Ab initio total-energy and phonon calculations of Co at high pressures

P. Modak,[1] A. K. Verma,[1] R. S. Rao,[1] B. K. Godwal,[2] and R. Jeanloz[2]
[1]*High Pressure Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400085, India*
[2]*Department of Earth and Planetary Science, University of California, Berkeley, Berkeley, California 94720-4767, USA*
(Received 4 January 2006; revised manuscript received 22 March 2006; published 17 July 2006)

We present results of *ab initio* calculations on the high pressure phonon, magnetic anomalies, and structural instability in cobalt. Our calculations reproduce the magnetic collapse starting near 100 GPa and the hcp to fcc phase transition around this compression, agreeing with earlier calculations and with the experimental data. Our studies show anomaly in the E_{2g} mode phonon frequency variation near 75 GPa pressure, consistent with the measurements. We have demonstrated that phonon and magnetic anomalies are interrelated in cobalt and hence, the magnetoelastic coupling should be stronger in Co than in iron, which also undergoes a high pressure bcc to hcp transition with magnetic collapse but without showing any associated anomaly in the phonon frequency variation under compression.

DOI: 10.1103/PhysRevB.74.012103 PACS number(s): 64.70.Kb, 71.10.−w, 62.30.+d, 75.10.Lp

I. INTRODUCTION

The study of 3*d* magnetic metals under pressure is useful for a better understanding of the composition and structure of the Earth's interior. Among these elements Fe is the most widely studied both by experiments and theory, as it is the major constituent of the Earth's core. Comparatively, cobalt is less studied, although its study at Mbar pressures is crucial for the systematic understanding of the magnetic 3*d* elements, being at the center of the 3*d* transition metal series. Furthermore, studies on the phase diagram of Co can help in providing a better understanding of Fe, as both are magnetic at ambient pressure and transform to a nonmagnetic phase under high pressure.

Under ambient conditions Co crystallizes in the hexagonal-close-packed (hcp) structure (ε phase). A face-centered-cubic (fcc) structure (γ phase) becomes stable above 420 °C and can be quenched to room temperature as a metastable phase. With an increase of temperature it makes an isostructural transition to a paramagnetic phase with Curie temperature of 1400 K. The ε-Co phase is stable over a wide range of pressure at room temperature, but it transforms to the fcc phase (β) in the pressure range of 105–150 GPa.[1] This phase transition occurs due to the well-known collapse of the magnetic moment in transition metals and their compounds under high pressure.[2] A similar transition was also observed in iron at 10 GPa pressure.[3] The magnetic properties of these 3d transition metals are largely determined by the well-localized 3d orbitals. The crystal field in these metals together with interaction effects split the 3d band into a nearly filled majority band and a partially filled minority band. The filling factor of the minority 3d bands determines the structural and elastic properties of these metals.[4] As per the Stoner model, a magnetic state is stable if $IN(E_F) > 1$, where the Stoner integral I is determined by the self-consistent spin splitting of atomic d states induced by an applied magnetization m, and $N(E_F)$ is the density of states at the Fermi level. Generally, I changes little under compression, but $N(E_F)$ decreases as the bandwidth increases,[2] and after a critical pressure, the Stoner criterion does not get satisfied and the system becomes nonmagnetic. We have verified the validity of this model using the computed density of states under compression and the magnetic to nonmagnetic transition pressure in the hcp phase obtained by this model, in agreement with that estimated by our *ab initio* calculations.

Goncharov *et al.*[5] have recently measured the elastic and vibrational properties of Co up to 120 GPa using both impulsive stimulated light scattering and Raman scattering methods. They found that under pressure the elastic properties of hcp Co depart from the normal behavior well below the hcp to fcc phase transition pressure. They also found an anomalous change in the rate of increase of E_{2g} mode phonon frequency, and they suggested a magnetoelastic mechanism as the driving mechanism for the martensitic hcp-fcc phase transition. Recently Antonangeli and co-workers[6] have determined the longitudinal acoustic dispersion of polycrystalline cobalt by inelastic x-ray scattering up to 99 GPa, throughout the entire stability field of the hcp phase. They have compared the aggregate compressional and shear sound velocities with impulsive stimulated light scattering and ambient pressure ultrasonic measurements and also with results of first-principles calculations. They obtained linear variation of sound velocities with density up to 75 GPa followed by softening. To corroborate these findings theoretically we have carried out E_{2g} phonon frequency calculations of hcp Co under pressure within the quasiharmonic approximation using the plane-wave self-consistent field (PWSCF) method.[7] Using these calculated E_{2g} phonon frequencies we have evaluated the C_{44} elastic modulus and its high pressure behavior. We have also calculated the total energies and the magnetic moments for both hcp and fcc phases under compression, since some of the earlier theoretical estimates do not show much agreement among themselves.[8–10] From our calculations we confirm the anomalous high pressure behavior of the E_{2g} phonon well below the pressure range at which the magnetic collapse and the structural phase transition occur, consistent with recent experiments.[5,6]

II. TOTAL ENERGY AND PHONON CALCULATIONS

We have performed *ab initio* full potential total energy calculations using WIEN2k code[11] based on density functional theory (DFT), as it is an all electron method and can account

for any effect of core level shift to semicore or valence states under pressure. For the Brillouin zone (BZ) integration, 5000 **k** points (288 **k** points in the irreducible wedge of BZ) and 10 000 **k** points (286 **k** points in the irreducible wedge of BZ), respectively, for hcp and fcc phases were used. For the exchange-correlation terms we employed the generalized gradient approximation (GGA).[12] For all calculations we have taken R_{MT} as 1.8 a.u. and $R_{MT}K_{max}=9.0$. We carried out spin-polarized calculations both for hcp and fcc phases of Co. We obtained the equilibrium volume by optimizing the axial ratio (c/a) for different volumes from total energy calculations. We have also optimized the c/a ratio for each compression. We have fitted our calculated total energies (E) for various compressions to a polynomial to obtain the equilibrium volume, pressure, and bulk modulus, etc. For comparison of the calculated (P-V) curve with experimental data, we have also included the zero point and lattice thermal contributions at room temperature.[13]

We have calculated the Stoner factor $IN(E_F)$ for the hcp phase both at ambient and at high pressures. To evaluate this we have carried out fixed spin moment calculations as implemented in the WIEN2k code[11] in which the total energy $E(m)$ is calculated subject to the constrained moment (m). The behavior at small m can be written as

$$E(m) = (1/2)\chi^{-1}m^2, \tag{1}$$

where χ is the susceptibility and can be written as,

$$\chi = \chi_0/[1 - IN(E_F)], \tag{2}$$

where $\chi_0=2\mu_B{}^2N(E_F)$ is the bare susceptibility. By fitting our calculated fixed spin moment energy $E(m)$ to Eq. (1) we can obtain χ, and then by evaluating χ_0 directly from the band structure and using Eq. (2) we can obtain the Stoner factor $IN(E_F)$. For higher pressure, we evaluated it by multiplying ambient I with corresponding density of states at the Fermi level $N(E_F)$, in accordance with Ref. 2.

We performed the *ab initio* phonon calculations using the plane-wave self-consistent field program[7] based on density functional perturbation theory (DFPT), which is quite a convenient method for the quasiharmonic *ab initio* phonon calculations.We employed the same exchange-correlation term as used in WIEN2k. Note that the equilibrium properties obtained by WIEN2k and PWSCF match quite well (see discussion below and Table I). In PWSCF, the interactions between the ions and the valence electrons are described by using ultrasoft pseudopotentials.[14] We have used a plane wave basis set with 50 Ry energy cutoff for Bloch functions and 400 Ry cutoff for the augmentation charges. For the Brillouin zone integration a $24\times24\times12$ uniform Monkhorst-Pack **k**-point mesh (854 **k** points in the irreducible wedge of BZ) and a $24\times24\times24$ **k** point mesh (826 **k** points in the irreducible wedge of BZ) for hcp and fcc phases, respectively, were used. In order to deal with the possible convergence problems for metals, a smearing technique was employed using the Methfessel-Paxton scheme,[15] with a smearing parameter of 0.14 eV.

The C_{44} elastic modulus was calculated from the E_{2g}-mode phonon frequencies using the relation,

TABLE I. Calculated equilibrium properties of Co both in hcp and fcc phases.

Phase	V_0 (Bohr^3)	c/a	Bulk modulus B_0 (GPa)	Pressure derivative of B_0 B'	Reference
hcp	74.04	1.618	205		WIEN2k[a]
	74.37	1.618	189	4.8	PWSCF[a]
	74.90	1.623	190	3.6	Experimental[b]
		1.615	199	3.6	Experimental[c]
		1.620	194	4.6	Theory[d]
	73.60	1.615	212	4.2	Theory[e]
			242		Theory[f]
fcc	73.82		247		WIEN2k[a]
	74.00		214	3.2	PWSCF[a]
	70.37		224	5.8	Experimental[c]
	70.04		262	4.5	Theory[d]

[a]Present calculation.
[b]Reference 18.
[c]Reference 1.
[d]Reference 9.
[e]Reference 10.
[f]Reference 17.

$$C_{44} = 2\pi^2 M[\sqrt{3}c/6a^2]\nu^2 \tag{3}$$

where M is the atomic mass, c and a are the cell parameters, and ν is the E_{2g}-phonon frequency[16] at the Γ point.

III. RESULTS AND DISCUSSION

Our calculated properties of Co in hcp and fcc phases are given in Table I, along with the available experimental data and with those of other theoretical estimates.[9,10,17] We notice good agreement for equilibrium volume, c/a ratio, and bulk modulus, whereas the pressure derivative of bulk modulus is in reasonable agreement. The computed pressure (P)–volume (V) equation of state is also seen to be in good agreement with the experimental data of Yoo *et al.*[1] (see Fig. 1).

From our calculated P-V data, we have also evaluated the Gibbs free energy for hcp and fcc phases at 0 K. We find by the free energy estimates that hcp to fcc transition pressure is at 105 GPa, which is in agreement with the experimentally reported pressure range of 105–150 GPa.[1] Earlier full potential linear muffin-tin orbital (FPLMTO) calculations by Yoo *et al.*[9] found that the fcc phase would stabilize over the hcp phase at about 95 GPa, which agrees with our estimates. From Fig. 1 we find that there is no significant change of volume (about 1%) at the transition pressure, which is consistent with the experiments.[1]

We also calculated the pressure variation of magnetic moment for Co in both hcp and fcc phases (see Fig. 2). Our calculated magnetic moment of 1.62 μ_B/atom at ambient pressure agrees with the experimental value of 1.58 μ_B/atom

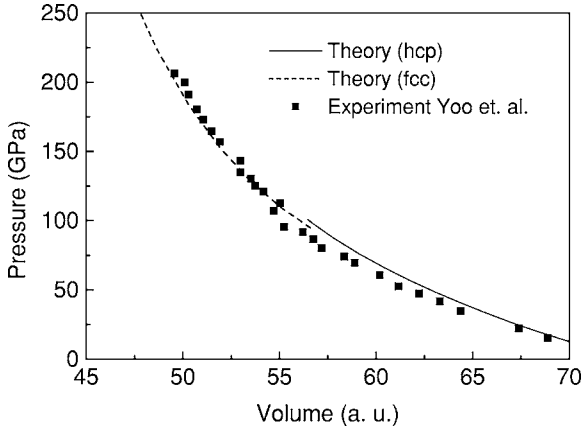

FIG. 1. Equation of states for hcp and fcc Co. Experimental data are from Yoo *et al.* (Ref. 1).

for the hcp phase[19] and with the results of earlier theoretical estimates.[8–10,17] From Fig. 2 it is seen that the hcp magnetic moment falls with pressure and at around 100 GPa, the rate of fall increases. For the fcc phase the magnetic moment remains almost constant up to 70 GPa and then suddenly falls to zero, resulting in a nonmagnetic fcc phase just below 125 GPa. Thus, at around 100 GPa pressure magnetic instability developes in hcp Co and it makes a transition to the fcc phase. This phase transition is similar to the bcc to hcp phase transition in Fe (Ref. 2). Similar qualitative results were obtained in other theoretical estimates, though some quantitative differences exist.[9,10,17] From our calculated Stoner factor, we find that at ambient pressure its value is 1.77 and at around the transition pressure it reduces to 1.15 in the hcp phase. The value of the Stoner factor falls below 1.0 at around 175 GPa pressure, and the magnetic moment in hcp phase reaches zero at that pressure, thus supporting the predictions of the Stoner model.

As mentioned earlier (Sec. I), recent Raman measurements[5] of the E_{2g} phonon frequency under high pressure show that the frequency of this mode increases linearly with pressure. However the slope of the variation changes discontinuously near 75 GPa, suggesting some lattice instability that could lead to phase transition at a higher pressure. Our

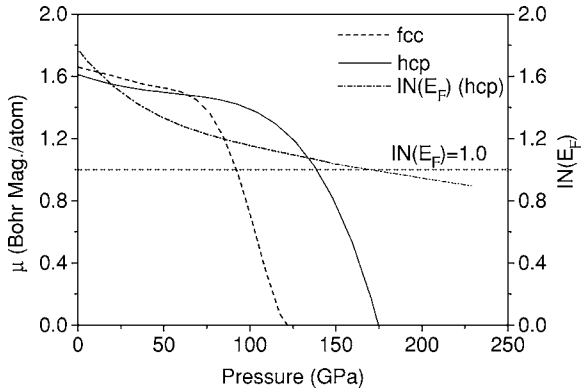

FIG. 2. High pressure variation of magnetic moments for both hcp and fcc phases of Co. The variation of the Stoner factor, $IN(E_F)$, is also shown.

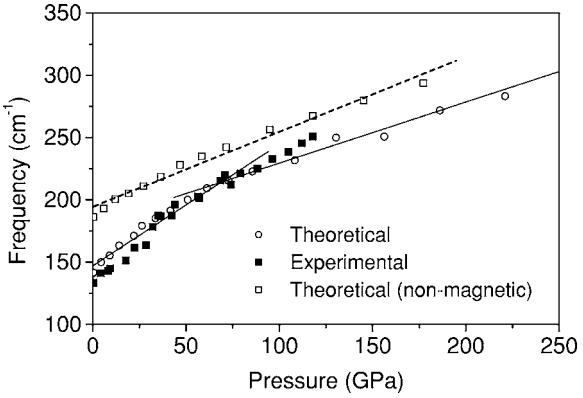

FIG. 3. E_{2g} phonon frequency as a function of pressure: theory and experiment (Ref. 5). Open squares are for nonmagnetic hcp-Co and the dotted line is the linear fit to the calculated frequencies.

calculated high pressure variations of E_{2g} phonon both for magnetic and nonmagnetic hcp-Co are shown in Fig. 3 along with experimental data[5] for comparison. We have made the linear fitting of our calculated results in view of the observations of Goncharov *et al.*[5] and found different slopes for lower pressure and higher pressure regions for the magnetic case, whereas an overall linear fitting suited well for our calculated data for the nonmagnetic case. It is evident that there is a change of slope near 75 GPa (magnetic case), in agreement with the phonon anomaly observed by Goncharov *et al.*[5] It is interesting to note that derived aggregate compressional and shear sound velocities from inelastic x-ray scattering data by Antonangeli *et al.*[6] scale linearly with density up to 75 GPa, and above it deviations in both are observed.

We have also estimated the C_{44} elastic modulus and its pressure variation from our calculated E_{2g}-phonon frequencies. At ambient pressure our calculated value for C_{44} is 70 GPa, which compares well with the experimental value of 75 GPa obtained from ultrasonic measurements by Schober and Dederichs[18] and 60 GPa inferred from Raman measurements by Goncharov *et al.*;[5] the theoretical calculations of Steinle-Neumann *et al.*[10] give an estimate of 90 GPa. In Fig. 4 we have presented the pressure variation of calculated C_{44} elastic moduli along with the experimental data of Goncharov *et al.*[5] and the shear moduli evaluated using the transverse sound velocity data of Antonangeli *et al.*[6] for comparison. We have made the linear fitting of our calculated results and found a slope change near 75 GPa pressure, also in good agreement with experimental measurements.

Hence, our theoretical phonon calculations for hcp Co reproduces the E_{2g} phonon anomaly observed by Goncharov *et al.*[5] The phonon anomaly can be attributed to a renormalization of the phonon frequency due to processes involving the particle-hole fluctuations. The magnon excitations of the magnetically ordered state also undergo renormalization of their spin stiffness due to processes involving particle-hole spin fluctuations. In a magnetically ordered ground state the transverse (particle-hole) spin excitations give rise to the magnons of the system. The phonon self-energies are weakly affected by the magnons due to spin-phonon coupling. The magnon spin stiffness softens at pressures just preceding the

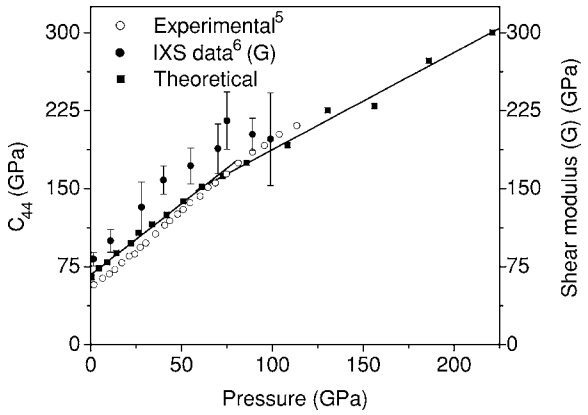

FIG. 4. Calculated pressure variation of C_{44} elastic moduli along with experimental data. We have made a linear fitting in the two regions of our calculated points (shown as filled squares). Open circles are experimental C_{44} data of Goncharov *et al.* (Ref. 5). The filled circles are shear moduli (G) obtained using the data of shear (transverse) sound velocity of Antonangeli *et al.* (Ref. 6). As C_{44} is not available from their data, and although G is a combination of all three, C_{11}, C_{12}, and C_{44} elastic constants, it is believed that its pressure behavior is similar to that of C_{44}.

pressure at which the magnetic order is lost. This might be expected to show up in the phonon dispersion as a slight softening of the rate of increase of the E_{2g} phonon mode. This is in fact what our calculations show: There is a phonon anomaly at a pressure of 75 GPa in the hcp phase which precedes the destruction of magnetic order near 100 GPa. This scenario is further supported by our calculations for the hypothetical nonmagnetic hcp state depicted in Fig. 3, which shows no evidence of phonon anomaly. This is reasonable as the anomalous particle-hole fluctuations that destroyed the magnetically ordered state considered earlier are a consequence of broken rotational invariance. In the absence of a spontaneous magnetization the spin and charge particle-hole fluctuations are nearly identical and the excitations which cause softening of magnetization and the phonon anomaly in the former case are absent. It is thus clear that the phonon anomaly of the E_{2g} mode and the magnetic moment collapse are intimately connected. Note that iron also undergoes similar structural transition accompanied by magnetic collapse at about 10 GPa pressure, but unlike in Co, no phonon anomaly associated with it has been observed so far. This contrasting behavior indicates that the magnetoelastic coupling should be stronger in Co than in Fe.

IV. CONCLUSIONS

We have presented our *ab initio* total energy and phonon calculations for Co under high pressure. We find an E_{2g} phonon anomaly near 75 GPa pressure which correlates well with the experimental measurements of phonon frequencies and with variation of aggregate sound velocities. We obtain a hcp to fcc phase transition at 105 GPa pressure, which agrees well with the experimentally determined pressure range of 105–150 GPa. From the pressure variation of magnetic moment we find that there is a change in the rate of variation of the magnetic moment for the hcp phase near 100 GPa pressure. Our calculations demonstrate that the lattice, magnetic, and structural instabilities are interrelated, pointing to the need to measure experimentally the magnetic moment of Co under pressure. This is important because a magnetoelastic mechanism has been proposed earlier for the hcp-fcc martensitic transition,[5] and our work confirms that the soft magnon excitations that precede the magnetic transition trigger the elastic anomaly that could lead to a lattice instability in Co under pressure. We also conclude that magnetoelastic coupling should be stronger in Co than in Fe, as no anomaly in the variation of phonon frequency accompanying the magnetic collapse under compression has been observed in the latter so far.

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