**Ab initio Total Energy and Phonon Calculations of hcp Co up to 250 GPa Pressure**

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**ABSTRACT**

We present the high pressure variation of $E_{2g}$ mode phonon frequency at $\Gamma$ point of Co calculated within the density functional perturbation theory. Using quasiharmonic approximation our calculations show an anomalous high pressure behaviour near 75 GPa as observed in phonon frequency measurements using impulsive stimulated light scattering and the derived aggregate compressional and shear sound velocities from inelastic X-ray scattering measurements. We find the rapid magnetic moment reduction beyond 100 GPa. We also calculated total energy both for hcp and fcc phases and confirm the structural phase transition as observed in earlier theoretical studies. Our finding reveal that magneto-elastic mechanism proposed for martensitic hcp-fcc phase transition in Co above 125 GPa need to be supplemented with direct experimental determination of pressure evolution of magnetic moment.

**INTRODUCTION**

The study of 3d 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 most widely studied both by experiments and theory, which is the major constituent of the Earth’s core. Many new phases including $\beta$-Fe have been observed though there are still controversies regarding the structure of iron at high pressure and high temperature. The structure of $\beta$-Fe has been proposed as orthorhombic [Andrault et al 1997] and has been contradicted by Shen et al [1998] or dhcp [Saxena et al 1995] though both of these structures are absent for all other transition metals [Skriver 1985, Moriarty 1985]. Comparatively cobalt is less studied by both theory and experiments, though the study of cobalt at Mbar pressures is crucial for the systematic understanding of the magnetic 3d elements as it is situated at the centre of the 3d transition metal series. Furthermore, the behaviour of Co in particular is closely associated with the physical properties of Fe. Hence the study of Co at high pressure may provide better understanding on the phase diagram of iron.

Under ambient condition Co crystallizes in the hexagonal close packed (hcp) structure (ε phase). A face centred cubic (fcc) structure (γ phase) becomes stable at high temperature above 420 °C and can be quenched at room temperature as a metastable phase. With 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 [Yoo et al 2000]. This phase transition is attributed to the theoretically known collapse of the magnetic moment under high pressure [Steinle-Neumann et al 1999, Cohen et al 2002]. Similar transition was also observed in iron at 10 GPa pressure [Mao et al 1987]. The magnetic properties of these 3d transition metals are largely determined by the well localized 3d orbitals. The crystal field in these metals splits the 3d band into a nearly filled majority and a partially filled minority bands. The filling factor of the minority 3d bands determines the structural and elastic properties of these metals [Söderlind et al 1994]. In the Stoner model, a
magnetic state is stable if \( I N(0) > 1 \), where the Stoner integral \( I \) is determined by the self-consistent spin splitting of atomic \( d \)-states induced by an applied magnetization \( M \), and \( N(0) \) is the density of states at the Fermi level. Under compressions \( I \) changes little but \( N(0) \) decreases as the bandwidth increases, and after a critical pressure, the Stoner criterion is not satisfied, and the system becomes nonmagnetic.

Goncharov et al [2004] have 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 departed from the normal behaviour well below hcp to fcc phase transition pressure. They also found an anomalous decrease in the \( E_{2g} \) mode frequency, which suggested magneto-elastic mechanism as the driving mechanism for the martensitic hcp-fcc phase transition. Recently Antonangeli and co-workers [2005] determined the longitudinal acoustic dispersion of polycrystalline cobalt by inelastic x-ray scattering up to 99 GPa, through out the entire stability field of hcp phase. They compared the aggregate compressional and shear sound velocities with impulsive stimulated light scattering and ambient pressure ultasonic measurements and with first principle calculations. They obtained linear variation of sound velocities with density upto 75 GPa and then found the softening. To corroborate these findings theoretically we have carried out \( E_{2g} \) phonon frequency calculations of hcp Co under pressure within quasi-harmonic approximations using plane wave self-consistent field (PWSCF) method. We have also calculated the total energy and magnetic moment for both hcp and fcc phases at different compressions. From our calculations we confirm the anomalous high pressure behaviour of \( E_{2g} \) phonon well below the pressures at which the magnetic collapse and the structural phase transition occurs, consistent with the recent experiments [Goncharov et al., 2004, Antonangeli et al., 2005].

**TOTAL ENERGY AND PHONON CALCULATIONS:**

We have performed *ab initio* total energy and phonon calculations using Plane Wave Self-Consistent Field (PWSCF) programs [Baroni et al., 2001]. Our total energy calculations are based on DFT and the phonon calculations are from density functional perturbation theory (DFPT). The interactions between the ions and the valence electrons are described using an ultrasoft pseudopotential [Vanderbilt 1990]. We have used a plane wave basis set with 50 Ry energy cut-off and 400 Ry cut-off is used for the expansion of augmentation charges. For the Brillouin zone (BZ) integration we have used a 24 x 24 x 12 uniform Monkhorst-Pack \( k \)-point mesh (854 \( k \)-point in the irreducible wedge of BZ) for hcp Co and 24 x 24 x 24 \( k \)-point mesh (826 \( k \)-point in the irreducible wedge of BZ) for fcc-Co. For the Exchange-correlation terms we have used generalized gradient approximation [Perdew et al., 1996]. In order to deal with the possible convergence problems for metals, a smearing technique is employed using the Methfessel-Paxton scheme [Methfessel et al 1989], with a smearing parameter set equal to 0.14 eV. Both for hcp and fcc phase we have carried out spin polarized calculations. We have optimized the hcp structure both with respect to volume and \( c/a \) by calculating total energies at various volume and \( c/a \) values. For higher compressions \( c/a \) is kept constant, as its pressure variation is very small [Steinle-Neumann et al 1999]. We have fitted our calculated total energies (E) for various compressions to the third order Birch-Murnaghan equation of state to obtain the equilibrium volume, bulk modulus and its pressure derivative. For *ab initio* phonon calculations we have computed the phonon dynamical matrices on a 5 x 5 x 3 uniform \( q \)-point mesh of the BZ. The dynamical matrices at arbitrary \( q \)-points are then obtained by Fourier interpolation. We have repeated these calculations for each lattice constant to obtain the phonon frequencies for higher compressions.

**RESULTS AND DISCUSSION:**

Our calculated equilibrium properties of hcp and fcc Co are given in table-I and compared with the available experimental results, and we get very good agreement for equilibrium.
volume, c/a ratio, bulk modulus and magnetic moment whereas the pressure derivative of bulk modulus is quite off, this is mainly due to numerical error propagations as the second derivative of total energy with respect to volume is involved in its evaluation. From our calculated P-V data, we have also calculated the Gibbs free energy for hcp and fcc phases at 0 K. The free energy for fcc phase with respect to that of hcp phase is shown in Fig.1. From this figure we find that hcp to fcc transition pressure is around 125 GPa, which is in good agreement with the experimentally determined pressure range of 105 to 150 GPa [Yoo et al 2000]. It is to be noted that the calculated free energy difference for hcp and fcc phases is less than 1mRy/atom in the pressure range of 105 – 150 GPa pointing out the possibility of mixed phase region.

Table-I Calculated equilibrium properties of Co both in hcp and fcc phase

<table>
<thead>
<tr>
<th>Phase</th>
<th>$V_0$ (Bohr$^3$)</th>
<th>c/a</th>
<th>Bulk modulus $B_0$ (GPa)</th>
<th>Pressure derivative of $B$ $B'$</th>
<th>Magnetic moment $\mu$ (Bohr mag./atom)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hcp</td>
<td>74.37</td>
<td>1.618</td>
<td>189</td>
<td>4.8</td>
<td>1.62</td>
<td>Present cal.</td>
</tr>
<tr>
<td></td>
<td>74.90</td>
<td>1.623</td>
<td>190</td>
<td>3.6</td>
<td>1.58</td>
<td>Experiments [Schober et al 1979, Meyer et al 1951]</td>
</tr>
<tr>
<td>Fcc</td>
<td>74.00</td>
<td>214</td>
<td>3.2</td>
<td>5.8</td>
<td>1.67</td>
<td>Present cal.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>224</td>
<td></td>
<td></td>
<td></td>
<td>Experiments [Yoo et al 2000]</td>
</tr>
</tbody>
</table>

Fig.1 Pressure variation of free energy differences for Co in fcc phase with respect to that of hcp phase.

We have also calculated the pressure variation of magnetic moment for Co in both hcp and fcc phases. We find that the hcp magnetic moment falls with pressure and around 100 GPa, the rate of fall increases and finally it becomes zero at around 260 GPa, whereas for fcc
phase it remains almost constant up to 100 GPa and then suddenly falls to zero. Hence the fcc phase at 125 GPa is nonmagnetic. Hence at around 100 GPa pressure some magnetic instability develops in hcp Co and around 125 GPa pressure it finally makes a transition to a nonmagnetic fcc phase. This phase transition is similar to the bcc to hcp phase transition in Fe.

In table-II we compare our calculated phonon frequencies at some high symmetry q-points of the BZ with those obtained from neutron scattering experiments by Wakabayashi et al [1982]. We find that at Γ and A points the phonon frequencies match well with experimental values whereas at M-point the agreement is poor. Our calculated $E_{2g}$ phonon frequency at ambient pressure also compares well with that of Raman measurements by Goncharov et al. [2004].

Table-II Comparison of calculated phonon frequencies with experimental measurements at few high symmetry q-points of BZ.

<table>
<thead>
<tr>
<th>Γ-point</th>
<th>Our calculations (THz)</th>
<th>0.00</th>
<th>0.00</th>
<th>0.00</th>
<th>4.22</th>
<th>4.22</th>
<th>6.32</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experimental values of</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>4.21</td>
<td>4.21</td>
<td>7.45</td>
</tr>
<tr>
<td>Wakabayashi et al [1982] (THz)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Experiment values of</td>
<td></td>
<td></td>
<td></td>
<td>3.96</td>
<td>3.96</td>
<td></td>
</tr>
<tr>
<td>Goncharov et al [2004] (THz)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>Our calculations (THz)</td>
<td>2.29</td>
<td>3.99</td>
<td>4.68</td>
<td>5.85</td>
<td>6.56</td>
<td>6.74</td>
</tr>
<tr>
<td></td>
<td>Experimental values of</td>
<td>3.93</td>
<td>4.59</td>
<td>5.86</td>
<td>6.90</td>
<td>7.48</td>
<td>7.83</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>Our calculations (THz)</td>
<td>3.11</td>
<td>3.11</td>
<td>3.11</td>
<td>3.11</td>
<td>7.15</td>
<td>7.15</td>
</tr>
<tr>
<td></td>
<td>Experimental values of</td>
<td>2.97</td>
<td>2.97</td>
<td>2.97</td>
<td>2.97</td>
<td>6.55</td>
<td>6.55</td>
</tr>
<tr>
<td>Wakabayashi et al [1982] (THz)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 2.** $E_{2g}$ phonon frequency as a function of pressure: theory and experiment [Goncharov et al 2004].
The calculated high pressure behaviour of $E_{2g}$ phonon is shown in Fig.2 along with experimental data [Goncharov et al 2004] for comparison. We have made the line fitting of our calculated data in two regions. It is evident that there is a change of slope near 75 GPa in agreement with the phonon anomaly as observed by Goncharov et al [2004]. It is interesting to note that derived aggregate compressional and shear sound velocities from inelastic X-ray scattering data by Antonangeli et al [2005] scale linearly with density up to 75 GPa and above it deviation in both is observed.

We thus find the phonon softening around 75 GPa with almost no reduction of magnetic moment upto 100 GPa. It is interesting to understand whether the lattice, magnetic and structural instabilities are inter-related, pointing to the need to measure experimentally the magnetic moment of Co under pressure. This is important because magneto-elastic mechanism is proposed for the hcp-fcc martensitic transition [Goncharov et al 2004]. It is also possible that the phonon instability triggers magnetic collapse initiating the lattice instability.

CONCLUSIONS

We have presented our ab initio total energy and phonon calculations for Co under high pressure. We find a magnetic hcp to nonmagnetic fcc phase transition near 125 GPa pressure which agrees well with the experimentally determined pressure range of 105-150 GPa. From pressure variation of magnetic moment we find that there is a change in the rate of change of magnetic moment for hcp phase near 100 GPa pressure. We find an $E_{2g}$ phonon anomaly near 75 GPa pressure which correlates with the experimental measurements of phonon frequencies and with variation of aggregate sound velocities. We strongly suggest the need for magnetic moment measurements of Co under pressure for clarifying the mechanism responsible for hcp-fcc martensitic phase transition.

REFERENCES

Antonangeli et al [ preprint of the paper submitted to PRB 2005, on Aggregate and single crystalline elasticity of hcp cobalt at high pressure ]


