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SMR.1165 - 25

WORKSHOP ON CALCULATION OF MATERIAL PROPERTIES USING TOTAL ENERGY AND FORCE METHODS AND *AB INITIO* MOLECULAR DYNAMICS

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"Structural phase transitions" practice the calculations

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Practice the calculations

- Get D8-1
  i) mkdir /tmp/*user*
  *ii)cd/tmp/*user
  iii) cp ~ppw/D8-1.tar.gz .
  iv) Un-packing by gunzip -c DX.tar.gz| tar xvf -
  you will get:

  - /bin contains the executables *start*, *fhi98md*, *tp* and *vcalc.x*.
  - /doc contains the text and postscript files
  - /scripts contains the shell scripts *run-Si_di_bulk-lda.scr*, *run-Si_di_bulk-gga.scr*, *run-Si_bt_bulk-lda.scr*, *run-Si_bt_bulk-gga.scr*.
  - /input contains the pseudopotentials
  - /output contains the calculation examples
  - /tp-gga is used for calculating the transition pressure with gga
  - /tp-lda is used for calculating the transition pressure with lda
  - /work will be used for running the calculations
- Run *run-Si_di_bulk-lda.scr* for the diamond Si
  cd /D8-1/work
  cp ../scripts/run-Si_di_bulk-lda.scr .
  We use `foreach` to handle multiple lattice constants within

one run. Because suitable lattice constants are around the experimental value 10.26 a.u. = 5.43 Å, we may calculate the energy for 6–8 lattice constants which have a lattice spacing *e.g.* 0.15 a.u., thus *e.g.*, `foreach C (10.55 10.40 10.25 10.10 9.95 9.80 9.65)`. The variable `CDA` is the value of c/a. For the diamond structure, it is $\sqrt{2}$ or `1.41421356237`. We use $4\times4\times2$ **k**–point folding. Execute the calculation using `./run-Si_di_bulk-lda.scr`

- Run *run-Si_di_bulk-gga.scr* for the diamond Si
  This run is just replacing LDA with GGA; i) replace pseudo potential with `si:pbe:ham.cpi`, ii) change `i_xc` = 4 (for PBE-GGA), iii) change the filename. You may get it from /scripts **command line**: cp */scripts/run-Si_di_bulk-gga.scr* .

- Run *run-Si_bt_bulk-lda.scr* for the β-tin Si
  For this run the diamond structure has to be replaced with the β-tin structure. Therefore one needs to i) change c/a ratio from $\sqrt{2}$ to 0.552, which is the experimental value, used since we don't have time to search for the optimal c/a; ii) lattice constants should be around 5.0 a.u., thus *e.g.* `foreach C (5.45 5.30 5.15 5.00 4.85 4.70 4.55)`; iii) **k**–point set should be changed to folding $4\times4\times6$, since the shape of the supercell has changed; and iv) change the output filename. Run first with LDA, so do the reverse of last point (pseudo potential, `i_xc`, filename). You may get it from /scripts

command line: cp */scripts/run-Si_bt_bulk-lda.scr* .

- Run *run-Si_bt_bulk-gga.scr* for the β-tin Si
  Again just replace LDA with GGA; i) pseudo potential `si:pbe:ham.cpi`, ii) `i_xc` = 4, iii) the filename. You may get it from /scripts **command line**: cp */scripts/run-Si_bt_bulk-gga.scr* .
- Analyze the results
  To get the results ready for calculating the transition pressure:

  ```
  cd /work
  ./vcalc.x <Si-diamond-lda.dat> ../tp-lda/ve_1.data
  ./vcalc.x <Si-diamond-gga.dat> ../tp-gga/ve_1.data
  ./vcalc.x <Si-bt-lda.dat>../tp-lda/ve_2.data
  ./vcalc.x <Si-bt-gga.dat>../tp-gga/ve_2.data
  ```

  To calculate the transition pressure:
  For the LDA case

  ```
  cd ../tp-lda
  cp ../bin/tp .
  cp ../input/tp.in .
  ./tp
  ```

  For the GGA case

  ```
  cd ../tp-gga
  cp ../bin/tp .
  cp ../input/tp.in .
  ./tp
  ```

  You will get `ve_1.plot`, `ve_2.plot` (fitting total energy results), `dH.plot` (enthalpy difference) and `zero.plot` (reference) in /tp-lda and /tp-gga.

- plot the figures
  Use the commands `xmgr ve_1.data ve_1.plot` and `xmgr ve_2.data ve_2.plot` to see the fitting results. Use `xmgr dH.plot zero.plot` to see the enthalpy difference and get the transition pressure (I got the results 10.1 GPa/LDA and 12.2 GPa/GGA).

Workshop on calculation of material properties using total energy and force methods and *ab initio* molecular dynamics, Trieste, 1999

Practical Session D8-2

Structural Phase Transitions of Magnesium Telluride : Wurtzite and NiAs phases

- Aim of the session

  To study structural phase transitions under **hydrostatic pressure** for elements and compounds of **any crystal symmetry**

- Copying the directory tree

  To get started,
  first go to */tmp* and create a new subdirectory *YOURDIR*
  then go to */tmp/YOURDIR*
  then copy the archive $D8-2.tar.gz$ there

```
cp ~ppw/D8-2.tar.gz .
```

Extracting this archive creates the following directories

  - /**scripts** contains the shell scripts *run.overall, run.rw, run.murn, run.MgTe.nias, run.MgTe.wurt*
  - /**output** will contain the output files
  - /**doc** contains a README file
  - /**pseudo** contains the pseudopotential files *mg:lda:tm.cpi, te:lda:tm.cpi*

  - **/work** can be used for running the calculations
  - **/input** contains the input files *input.param*
  - **/bin** contains the executables *fhi98start, fhi98md, murn, rwener*
  - **/src** contains the fortran files *latgen.f, atpos.special.f, rwener.f, murn3new.f*

- Calculating the total energies for Wurtzite and NiAs phases each for 5 different volumes (lattice constants)

First, you MAY like to read the README file placed in ./doc. However you will get most of the "what to do's" here anyway! Only to know the background of the problem, README can be useful.

To submit the run, which will calculate the energies for the Wurtzite and NiAs phases for MgTe, do the following:

```
cd /tmp/YOURDIR/work
../scripts/run.overall
```

This will take you about **30 minutes** so meanwhile read on please....

Note : There are 6 celldm variables in the *start.inp* file. First three (for phases to be described here) are lattice constant a, c/a, and u (please look at the structures, given along with this write-up). To save your time, we have tested the convergence for the number of k-points, Energy cutoff and other parameters. We have also optimised the a, c/a and u parameters. You are running here just the final **Total energy vs. volume** runs to get the curves you have heard in the lectures already. Please note that good experimental agreements are obtained (within 1-3 percent) for the experimental structures (Li et. al. PRL, 1995).

There are two source files, **latgen.f** and **atpos.special.f** in ./src directory

---

If you go through these files, you get idea about how to change these files (at a later time, not now!) for your **own** symmetries or crystal structures, if already that option is not there!

Please read the comments made in the files. Search for a variable **ibrav**. Each **ibrav** is responsible for **each different crystal structures** : surface or bulk.

- Run is done by now?

You may look into the files created in the ./output and ./work directories.

To get the final Murnaghan-fits for the **Total energy vs. Volume** plots directly on the display,

---

```
../scripts/run.rw
../scripts/run.murn
```

RED curve is for NiAs phase and BLUE for Wurtzite phase. Note the slightly lower energy minimum for the NiAs phase : which predicts that the ground state at standard temperature and pressure(STP) for MgTe is a NiAs phase!

Now you can change the parameters and run your own tests. May be you would want to see how stable is NaCl or CsCl structure with respect to the Wurtzite phase here? And get the transition pressure between the two, if there's any!

You already heard from afternoon's talk, how to calculate transition pressure, so........

Questions:

1. Can you guess what should be the sign of the transition pressure of the Wurtzite phase to the NiAs phase for MgTe? What it is for Si, diamond to β-Tin phase?

2. Can you think why for certain semiconductors, certain structures are ground state phase, whereas in others, it is another structure? For example CuCl, ground state at STP is NaCl, whereas for GaAs it is Zinc Blende, where both are isocoric?

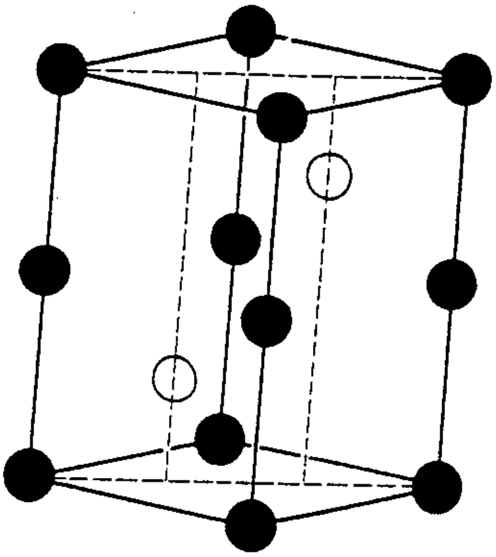
NiAs

but the axial ratios and values of u are so different that the resulting atomic groupings are not similar.

These positions for the NiAs arrangement are:

$$\begin{array}{lll} R: & (2a) & 000;\ 0\,0\,\tfrac{1}{2} \\ X: & (2b) & \tfrac{1}{3}\,\tfrac{2}{3}\,u;\ \tfrac{2}{3},\tfrac{1}{3},u+\tfrac{1}{2} \end{array}$$

where R is the metallic and X the metalloid element (Fig. III,15).



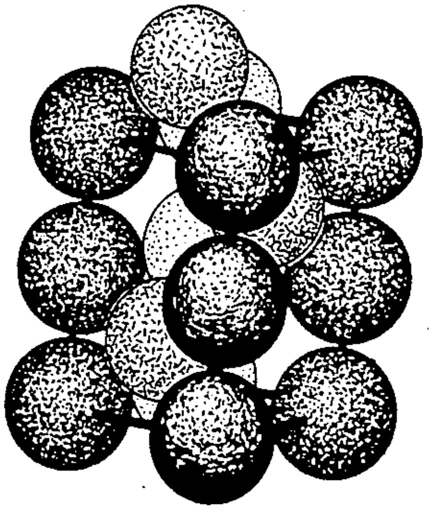


Fig. III,15a (left). The arrangement of the atoms in the hexagonal cell of NiAs. Black circles represent the nickel, open circles the arsenic atoms.

Fig. III,15b (right). A perspective packing drawing of the NiAs arrangement. The nickel atoms are dot-shaded, the arsenic atoms are line-shaded.

With $u = \tfrac{1}{4}$, each X atom is surrounded by six equidistant R atoms situated at the corners of a right trigonal prism. Each R atom on the other hand has eight close neighbors, six of which are X atoms while the other two are those R atoms immediately above and below it. It is usual to find the more metallic atom of a compound in the R position, but this is not necessary and thus there arises the possibility of an anti as well as the normal NiAs structure. A few of these anti arrangements are now known.

In contrast with the ZnO arrangement (III,c2) with its very constant axial ratio, c/a for NiAs-like crystals ranges between 1.2 and 1.7. The composition of many of these crystals is highly variable, and this excess of one or the other kind of element leads to large variations in the observed cell dimensions. Both these factors must be borne in mind when evaluating the data of Table III.7, which lists the various

Wurtzite

2. Halides, oxides, nitrides, etc. of transitional and less electropositive metals. With many it cannot be inferred that ionization is sufficiently complete to give meaning to a calculated radius-ratio. An additivity of interatomic distances has, however, been observed and this is usually expressed through the use of nonionic, "tetrahedral radii." In many of the compounds and structures for which such radii are approximately valid there are X–X as well as R–X close contacts and it is these that give the basis for the atomic radii chosen.

III,c2. The atoms in the two-molecule hexagonal unit of the *zincite*, ZnO, arrangement are in the positions:

$$\begin{aligned} R&:\ 000;\ {}^1/_3\,{}^2/_3\,{}^1/_2 \\ X&:\ 00u;\ {}^1/_3,{}^2/_3,u+{}^1/_2 \end{aligned}$$

which are derived from two sets of special positions of C_{6v}^4 ($C6mc$):

$$(2b)\quad {}^1/_3\,{}^2/_3\,v;\ {}^2/_3,{}^1/_3,v+{}^1/_2$$

by a change of origin to the point ${}^2/_3\,{}^1/_3\,0$. The axial ratios of crystals with this structure have always been close to $c/a = 1.63$ and the parameter u to 0.375. Under these circumstances (Fig. III,13), each atom has about it a tetrahedron of atoms of the opposite sort just as in the cubic ZnS arrangement.