Overall algorithm:

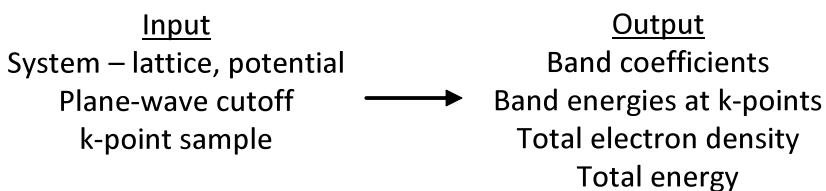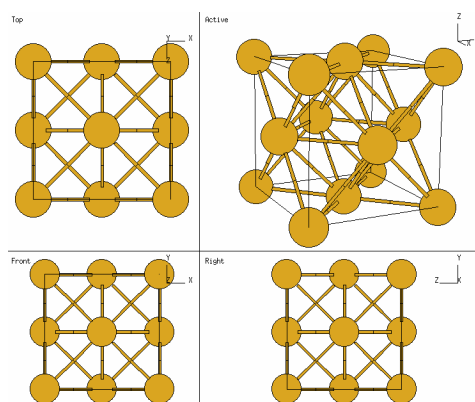| Input | Output |
|---|---|
| System – lattice, potential | Band coefficients |
| Plane-wave cutoff | Band energies at k-points |
| k-point sample | Total electron density |
| | Total energy |

## 1. FCC metal

Late transition metals commonly crystallize in FCC lattice.

### *Face-centered cubic*

$$\mathbf{a}_1 = a \begin{pmatrix} 0 \\ 1/2 \\ 1/2 \end{pmatrix}, \qquad \mathbf{a}_2 = a \begin{pmatrix} 1/2 \\ 0 \\ 1/2 \end{pmatrix}, \qquad \mathbf{a}_3 = a \begin{pmatrix} 1/2 \\ 1/2 \\ 0 \end{pmatrix},$$

$$r = a/\sqrt{2}$$

Primitive cell has one atom.

## 2. Energy calculation

POSCAR:
```
Pure FCC metal
 3.9239
 0.  .5   .5
 .5  0   .5
 .5 .5  0.
   1
Direct
   .0000000000000000    .0000000000000000    .0000000000000000
```

KPOINTS:
```
10x10x10
0
Monkhorst-Pack
10 10 10
0. 0. 0.
```

INCAR:
```
System = Au, FCC
NWRITE = 1
LWAVE  =  .FALSE.   ! write WAVECAR?
LCHARG = .FALSE.     ! write CHGCAR?
LVTOT =   .FALSE.   ! write LOCPOT?

Electronic relaxation
ALGO   = Fast   ! use fast algorithm for electronic convergence
ISMEAR = 0       ! 0: Gaussian smearing of states near Fermi level
```

```
SIGMA  = 0.1     ! smearing parameter, eV
PREC   = normal
    ! set FFT mesh, cutoffs
ENCUT  = 350     ! set plane-wave cutoff
ISTART = 0       ! start from scratch
EDIFF  = 1e-4    ! electronic convergence parameter
ISPIN  = 1       ! polarization? 1, no; 2, yes
```

POTCAR:
Depends on the metal you are doing.

Look at output file

Example of FCC Au, PAW GGA.  Note symmetry unique k points do not grow monotonically.
Timings scale with number of k points.  Also would scale (more severely) with energy cutoff.

| | Unique k points | Free Energy (eV) | Total Energy | Delta | Time (s) |
|---|---|---|---|---|---|
| 6x6x6 | 28 | -2.841 | -2.837 | 0.004 | 6.0 |
| 7x7x7 | 20 | -2.912 | -2.911 | 0.001 | 4.5 |
| 8x8x8 | 60 | -2.859 | -2.858 | 0.001 | 12.2 |
| 10x10x10 | 110 | -2.858 | -2.857 | 0.001 | 21.6 |

With Gaussian smearing, look for difference between free energy (finite sigma) and total energy (sigma neglected) to ~0.001 eV/atom.  For Au does so at modest k point sizes.

## 3.  Lattice constant optimization

Two approaches:
By hand: Calculate energy vs. lattice parameter.

Au, primitive FCC, 8x8x8 mesh (a bit too small):

```
3.7: 1 F= -.15522197E+01 E0= -.15517255E+01  d E =-.988329E-03
3.8: 1 F= -.23013630E+01 E0= -.23008848E+01  d E =-.956338E-03
3.9: 1 F= -.27777703E+01 E0= -.27773039E+01  d E =-.932702E-03
4.0: 1 F= -.30520956E+01 E0= -.30516339E+01  d E =-.923270E-03
4.1: 1 F= -.31785731E+01 E0= -.31780922E+01  d E =-.961871E-03
4.2: 1 F= -.31986333E+01 E0= -.31976437E+01  d E =-.197911E-02
4.3: 1 F= -.31463591E+01 E0= -.31454782E+01  d E =-.176166E-02
4.4: 1 F= -.30443417E+01 E0= -.30434732E+01  d E =-.173691E-02
```

Could fit to a quadratic, but Burch-Murnaghan equation of state better choice.

$$E_{tot}(a) = E_0 + \frac{9V_0 B_0}{16}\left[\left(\left(\frac{a_0}{a}\right)^2 - 1\right)^3 B_0' + \left(\left(\frac{a_0}{a}\right)^2 - 1\right)^2 \left(6 - 4\left(\frac{a_0}{a}\right)^2\right)\right]. \quad (2.3)$$

$E_0$: total energy
$a_0$: equilibrium lattice constant
$V_0$: equilibrium volume
$B_0$: bulk modulus

$B_0'$:

"murg" program performs this fit.  fort.2 input:

```
8.0          ! lattice guess, bohr
         0. .5  .5    ! lattice vectors
         .5  0  .5
         .5 .5  0.
  7             ! number of energies
7.180962136    -0.169108099368        ! lat in bohr, E in Ryd
7.369934823    -0.204123467588
7.558907511    -0.224285895928
7.747880199    -0.233580199912
7.936852887    -0.235017176246
8.125825574    -0.23118316919
8.314798262    -0.22368610907
-3.2
```

fort.10 output:
```
Total energy murnaghan fit
        the four parameters are E0,B,BI,V0

        value of Eo  :       2.96474621
        value of B   :       0.00913914
        value of BI  :       5.43623555
        value of V0  :     122.90870968
        value of rms :   0.40775044E-07

  Vol          Etot              Efit            residual
     7.181   92.574          -0.169108        -0.169052        -0.0561
     7.370  100.076          -0.204123        -0.204307         0.1837
     7.559  107.973          -0.224286        -0.224187        -0.0991
     7.748  116.276          -0.233580        -0.233408        -0.1725
     7.937  124.993          -0.235017        -0.235098         0.0808
     8.126  134.135          -0.231183        -0.231351         0.1682
     8.315  143.713          -0.223686        -0.223581        -0.1051


        Bulk modulus    (Mbar) :       1.34520849
        Bulk derivative        :       5.43623555
        Equilibri volume  (au^3) :     122.90870968
        lattice constant (au)   :       7.89249321
        lattice constant (Ang)  :       4.17644695
             rws (au)           :       3.08435731
             rws (Ang)          :       1.63214010

        energy mininum    (Ryd) :      -0.23525379
        energy mininum     (eV) :      -3.20079209
```
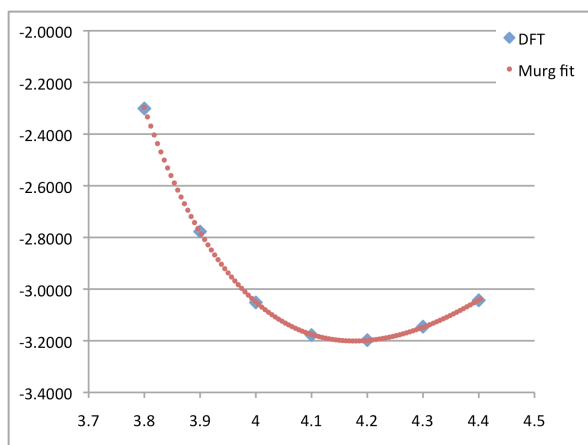
Gives lattice constant (4.176 Å), compare to experiment of 4.078 Å.  Typical of GGA to slightly overestimate this.

Since energy of atom within PAW model is ~0, can get cohesive energy directly from minimum energy point, 3.20 eV vs. exp't of about 3.8 eV, not too bad.

Gradient-based: Calculate "stress tensor" and use to optimize cell.  Problem is that basis set size is determined by cell size, through energy cutoff.  Can either let basis set size float and fix energy cutoff as cell changes size, or fix basis set size and let cutoff effectively float.  Vasp does the latter.  Have to apply more carefully, iteratively optimize and calculate final total energy in a single point.

In this case, converges in six steps to give lattice constant of 4.161 Å and energy of -3.18 eV.

Sometimes only choice if cell has multiple internal degrees of freedom.

## 4.  Band structure and density of states

Calculation gives band energies and occupations in OUTCAR and total density of states in DOSCAR.  Note that absolute band energies are arbitrary; in an infinite solid, there is no vacuum to reference the energy of an electron to!  Typically put Fermi level at 0 eV.

(Density and total energy converges faster than band energies; common to converge calculation with some **k** point mesh, and then use computed density to get band energies along directions of interest non-self-consistently.)

Frequently helpful to decompose bands/DOS into atomic components.  Done by projecting onto atom-centered spherical harmonics, either within a sphere of given radius (RWIGS) or with an intelligently selected radius (LORBIT = 11).

PROCAR gives projection of bands, kind of like an orbital population.  Example output:

```
PROCAR lm decomposed
# of k-points:   60        # of bands:   9        # of ions:   1

 k-point    1 :     0.06250000 0.06250000 0.06250000     weight = 0.00390625
```

```
band    1 # energy    -4.18713668 # occ.  2.00000000

ion     s     py     pz     px     dxy    dyz    dz2    dxz    dx2    tot
  1  0.565  0.002  0.002  0.002  0.000  0.000  0.000  0.000  0.000  0.570

band    2 # energy     0.32959685 # occ.  2.00000000

ion     s     py     pz     px     dxy    dyz    dz2    dxz    dx2    tot
  1  0.000  0.000  0.000  0.000  0.306  0.306  0.000  0.306  0.000  0.918

band    3 # energy     0.40770609 # occ.  2.00000000

ion     s     py     pz     px     dxy    dyz    dz2    dxz    dx2    tot
  1  0.000  0.000  0.000  0.000  0.482  0.001  0.001  0.437  0.000  0.922

band    4 # energy     0.40770634 # occ.  2.00000000

ion     s     py     pz     px     dxy    dyz    dz2    dxz    dx2    tot
  1  0.000  0.000  0.000  0.000  0.132  0.612  0.000  0.176  0.001  0.922

band    5 # energy     1.65915418 # occ.  2.00000000

ion     s     py     pz     px     dxy    dyz    dz2    dxz    dx2    tot
  1  0.000  0.000  0.000  0.000  0.000  0.001  0.278  0.000  0.677  0.956

band    6 # energy     1.65915431 # occ.  2.00000000

ion     s     py     pz     px     dxy    dyz    dz2    dxz    dx2    tot
  1  0.000  0.000  0.000  0.000  0.000  0.000  0.677  0.001  0.278  0.956

band    7 # energy   20.13821541 # occ.  0.00000000

ion     s     py     pz     px     dxy    dyz    dz2    dxz    dx2    tot
  1  0.000  0.001  0.001  0.001  0.007  0.007  0.000  0.007  0.000  0.024

band    8 # energy   22.38990576 # occ.  0.00000000

ion     s     py     pz     px     dxy    dyz    dz2    dxz    dx2    tot
  1  0.022  0.073  0.073  0.073  0.008  0.008  0.000  0.008  0.000  0.265

band    9 # energy   23.48253361 # occ.  0.00000000

ion     s     py     pz     px     dxy    dyz    dz2    dxz    dx2    tot
  1  0.000  0.015  0.141  0.086  0.006  0.004  0.005  0.001  0.001  0.259
```

Note that Au is $d^{10}s^1$, yet there are 12(!) electrons here. We must have screwed up! No...other bands ("orbitals") would have lower occupancies, so that average works out correctly.

DOSCAR gives total density of states summed over **k** points, and similar type of atomic and lm projection. EMIN, EMAX, and NEDOS in INCAR specify lower and upper energy bounds and total number of points, respectively. File first gives total and integrated DOS, then gives site and angular momentum projection.

FCC Au, 10x10x10: 11 valence electrons, as indicated by where Fermi level crosses integrated DOS. Kind of dull electronic structure.
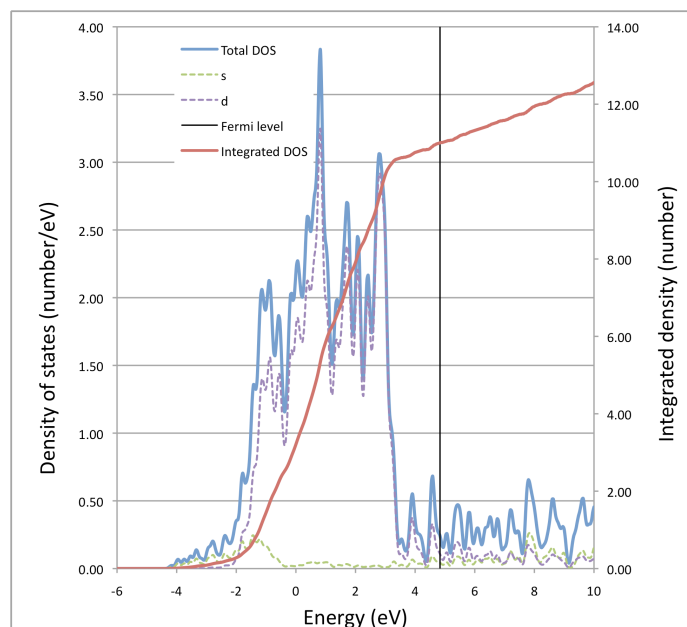
## 5. Supercells and phonon calculations
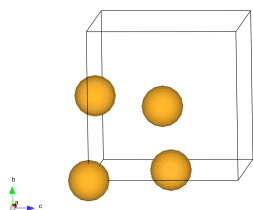


Four atom conventional supercell.  Lattice constant becomes 2^0.5 times primitive one, basis becomes four atoms rather than one.  Increasing lattice constant, can decrease k points proportionally, eg 8x8x8 becomes 6x6x6.

```
Pure FCC metal
 4.176
 1.  0.  0.
 0.  1.  0.
 0.  0.  1.
    4
Direct
   .0000000000000000    .0000000000000000    .0000000000000000
   .5000000000000000    .5000000000000000    .0000000000000000
   .5000000000000000    .0000000000000000    .5000000000000000
   .0000000000000000    .5000000000000000    .5000000000000000
```

10 irreducible k points.  Calculation takes longer, energy becomes -12.759/4 = -3.19 eV/atom, same as above.  Why bother to do this?

Larger cell, more internal degrees of freedom (remember H chain dimerization), lower symmetry constraints.

Also important for phonon (vibrational frequency) calculations. Bloch's theorem applies to vibrational modes: any mode in a cell can be propagated with range of wavelengths, picture

completely analogous to electronic wavefunctions, **k** space becomes **q** space. No simple way, though, to evaluate frequencies at various **q**. Alternative approach:

1. multiply supercell (larger cell, more modes that are included)
2. "dynamical matrix" in harmonic approximation (like a Hessian)
3. finite difference approximation

Controlled with IBRION and NFREE options. Vasp 4.6 does not take advantage of symmetry in displacement calculations; 5.2 does. Vasp 5.2 also includes linear response method.

INCAR:
```
System = Au, FCC
NWRITE = 1
LWAVE =  .FALSE.  ! write WAVECAR?
LCHARG = .TRUE.   ! write CHGCAR?
LVTOT =  .FALSE.  ! write LOCPOT?


Electronic relaxation
ALGO   = Fast   ! use fast algorithm for electronic convergence
ISMEAR = 0      ! 0: Gaussian smearing of states near Fermi level; -5: tetrahedron + Blochl
SIGMA  = 0.1    ! smearing parameter, eV
PREC   = normal ! set FFT mesh, cutoffs
ENCUT  = 350    ! set plane-wave cutoff
ISTART = 0      ! start from scratch
EDIFF  = 1e-4   ! electronic convergence parameter
ISPIN  = 1      ! polarization? 1, no; 2, yes
! LORBIT = 11    ! site-projection of DOS


Geometry relaxation
NSW    = 10     ! # of steps in optimization (default 0!)
ISIF   = 2      ! 0: relax ions, 1,2:relax ions,calc stresses, 3:relax ion+cell
IBRION = 5      ! 1: quasi-NR, 2:CG algorithm for ions, 6:symmetrized phonons
NFREE  = 2      ! number of DIIS vectors to save, or number of dynamical matrix displacements
POTIM  = 0.35   ! reduce trial step in optimization
EDIFFG = -0.05  ! >0: converge on energy (eV); <0: converge on gradient (eV/Ang)
```

OUTCAR gives
```
Eigenvectors and eigenvalues of the dynamical matrix
 -------------------------------------------------


   1 f  =     4.265170 THz    26.798856 2PiTHz  142.270765 cm-1    17.639333 meV
           X          Y          Z           dx         dy          dz
     0.000000   0.000000   0.000000     -0.486404    0.115808    0.000000
     2.088000   2.088000   0.000000      0.486404   -0.115808    0.000000
     2.088000   0.000000   2.088000      0.486404    0.115808    0.000000
     0.000000   2.088000   2.088000     -0.486404   -0.115808    0.000000

   2 f  =     4.265170 THz    26.798856 2PiTHz  142.270765 cm-1    17.639333 meV
           X          Y          Z           dx         dy          dz
     0.000000   0.000000   0.000000      0.000000    0.000000    0.500000
     2.088000   2.088000   0.000000      0.000000    0.000000    0.500000
     2.088000   0.000000   2.088000      0.000000    0.000000   -0.500000
     0.000000   2.088000   2.088000      0.000000    0.000000   -0.500000

   3 f  =     4.265170 THz    26.798856 2PiTHz  142.270765 cm-1    17.639333 meV
           X          Y          Z           dx         dy          dz
```

```
   0.000000   0.000000   0.000000     0.115808    0.486404    0.000000
   2.088000   2.088000   0.000000    -0.115808   -0.486404    0.000000
   2.088000   0.000000   2.088000    -0.115808    0.486404    0.000000
   0.000000   2.088000   2.088000     0.115808   -0.486404    0.000000

 4 f  =    2.738963 THz     17.209413 2PiTHz   91.361973 cm-1    11.327445 meV
           X          Y          Z          dx          dy          dz
   0.000000   0.000000   0.000000     0.171709   -0.181306    0.196340
   2.088000   2.088000   0.000000     0.184840    0.590661   -0.196340
   2.088000   0.000000   2.088000    -0.184840    0.181306   -0.126684
   0.000000   2.088000   2.088000    -0.171709   -0.590661    0.126684

 5 f  =    2.738963 THz     17.209413 2PiTHz   91.361973 cm-1    11.327445 meV
           X          Y          Z          dx          dy          dz
   0.000000   0.000000   0.000000     0.139045    0.020405   -0.330128
   2.088000   2.088000   0.000000    -0.555876    0.249534    0.330128
   2.088000   0.000000   2.088000     0.555876   -0.020405    0.000000
   0.000000   2.088000   2.088000    -0.139045   -0.249534    0.000000

 6 f  =    2.738963 THz     17.209413 2PiTHz   91.361973 cm-1    11.327445 meV
           X          Y          Z          dx          dy          dz
   0.000000   0.000000   0.000000     0.630812   -0.143663   -0.046407
   2.088000   2.088000   0.000000     0.065887   -0.254373    0.046407
   2.088000   0.000000   2.088000    -0.065887    0.143663   -0.101179
   0.000000   2.088000   2.088000    -0.630812    0.254373    0.101179

 7 f  =    2.738963 THz     17.209413 2PiTHz   91.361973 cm-1    11.327445 meV
           X          Y          Z          dx          dy          dz
   0.000000   0.000000   0.000000    -0.102597    0.149812   -0.152806
   2.088000   2.088000   0.000000     0.055759   -0.033029    0.152806
   2.088000   0.000000   2.088000    -0.055759   -0.149812   -0.662933
   0.000000   2.088000   2.088000     0.102597    0.033029    0.662933

 8 f  =    2.738963 THz     17.209413 2PiTHz   91.361973 cm-1    11.327445 meV
           X          Y          Z          dx          dy          dz
   0.000000   0.000000   0.000000     0.177086    0.535721    0.394746
   2.088000   2.088000   0.000000    -0.157676    0.028511   -0.394746
   2.088000   0.000000   2.088000     0.157676   -0.535721   -0.012013
   0.000000   2.088000   2.088000    -0.177086   -0.028511    0.012013

 9 f  =    2.738963 THz     17.209413 2PiTHz   91.361973 cm-1    11.327445 meV
           X          Y          Z          dx          dy          dz
   0.000000   0.000000   0.000000    -0.106646   -0.369637    0.413688
   2.088000   2.088000   0.000000    -0.352880   -0.149143   -0.413688
   2.088000   0.000000   2.088000     0.352880    0.369637   -0.184633
   0.000000   2.088000   2.088000     0.106646    0.149143    0.184633

10 f/i=    0.000000 THz      0.000001 2PiTHz    0.000003 cm-1     0.000000 meV
           X          Y          Z          dx          dy          dz
   0.000000   0.000000   0.000000    -0.048248   -0.127059   -0.481174
   2.088000   2.088000   0.000000    -0.048248   -0.127059   -0.481174
   2.088000   0.000000   2.088000    -0.048248   -0.127059   -0.481174
   0.000000   2.088000   2.088000    -0.048248   -0.127059   -0.481174

11 f/i=    0.000000 THz      0.000001 2PiTHz    0.000003 cm-1     0.000000 meV
           X          Y          Z          dx          dy          dz
   0.000000   0.000000   0.000000     0.448013   -0.221585    0.013589
   2.088000   2.088000   0.000000     0.448013   -0.221585    0.013589
   2.088000   0.000000   2.088000     0.448013   -0.221585    0.013589
   0.000000   2.088000   2.088000     0.448013   -0.221585    0.013589
```

```
 12 f/i=    0.000000 THz      0.000001 2PiTHz    0.000004 cm-1     0.000000 meV
          X          Y          Z          dx          dy          dz
     0.000000  0.000000  0.000000    -0.216695   -0.429833    0.135230
     2.088000  2.088000  0.000000    -0.216695   -0.429833    0.135230
     2.088000  0.000000  2.088000    -0.216695   -0.429833    0.135230
     0.000000  2.088000  2.088000    -0.216695   -0.429833    0.135230
```

Note three zero frequency modes and degeneracies in other modes.

## 6. Bulk reactions

One common application of supercell DFT is to look at the stability of bulk compounds.  AuCu system makes a nice example.  Consider compounds of form $Au_xCu_{1-x}$ using the FCC supercell above (called the $L1_2$ and $L1_0$ structures in the alloy literature, see http://cst-www.nrl.navy.mil/lattice/alloys/aucu.html).  Calculate "formation energies" for reactions

$x$ Au (s) + (1-$x$) Cu (s) → $Au_xCu_{1-x}$

and plot against x.  Use 6x6x6 k points, 350 eV cutoff, PAW potentials, gradient optimization of supercells and atom positions.
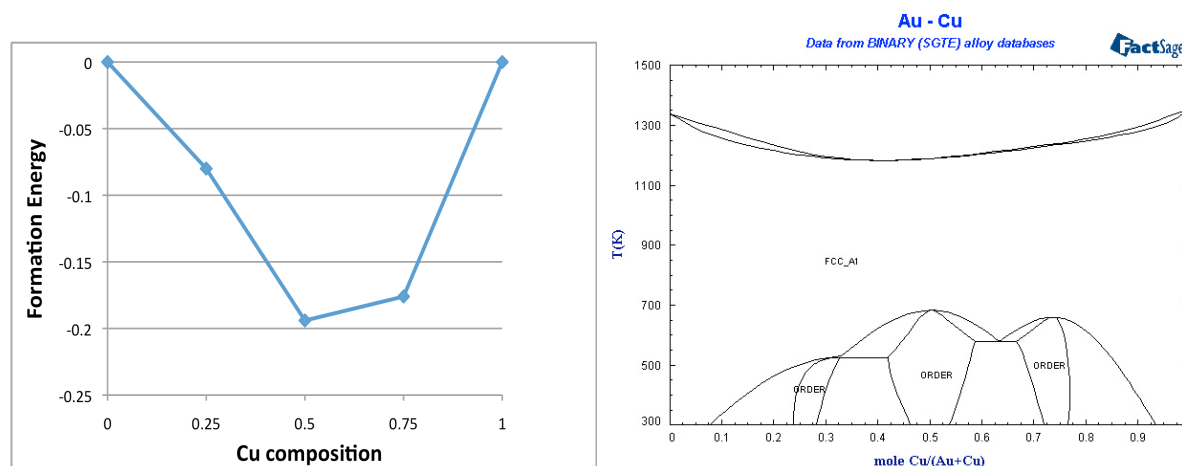


According to this, AuCu and $AuCu_3$ are stable structures, $Au_3Cu$ is not.  Phase diagram shows that this is not correct.  Probably a consequence of insufficiently converged computational parameters.

## 7. Other structures

Many, *many* known crystal structures (see e.g. http://cst-www.nrl.navy.mil/lattice/).  Using DFT to calculate bulk structures, stability, phonon and electronic spectra, …, is now a cottage industry.

## 8. Visualization tools that may be helpful:

vmd: http://www.ks.uiuc.edu/Research/vmd/
Vesta: http://www.geocities.jp/kmo_mma/crystal/en/vesta.html
XCrysDen: http://www.xcrysden.org/