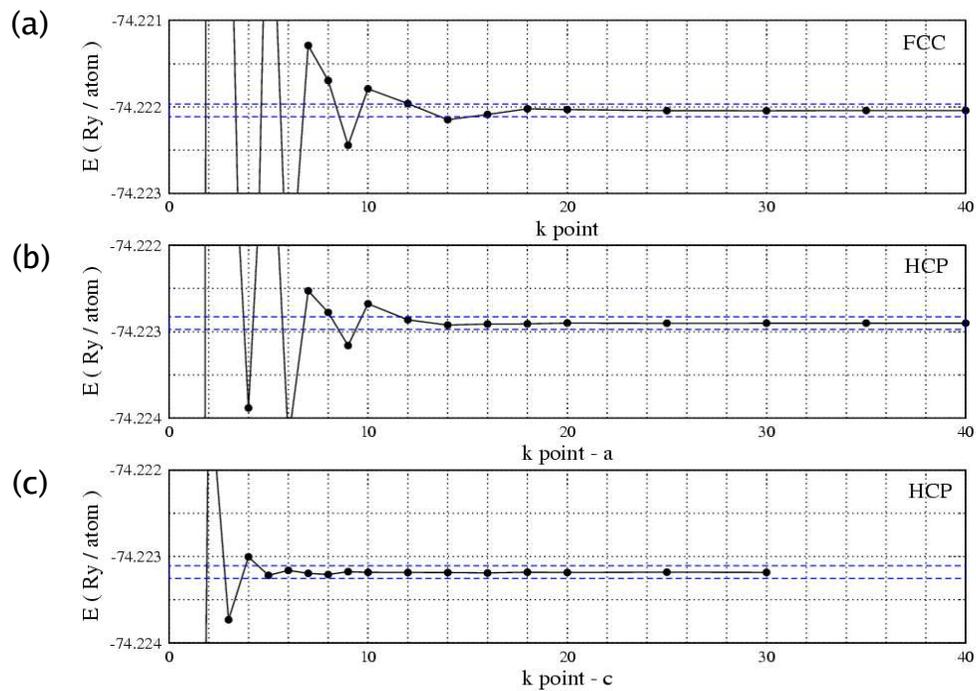


### 3.320 Atomistic Modeling of Materials Spring 2005 Solution set 3: First-principles energy methods II

**Problem 1** (50 pts): Cobalt in HCP and FCC structures.

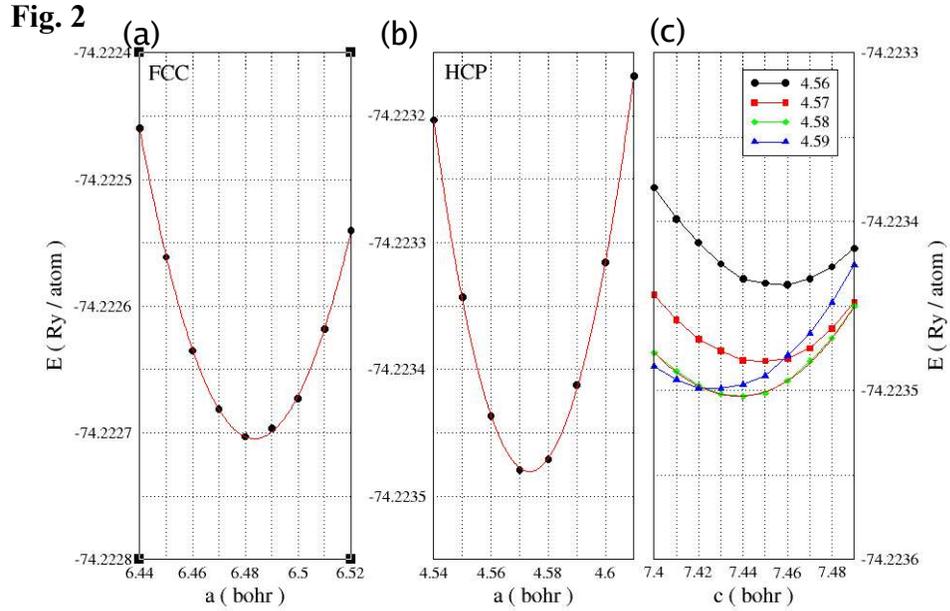
$\vec{k}$  -point mesh :

**Fig. 1**



The dashed blue lines indicate a  $\pm 1$  meV window around the fully converged energy. According to the graph, we can choose  $16 \times 16 \times 16$  for the FCC and  $12 \times 12 \times 6$  for the HCP structure.

Note that for the HCP structure you should check convergence in *both* the  $a$  and  $c$  directions. In Fig. 1(c), 9 k-points are sampled in  $a$  while a varying number of k-points are sampled in  $c$ .



1. Fig.2(a) :  
The lattice parameter  $a$  is approximately 6.483 bohr.
2. Fig.2(b) : Ideal  $c/a$  ratio =  $\sqrt{8/3} = 1.632993$   
The minimum point is approximately 4.57 bohr.

Fig.2(c) :

Four values of  $a$  around 4.57 bohr are tested. The line with  $a=4.58$  bohr shows a minimum at  $c=7.438$  bohr.

Compared to the experimental values, all of the lattice parameters are underestimated, which is often the case for the LDA exchange-correlation functional.  $c/a$  is very similar to the experimental value because of an error cancellation. Also note that unlike our calculated values, the experimental values are not obtained at zero temperature and pressure.

	FCC	HCP		
( Å )	$a$	$a$	$c$	$c/a$
LDA	3.43	2.42	3.94	1.624
Exp.	3.54	2.51	4.07	1.623

## 3. The energies are:

FCC : - 74. 22270 Ry / atom

HCP : - 74. 22350 Ry / atom

HCP is more stable by 11 meV/atom. The energy difference is very small, which is why we need a highly accurate k-point sampling.

The volumes are:

FCC : 68.12 bohr<sup>3</sup> / atomHCP : 67.56 bohr<sup>3</sup> / atom

Higher pressure will favor the structure with a smaller volume, so a phase transition is not likely to occur. On the other hand, higher temperature will favor the one with a larger volume since it is usually softer and has higher entropy. Therefore, an HCP-to-FCC transition could happen at high temperature. If you think about the pressure-temperature phase diagram, it is possible that  $dP/dT = \Delta S_{\text{FCC-HCP}} / \Delta V_{\text{FCC-HCP}} > 0$  at the two-phase equilibrium, which would place the HCP phase in the high-pressure, low-temperature regime. Still, this is a very crude argument and we definitely need more calculations to test it.

## 4. In a hexagonal cell, the A and B sites are given as the following:

A 0.3333333333 0.6666666667

B 0.6666666667 0.3333333333

and the C position is

C 0.0000000000 0.0000000000

The relationship between the lattice parameter  $a$  for the FCC in a cubic system and the corresponding value for the FCC in a hexagonal system is

$$a(\text{hex}) = (1/\sqrt{2}) * a(\text{FCC})$$

In our case,  $a(\text{hex}) = (1/\sqrt{2}) * 6.483 = 4.584$  bohr, which is very close to the lattice constant  $a$  of HCP.

The  $c/a$  ratio is simply 1.5 times the ideal  $c/a$  ratio of HCP, since we now have three atoms per unit cell.

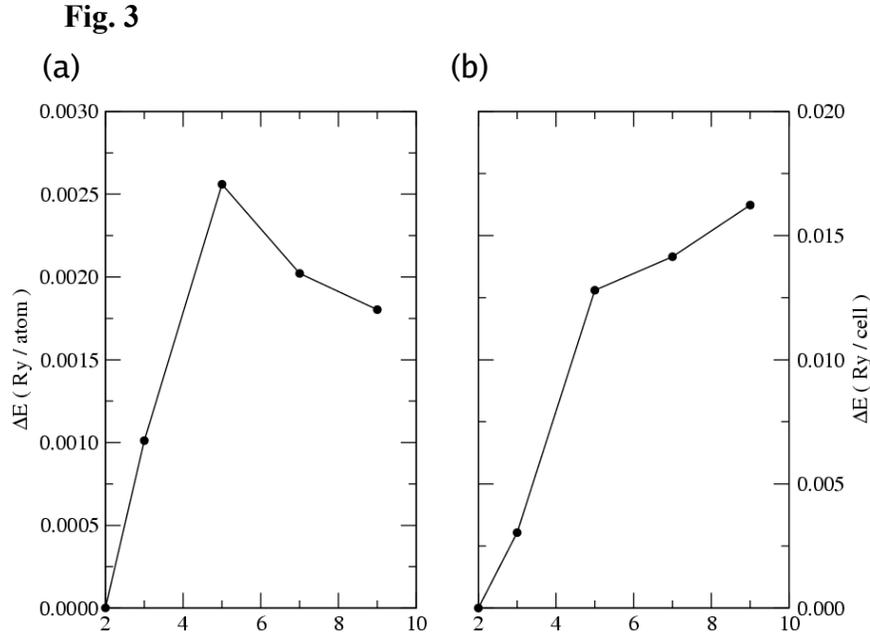
$$c/a = 1.5 * \sqrt{(8/3)} = 2.449490$$

To calculate the energy, a 12x12x4 k-point grid is used.

$E(\text{FCC in a hexagonal cell}) = -74.22259$  Ry / atom

which is higher by 12 meV / atom when compared to  $E(\text{HCP})$ .

This value is almost the same as what we have seen in #3 to within the k-point energy convergence threshold, which confirms that we composed the structure correctly.



5. ABABABAB  
 AB|CACACAC.....

Since we are using periodic boundary conditions, we should add two “AC” layers at a time.

- 2 : AB           ⇒ HCP  
 3 : ABC         ⇒ FCC  
 5 : ABCAC  
 7 : ABCACAC  
 9 : ABCACACAC ( This is the point where you stop the calculations)

When the number of layers  $n$  is very large, the next two “AC” layers should feel like that they are in the HCP structure.

$$E(n+2) - E(n) \approx E(2)$$

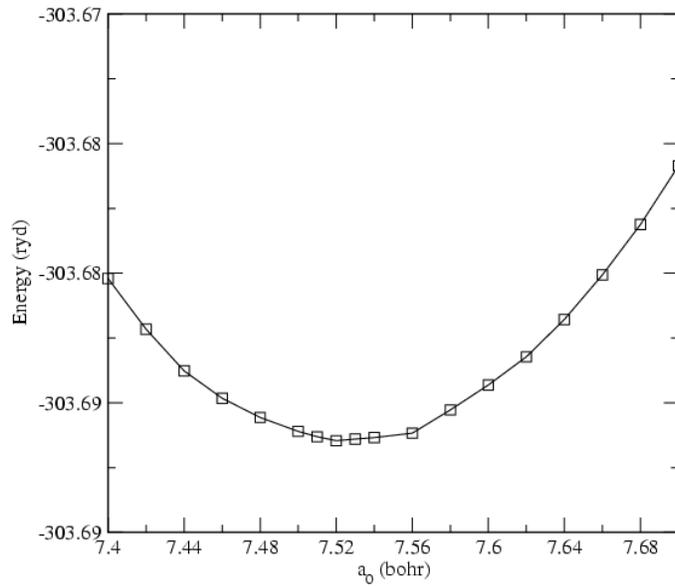
Fig.3(a) is a plot of  $\Delta E(\text{atom}) = E(n)/n - E(2)/2$  as a function of  $n$ , which should reach 0 for a sufficiently large number of layers.

Fig.3(b) is a plot of  $\Delta E(\text{cell}) = E(n) - n * E(2) / 2$  as a function of  $n$ , and this  $\Delta E$  should converge to a value which represents the extra energy introduced by the stacking fault.

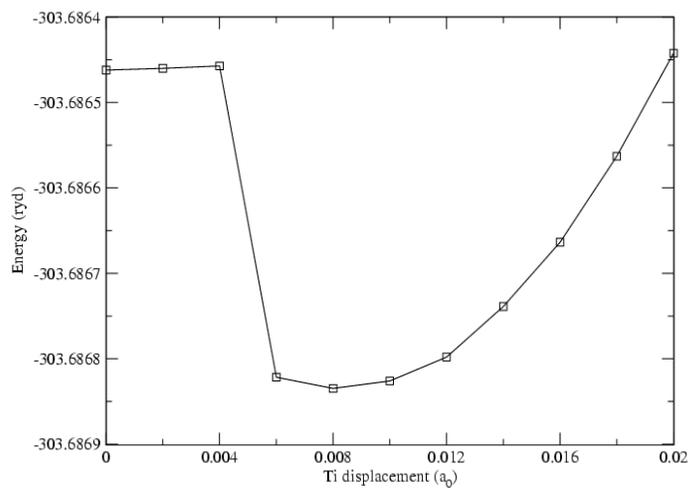
As is obvious from  $\Delta E(\text{atom})$ , which is much higher than 0,  $\Delta E(\text{cell})$  is still far from convergence.

**Problem 2** (50 pts): Stability of the perovskite structure: a case study of  $\text{BaTiO}_3$ .

1. The minimum-energy lattice parameter is about 7.52 bohr ( $3.979 \text{ \AA}$ ):



2. The energy is at a minimum for a Ti displacement of about  $0.08 \cdot a_0$  from  $(0.5, 0.5, 0.5) \cdot a_0$  along one of the cubic lattice directions. The corresponding energy difference is  $3.726 \cdot 10^{-4}$  ryd.



## 3. Final atomic positions:

ATOMIC\_POSITIONS (alat)

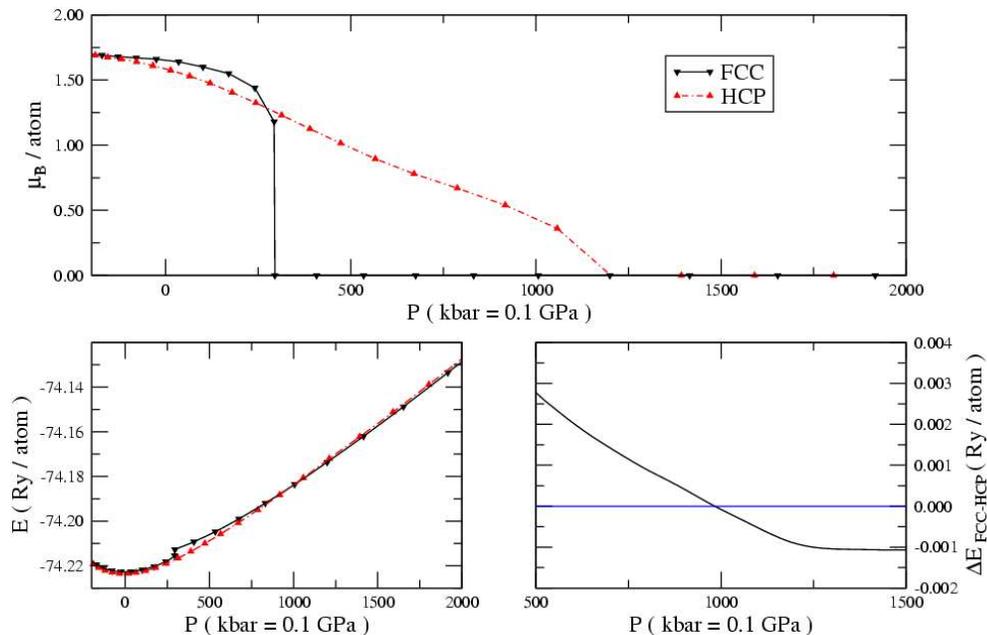
Ba	0.000000000	0.000000000	0.000000000
Ti	0.500000000	0.500000000	0.507394883
O	0.500000000	0.500000000	-0.019383444
O	0.500000000	0.000000000	0.485432812
O	0.000000000	0.500000000	0.485432812

Final energy: -303.6868329953 ryd

Note that this energy is essentially the same as the result of the previous section, to within the convergence threshold given in the script.

4.  $\text{BaTiO}_3$  is more stable in the broken-symmetry configuration for which the titanium atom is slightly displaced along one of the cubic directions with respect to the 'perfect' perovskite structure. Since the titanium atom is cationic, this results in a net polarization of the unit cell along the direction of titanium displacement. This permanent dipole moment is responsible for the ferroelectric behavior of  $\text{BaTiO}_3$ .

Extra credit (20 points): More on Cobalt : Co at high pressure.



The magnetic moment of the HCP Co is  $1.59 \mu_B$  / atom, and the experimental value is  $1.72 \mu_B$  / atom, so it seems that our DFT calculations give us a reasonable value (although we must pay attention to the experimental conditions).

Both HCP and FCC become nonmagnetic at high pressure.

Around 100 GPa, nonmagnetic FCC becomes more stable than HCP.

There is a phase diagram in Yoo et al., Phys. Rev. Lett. 84[18] 4132 (2000), and it would be interesting to compare it with what you have learned from your DFT calculations.