Johnson Labs   (abinit for CE and how to do CE --- using CE-toolkit)
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PART 1 ABINIT –
   Cu k-points convergence and c/a distortion for fcc ordered $L1_0$ CuAu

(1) First, we want to explore the importance of k-point sampling to get converged total energy ('*etotal*' in ABINIT). Do this for fcc Cu at fixed lattice constant $a = 3.677 A$ and plane-wave energy cutoff *ecut* = 120 *Ry*.
   i)   If not already done so, source the *mcc.cshrc* from *~/mcc-adm/public_html*:
          cat /nmnt/home2/m/mc/mcc/mcc-adm/mcc.cshrc >> .cshrc
          source .cshrc
   ii)   Copy *Johnson-abinit.tar* and unpack in your local */tmp* directory
          cp /nmnt/home2/m/mc/mcc/mcc-adm/public_html/ Johnson-abinit.tar ./
   iii)   Untar input files: *tar -xvf Johnson-abinit.tar*

(A) Calculate total cohesive energy, *etotal*, for Monkhorst-Pack k-meshes of *4x4x4* and *8x8x8*. To do this, simply modify the given input file, *FCC_Cu.in*, to alter the lines controlling the Monkhorst-Pack division, i.e., *ngkpt 4 4 4 , ngkpt 8 8 8.* and, finally, *ngkpt 12 12 12*.
          The Cu k point convergence your WORKING DIRECTORY *~/tmp/Cu/*
          Run the code, using: *abinis < FCC_Cu > /dev/null &*
          Make sure you copy outputs to other names to avoid overwriting data.

Important note: While waiting for *ngkpt   12 12 1*2, which alone takes about 10 minutes for just one lattice constant*, start the analytic part (See #3) of exercise involving cluster expansion for near-neighbors using DFT calculated data*.
Second note*:* When part (1) has completed running, do part (B and C) below. Then start exercise #2 such that when it is set up and running, finish the analytic work in #3.

(B) Using gnuplot, plot *etotal* versus the x-component of *ngkpt (*number of division per k_x). Here is data to complete plots (it is too CPU intensive to run all this for lab):
          Hartree   *Nx Ny Nz*
          -44.04249   *16 16 16*
          -44.04251   *20 20 20*
          -44.04252   *24 24 24*

(C) From plot, what k-mesh provides convergence to ~*0.3 mRy*? From morning lecture, what plane-wave energy cutoff, *ecut*, provides similar convergence?

For metallic alloys, now you have some appreciation for the care needed to obtain "reliable" formation enthalpies for thermodynamic modeling.

(2) **Structural relaxations for $L1_0$ CuAu c/a.**   Note that both Cu ($a = 3.677 A$) and Au ($a = 4.162 A$) are cubic structures with lattice constants determined by minimizing

volume (or lattice constant) using *ABINIT*. But, most ordered alloy unit cells are not cubic and structural parameters must be found that minimize the total energy.

As a example, $L1_0$ ordered CuAu (having layers of Cu and Au along z-axis, see figure) can be represented as a *body-centered tetragonal* (bct) with 2 atoms, where x-y plane along the cube axes has lattice contant *a* and c-axis has possible tetragonal *c/a*. (To see this, draw two adjacent $L1_0$ 4-atom cells. Connect the two corner atoms and two face atoms in the top and bottom z-planes such that the original face atom that is in between is in a body-centered position in a cell rotated by 45 degrees from fcc lattice vectors.)

> Show that $L1_0$, as represented by bct cell in coordinates of the original fcc unit cell, has c/a = 1, while bcc has c/a =1/sqrt(2). This is called the **Bain transformation path**, as found in Martensites. Energy will be lowered.
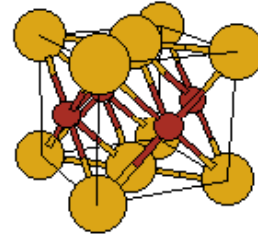
(A) Determine c/a by calculating energies along the Bain path. Structural parameters can often, but not always, be estimated from coarse k-points and lower *ecut* than fully converged values. So, for four c/a values (bcc, fcc, and two in between) calculate the optimal *c/a* for fixed *a* and *b (a=b)*?

Use a 4x4x2 k-mesh and given *a* = *b* = *4.059 A*. For *ecut*, a reduced value of *80 Ry* will suffice for rapid convergence (and limit CPU). Vary *c* for a few test cases, between a range of values: *c_low = (1/√2)*a* (for bcc) up to *c_high = a*.

In "***FCC_CuAu.in***", change the lines "*acell*" for a series of data: "*ndtset 4*"
        acell1 4.059 4.059 2.870 Angstr   # This is bcc. (c = 2.870 = 4.059 /sqrt(2))
        acell2 4.059 4.059 ????? Angstr
        acell3 4.059 4.059 ????? Angstr
        acell4 4.059 4.059 4.059 Angstr   # This is fcc (c =4.059 /1).

The code will automatically generate energies for all four structures using:
        WORKING DIRECTORY *~/tmp/CuAu/*
        abinis < FCC_CuAu > /dev/null &
(remember, avoid overwriting your outputs by moving files to new names.)

Using gnuplot, plot the results: *etotal* versus *c/a*. **What is the minimum c/a?**
How much is the energy reduced by structural relaxation?
 Recall there is none in the cubic L12 alloys, by symmetry.

Please note that if you wanted to use the resulting energies for thermodynamics, then a careful convergence of total energy (and minimization of structural parameters *a and c*) versus k-points is required, as in part I.

                But you now get the idea!

Analytic Cluster Expansion (following original Connolly-Williams paper)

(3) Perform analytically a cluster expansion for near-neighbors only (i.e., *empty, point, pair, triplet and tetrahedron* clusters) using DFT calculated data.

First, ABINIT energies of relaxed Cu, $L1_2$ Cu_3Au, $L1_0$ CuAu, $L1_2$ Au_3Cu, and Au are:

fcc	c	total energy (eV/atom)
Au	0.00	−899.15897
Au_3Cu	0.25	−974.02126
CuAu	0.50	−1048.87730
Cu_3Au	0.75	−1123.68897
Cu	1.00	−1198.46585

(A) What are the five formation energies (in meV/atom) for ordered fcc Cu-Au systems?

(B) With these formation energies, calculate the cluster correlation functions for fcc-based Cu, $L1_2$ Cu_3Au, $L1_2$ Au_3Cu, and Au, as done in lecture for $L1_0$. Take Cu as (+1) spin and Au as (-1). Recall that correlation vector for *empty, point, pair, triplet and tetrahedron* clusters in $L1_0$ are, respectively, [1, 0, −1/3, 0, 1]. You need four more to get the correlation matrix.

(C) The inverse of the correct correlation function (a matrix) is:

$$\Phi^{-1} = \frac{1}{16}\begin{pmatrix} 1 & 4 & 6 & 4 & 1 \\ 4 & 8 & 0 & 8 & 4 \\ 6 & 0 & -12 & 0 & 6 \\ 4 & -8 & 0 & 8 & -4 \\ 1 & -4 & 6 & -4 & 1 \end{pmatrix}$$

What are the interactions J_{0-4} for the clusters based upon the ABINIT total energies? Based on magnitude, how do the interactions fall with order, starting with pairs (J_0 is zero of energy and J_1 is chemical potential)?

(D) What is the formation energy of homogeneously "disordered" $Cu_{0.5}Au_{0.5}$ based upon these relaxed total energies? (Note: the disordered state correlations are products of the spin-variables, e.g. $\langle\sigma\sigma\rangle = \langle\sigma\rangle\langle\sigma\rangle = \langle\sigma\rangle^2$, or $(c_{Cu} - c_{Au})^2$. More generally, it is to power "n", where is the order of the cluster. If $(\Delta H_D - \Delta H_O) \sim k_B T_{o/d}$, as we suggested in lecture, what is $T_{o/d}$ (experimentally it is ~680 K)?

(E) Why should higher-order compact clusters not contribute to energy of the ordered states? What cases do higher-order compact clusters contribute?

(F) Considering that at varying composition the local clusters are made of various probabilities of Cu ($a = 3.677$ A) and Au ($a = 4.162$ A), can you think of why your results in (D) is wrong for Cu-Au system? The correct answer for enthalpy of mixing in disordered CuAu is about −4 meV! So, now, if $(\Delta H_D - \Delta H_O) \sim k_B T_{o/d}$, what is $T_{o/d}$?

ANSWER PAGE:

From part 1, problem 1:
(A) The correct ABINIT energies for a= 3.677 A at 120 Ry Ecut.
Note that Hartree = 2*Rydberg = 2*13.6 eV!

Hartree	Nx Ny Nz
-44.03639	4 4 4
-44.04134	8 8 8
-44.04233	12 12 12
-44.04249	16 16 16
-44.04251	20 20 20
-44.04252	24 24 24

(B) Hence, for sub-mRy accuracy, need minimally 12 x 12 x 12 for Cu. (see plot below)
(C) From lectures, since ABINIT does not use Ultrasoft PP, need 160 Ry (80 Hartree)
energy cutoff for required accuracy!   Below is output of ABINIT (in Hartrees).
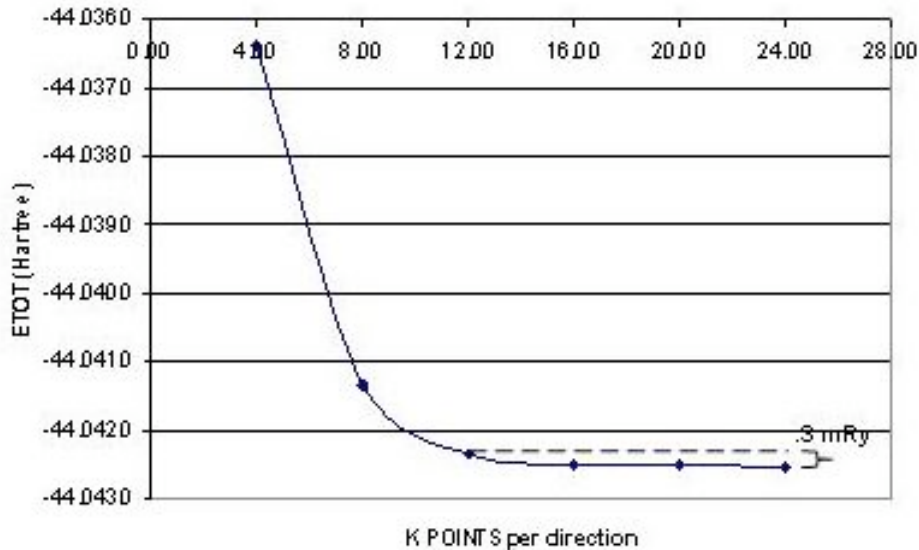
From part 1, problem 2:
(A) The c/a = 0.913, so $L1_0$ CuAu is distorted substantially from ideal fcc.

From part 1, problem 3:
(A) The formation energies in same order as energies given are:

fcc	c	Formation Energy (meV/atom)
Au	0.00	0.0
Au_3Cu	0.25	−35.6
CuAu	0.50	−64.9
Cu_3Au	0.75	−49.8
Cu	1.00	0.0

(B) The correct correlation for the analytic cluster expansion is:

$$\Phi = \begin{pmatrix} 1 & 1 & 1 & 1 & 1 \\ 1 & 1/2 & 0 & -1/2 & -1 \\ 1 & 0 & -1/3 & 0 & 1 \\ 1 & -1/2 & 0 & 1/2 & -1 \\ 1 & -1 & 1 & -1 & 1 \end{pmatrix}$$

(C) The interactions J_{0-4} (in meV) for the clusters are, using

$$J = \Phi^{-1}E \qquad \text{with} \quad \Phi^{-1} = \frac{1}{16} \begin{pmatrix} 1 & 4 & 6 & 4 & 1 \\ 4 & 8 & 0 & 8 & 4 \\ 6 & 0 & -12 & 0 & 6 \\ 4 & -8 & 0 & 8 & -4 \\ 1 & -4 & 6 & -4 & 1 \end{pmatrix},$$

$J0 = -45.7$ (energy zero), $J1 = -7.1$ (chemical potential), *J2 = +48.7, J3 = 7.1 and J4 = –3 meV*. As $J2 > J3 > J4$, there is rapid convergence of the cluster expansion here, as physically must be the case because this is nothing more than a *cumulant-type expansion* of correlations. Note that above phase transitions the correlations decay exponentially in distance, e.g., the pair correlation $<\sigma_i\sigma_j>-<\sigma_i><\sigma_j>$ describe Short-Range Order, which extends only locally.

(D) Since $<\sigma\sigma> = <\sigma><\sigma> = <\sigma>^2$, or $(c_{Cu} - c_{Au})^2$, the correlations are all zero on average in the disordered phase at 50% Au. Hence $J_0 = -45.7$ meV is the enthalpy of the disordered phase at 50%, in this example. If $(\Delta H_D - \Delta H_O) \sim k_B T_{o/d}$, so $k_B T_{o/d} \sim (-46 + 66)$ meV $=20$ meV, so that $T_{o/d}, \sim 230$ K. Experimentally it is ~680 K, so prediction is **bad**!

(E) Ordered states do not exihibit local clustering. So J4 represents segregated Cu or Au, which do not happen in ordered state except with small probability (less than c^4). Higher-order compact clusters contribute for clustering alloys.

(F) The correlations Φ's are V-independent, but J(V) are not. Local relaxations of the clusters were not considered, i.e. minimization of each structure (here disordered state) must include relaxation effects. (See appropriate references and lectures, e.g., Terakura et al., Ozolins et al., and van der Walle et al..) The correct answer for enthalpy of mixing in disordered CuAu is about –4 meV! So, now, if $(\Delta H_D - \Delta H_O) = (-2 + 66)$ meV $\sim k_B T_{o/d}$, so $T_{o/d} \sim 720$ K. Result is now much more realistic and close to experiment, even without phonons.

Upcoming lectures will focus on this strain, relaxation, phonons, etc.