principles predictions of the magnetic moment of FCC Co plotted alongside the energy difference between the FM and NM states. The FM to NM transformation for FCC Co is first order since metastable FM states are present. The dashed lines correspond to the volumes where magnetic moment calculations were performed. (Bottom) first-principles predictions of the energy of FCC Co as a function of magnetic moment at fixed volumes (in Å^3/atom) with respect to the energy at zero moment. The inset shows the local FM minimum at $V = 8.5$ Å^3.

ground state and NM becomes unstable. HCP Co does not exhibit a FM local minimum, as FM becomes the ground state simultaneously as the minimum in the energy appears, confirming the prediction of the second-order transformation. The fixed moment method to determining the order of magnetic transformations is consistent with the E–V curve method from the previous paragraph. The latter is more efficient in practice since no calculations beyond the E–V curves are required and is thus used in the present work. It can also be readily applied to antiferromagnetic states.

3.2. Equation of state fitting

The stability of the FM and NM states of HCP and FCC Co as a function of volume are examined by calculating the energy versus volume (E–V) curves for FM and NM HCP and FCC Co, which are shown in figure 4. EOS's (EOS) must be fitted to these curves to determine the pressure dependence of their properties, including transformation pressures. Uncertainty is introduced into an EOS when a magnetic transformation takes place within the volume range of the E–V curve since two or more distinct magnetic states are present, such as the transformation from FM to NM with decreasing volume.

Three approaches to fitting an EOS to an E–V curve with magnetic transformations are examined. The first is to include all of the calculated values on either side of the

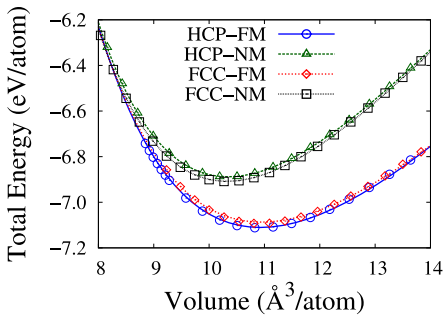

Figure 4. Energy versus volume curves for Co from first-principles calculations (points) and fitted EOS's (lines).

transformation (FM-All). However, this scheme would be inappropriate since there is a discontinuous behavior in the energy versus volume at the transformation pressure. The second is to include only data that retain a magnetic moment (FM-Mag). For large volumes, the moment (M) is fairly linear with V, with $\mathrm{d}M/\mathrm{d}V \sim 0.1\ \mu_B$ Å^{-3} for HCP and FCC Co. At smaller volumes, $\mathrm{d}M/\mathrm{d}V$ increases by an order of magnitude and changes greatly with volume, which is predicted to occur by about 9 Å^3 for both HCP–FM and FCC–FM (about 70 and 65 GPa, respectively), as seen in figures 2 and 3. The significant variability in $\mathrm{d}M/\mathrm{d}V$ has been thought to be indicative of mixing between NM and FM magnetic states [16, 17]. Indeed, this change in slope has

Table 1. EOS's for the phases of Co, comparing the current 0 K first-principles calculations employing different fitting schemes for the FM state. Experimental data at room temperature and previous calculations in the literature are provided for comparison.

Structure	Method	V_0 (Å^3/atom)	B (GPa)	B′ (GPa)	Source
HCP	Exp	11.00	199	3.6	[13]
HCP	Exp	11.10	199	3.6	[20]
HCP	Exp	11.07	203	3.6	[19]
HCP–FM-All	FP	10.93	206	4.3	Current work
HCP–FM-Mag	FP	10.92	206	4.4	Current work
HCP–FM-Linear	FP	10.88	210	4.8	Current work
HCP–FM	FP	10.90	210	4.1	[2]
HCP–NM	FP	10.35	248	4.8	Current work
HCP–NM	FP	10.31	256	4.7	[2]
FCC	Exp	10.33	224	5.8	[13]
FCC–FM-All	FP	10.95	197	4.4	Current work
FCC–FM-Mag	FP	10.93	205	4.8	Current work
FCC–FM-Linear	FP	10.92	206	4.8	Current work
FCC–FM	FP	10.95	198	4.3	[2]
FCC–NM	FP	10.32	249	4.8	Current work
FCC–NM	FP	10.28	258	4.7	[2]

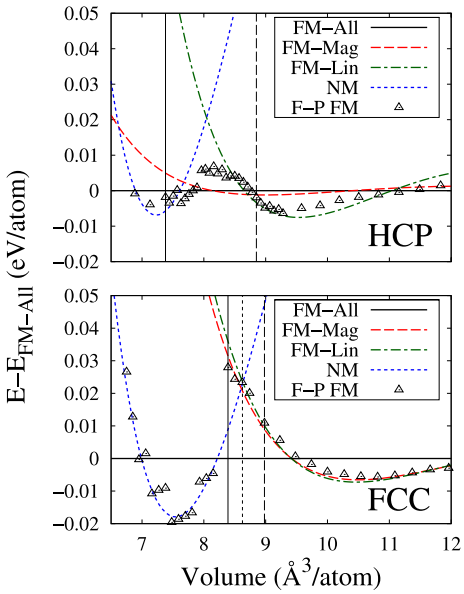

Figure 5. Comparison of the E–V curves of FM Co for three EOS fitting schemes. The EOS scheme including all the volumes in the fitting (FM-All) is taken as the reference state. Empty triangles refer to first-principles calculations. The solid vertical line represents the smallest volume where a magnetic moment is predicted by first-principles, the dashed vertical line is the smallest volume where a linear magnetic behavior is predicted, and the dotted line is the first-order FCC transition volume shown in figure 3.

been linked to a measured phonon anomaly in HCP Co at finite temperatures [3, 18]. The third scheme, therefore, is to include only those volumes where the magnetic moment is not only nonzero but also linearly or near linearly decreasing with volume (FM-Linear). This approach is similar to a recent method to fit the FM EOS for Co by including a 'magnetic pressure' into the NM EOS based on a linear fit to the magnetization energy [2].

A comparison of the fitting schemes with experiments [13, 19, 20] and recent calculations [2] is given in table 1, where the results are comparable to previous work, for both FM and NM calculations. Furthermore, only small differences are observed between the different fitting schemes. Besides the fitting parameters themselves, there are two other important properties of the fitted EOS to consider when judging the quality of the fitting, particularly for use in predicting stability and transition pressures. The first is the accuracy of the EOS in reproducing the calculated energies. The second is the stability of the extrapolated curve into smaller volumes, specifically if the EOS erroneously predicts that the FM state becomes stable again at very small volumes.

As shown in figure 5, the FM-All scheme, in both FCC and HCP, attempts to describe two phases, NM at small volumes and FM at larger volumes, thereby failing to reproduce either near the FM–NM transformation volume. This scheme also predicts that FM is more stable than NM at smaller volumes where NM should be stable. For this reason, this approach is not suitable.

For FCC Co, the FM-Mag and FM-Linear schemes are able to reproduce the E–V curve of the magnetic states while also remaining metastable below the transformation volume. Since the FM to NM transformation for FCC is first order, a pronounced kink is present in the E–V curve at the transformation volume, allowing a clear fitting of the magnetic states. The FM-All scheme fails to reproduce the magnetic transition volume, described in section 3.1, whereas the FM-Mag and FM-Linear schemes show good agreement, as shown in figure 5. Since the FM to NM transformation is second order for HCP, the fitting region for the FM state is less obvious because it transitions into the NM state more smoothly. The FM-Mag and FM-Linear schemes, therefore, produce quite different results. Although the FM-Mag scheme reproduces more accurately the first-principles data near the transformation volume, the FM-Linear scheme is more accurate for where there is a linear change to the magnetic moment. Furthermore, the FM-Mag fitting predicts that the FM state becomes stable again at smaller volumes, whereas the FM state in the FM-Linear scheme remains metastable. These results suggest that the FM-Linear approach offers the more physical results of the three fitting schemes for HCP and FCC Co. For the remainder of the discussion the FM-Linear fitting approach is employed.

3.3. Predicted 0 K phase transformations

With the EOS's thus obtained, the Gibbs energy versus pressure can be plotted for the different states by using the following relations, noting that the Gibbs energy at 0 K is equivalent to the enthalpy: $H = E + PV$ where $P = -\mathrm{d}E/\mathrm{d}V$. The Gibbs energies for HCP and FCC–FM and NM Co as a function of pressure are given in figure 6 with HCP–FM taken as the reference state. From this plot, the transformation pressures between two phases are simply the intersections of their Gibbs energy curves. Five such transformations are predicted and are summarized in table 2.

Two of the predicted phase transformations are stable structural transformations and would be observed at 0 K as

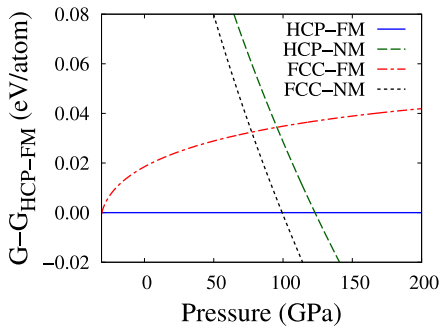

Figure 6. Gibbs energy versus pressure for different Co phases with HCP–FM as the reference state. HCP–FM is the most stable phase up to 105 GPa, at which point FCC–NM becomes stable.

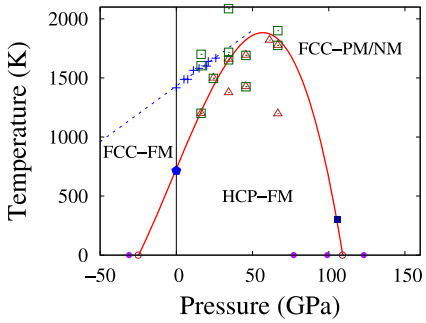

Figure 7. Co pressure–temperature phase diagram with extrapolation to 0 K (○). Experimental data for the FCC Curie transformation (+) [21], where HCP (△) and FCC (□) were observed [22], the zero pressure FCC to HCP transformation temperature (⬟) [31], and the room temperature FCC to HCP transformation (■) pressure [13] are included. The dashed line is the second-order FCC–FM to FCC-PM/NM Curie transformation and the solid line is the first-order FCC–FM to HCP–FM structural transformation, fitted to the experimental data. The 0 K transformation pressures from first-principles (●) are also shown.

Table 2. Pressures of Co phase transformations predicted from current first-principles calculations (employing the FM-Linear fitting scheme) and extrapolation of the experimental phase diagram [13] to 0 K (see figure 7).

Transformation	Source	Pressure (GPa)
Stable		
FCC–FM–HCP–FM	FP	−31
	Exp (0 K extrap)	∼−25
HCP–FM–FCC–NM	FP	99
	Exp (0 K extrap)	∼109
Metastable		
FCC–FM–FCC–NM	FP	77
HCP–FM–HCP–NM	FP	123

they have the lowest energies at the given pressure, namely the transitions between HCP–FM and FCC–NM at 99 GPa and between FCC–FM and HCP–FM at −31 GPa. These two predictions are in qualitative physical agreement with linear extrapolations of the experimental Co P–T phase diagram [13, 21, 22] to 0 K, shown in figure 7, where the parabolic shape of the FCC–HCP transformation curve suggests both a high pressure transformation and a negative pressure transformation. The first-principles predicted 0 K high pressure transformation is also consistent with suspicions that the high pressure phase of FCC is NM [13] and suggests that the slope of this phase boundary in the P–T phase diagram must be very steep as the 99 GPa transformation pressure remains almost unchanged from 0 K to room temperature [13], when defined as the onset of the observed experimental FCC/HCP metastable coexistence region. Concerning the negative pressure prediction, such conditions have been produced experimentally in solids and liquids, albeit of a smaller magnitude than discussed here, and are thought to offer new opportunities in materials engineering [23–26]. However, very large values of negative pressure may no longer be physical. This may be the case for the extrapolation of the experimental FCC Curie transformation data to ∼−150 GPa, which is much less than the minimum pressure suggested by the linear regime of the E–V curves at large volumes (−31 GPa for FCC).

Two other predicted phase transformations are the metastable magnetic transformations from FM to NM for FCC and HCP at 77 and 123 GPa, respectively. These predictions are consistent with experimental observations that HCP phase retains a magnetic moment up to the structural transformation of 105 GPa at room temperature [13] and the FM to NM transformation in HCP Co is estimated to be 150 GPa from the experimental slope of magnetic moment with pressure at room temperature [27]. Furthermore, measurements indicate the high pressure FCC phase to be NM [13], consistent with the current prediction that the moment goes to zero at lower pressures than the FCC to HCP transformation pressure.

The only experimentally observed magnetic transformation in Co is the Curie transformation between the FCC–FM and paramagnetic (PM) states, at 1400 K at zero pressure, which increases and then flattens with pressure [21, 22]. In general, as a Curie transformation nears 0 K, it is manifested as a phenomenon known as a quantum phase transition, where the thermally excited magnetic states dwindle and spin fluctuations due to Heisenberg uncertainty dominate [28]. Since the pressure range of the phenomenon is typically fairly small, 15 GPa for iron [29] and less than 10 GPa for several compounds [30], the FCC Co Curie transformation pressure at 0 K is approximated by the calculated FM/NM transformation pressure at 77 GPa.

The experimental P–T diagram confines the 0 K FCC Co Curie transformation pressure to be between the highest pressure it is observed, 70 GPa [21], and the room temperature HCP to FCC transformation pressure where NM is observed, 105 GPa [13], consistent with the current prediction of 77 GPa from FM to NM. Therefore, a sharp drop in the Curie transformation is expected from high temperatures at 70 GPa to close to 0 K by 77 GPa. Indeed, a quantum phase transition has been theorized to be present near the HCP–FM to FCC–NM transformation [18]. A similar deduction can be made for HCP. Since no magnetic transformation is observed for HCP up to the HCP–FCC transition pressure [27], the 0 K FM to NM transformation pressure (and that for any possible quantum phase transition) must be higher than 99 GPa, which is consistent with the predicted value of 139 GPa.

The last phase transformation predicted from figure 6 is between FCC–FM and HCP–NM at 96 GPa. Since FCC–FM has already become NM by this pressure, this prediction is likely an artifact of extrapolating the EOS of FCC–FM into volumes where it has already become NM.

4. Summary

The 0 K stable and metastable phase stability of Co is predicted by first-principles calculations. Various EOS fitting schemes were tested to determine which best reproduced the behavior the FM states both near the transformation volume and smaller volumes where FM is metastable. It was found that the best scheme is to include only volumes in the EOS fitting where the magnetic moment decreases with volume with near constant slope. The metastable phase transformations from FM to NM for FCC and HCP are predicted to be at 77 GPa and 123 GPa, respectively, using this scheme. By analyzing how the magnetic moment compares to the energy difference between the NM and FM states, the FM to NM transition at 0 K is predicted to be first order for FCC and second order for HCP. These results, and those for the structural transformations at −31 and 99 GPa, are consistent with the experimental P–T phase diagram.

Acknowledgments

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