First-Principle Calculations

Lab Test Report

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❖ Objective:

Phonon Band Structure Calculation of a TiNiSn system

❖ Procedure:

A. Structural Optimization:

1. Please refer to the publication titled "***Electron-dominated thermoelectric response in MNiSn***" by Gandi and Schwingenschlögl (2016) and the accompanying README file.
2. Download the **Standard Solid-State Pseudo-potentials (SSSP)** from 'https://www.materialscloud.org/discover/sssp/table/efficiency' for the elements Ti, Ni and Sn.
    - These are the **ultrasoft potentials** and correction used here is **nonlinear core correction**
    - **Perdew-Burke-Ernzerhof (PBE)** exchange-correlation functionals are used
    - Potentials used for the calculations are:
        - **ni_pbe_v1.4.uspp.F.UPF**
        - **ti_pbe_v1.4.uspp.F.UPF**
        - **Sn_pbe_v1.4.uspp.F.UPF**
        - For further information, refer to the following website:
            - https://www.physics.rutgers.edu/gbrv/

3. After downloading pseudo-potentials, transfer them to a newly formed folder named '**pseudo**'. Additionally, create a folder called '**tmp**' to hold all the output files, which will be used as the '*outputdir*'.

4. **Self-consistent field calculations:**
    - The real wavefunction of a system is typically too complex to find directly, but a simpler wavefunction can approximate it.
    - This then enables the electronic Schrödinger equation to be solved numerically.
    - The self-consistent field method is an *iterative method* that involves selecting an approximate Hamiltonian, *solving the Schrödinger equation to obtain a more accurate set of orbitals*, and then solving the Schrödinger equation again with theses *until the results converge*.
5. To do this task, generate the'scf.in' file and include folders for output and pseudo. The input parameters are explained here, along with the input file 'tinisn.scf.in'.
    - As the structure of TiNiSn is **cubic FCC**, *ibrav = 2*
    - As the **lattice parameter is 5.941**, convert it toan atomic unit, *celldm(1) = 11.227*
    - *nat and ntype = 3*, as there are **three different elements**
    - Add atomic species Ti, Ni, and Sn, there **atomic masses**, and respective **pseudo-potential files**
    - Add atomic positions as described in the paper according to **wyckoff positions** as mentioned for Ti, Ni and Sn which are **4b, 4c and 4a**, respectively
        - Reference: [Wyckoff Positions of Space Groups]
    - Add k-point mesh at the end, which here is '**12x12x12**' for the increased accuracy of the calculations
    - For further information related to input parameters, refer to the following website: https://www.quantum-espresso.org/Doc/INPUT_PW.html
    - Input file for the reference: (*which is used in the calculations*)

```
&control
```

```
                calculation='scf'
                prefix='tinisn',
                pseudo_dir =
          '/home/user11/Downloads/lab-test/pseudo'
                outdir='/home/user11/Downloads/lab-test/tmp'

           /
           &system
                ibrav= = 2, celldm(1) =11.227 , nat = 3, ntyp=
          3,
                ecutwfc =30.0

           /
           &electrons
           /

          ATOMIC_SPECIES
           Ti  47.867  ti_pbe_v1.4.uspp.F.UPF
           Ni  58.69354  ni_pbe_v1.4.uspp.F.UPF
           Sn  118.71  Sn_pbe_v1.uspp.F.UPF

          ATOMIC_POSITIONS
           Ti 0.50 0.50 0.50
           Ni 0.25 0.25 0.25
           Sn 0.00 0.00 0.00

          K_POINTS automatic
           12 12 12 0 0 0
```

6. Execute the below code for structural optimisation.

```
pw.x < tinisn.scf.in > tinisn.scf.out
```

B. Phonon Dispersion Calculations

7. **ph.x :** Calculates phonon frequencies and displacement patterns, dielectric tensors, and effective charges (*uses data produced bypw.x, which is stored in the 'tmp' directory*)
8. Create the 'tinisn.ph.in' file, change output directory and add masses of all the elements
   (Input parameters are explained in the code itself.)

```
phonons of tinisn
 &inputph
  tr2_ph=1.0d-12,  #Threshold for self-consistency.
  prefix='tinisn',
  ldisp=.true.,
  nq1=2, nq2=2, nq3=2  #Parameters of the Monkhorst-Pack grid
(no offset) used when ldisp=.true.
  amass(1)= 47.867   #Atomic mass [amu] of each atomic type.
  amass(2)= 58.69354
  amass(3)= 118.71
  outdir='/home/user11/Downloads/lab-test/tmp'
  fildyn='tinisn.dyn', #File where the dynamical matrix is
written.
  recover=.true.
 /
```

9. For further information, refer to Input File Description - ph.x
10. Execute the code for *phonon dispersion calculation.*

```
ph.x < tinisn.ph.in > tinisn.ph.out
```

C. Post-processing for real-space force constants

11. **q2r.x** : Calculates Interatomic Force Constants (IFC) in real space from dynamical matrices produced by **ph.x** on a regular **q**-grid
12. Create the file 'q2r.in' for post processing of real-space force constants (Input parameters are explained in the code itself.)

```
&input
   fildyn='tinisn.dyn', zasr='simple', flfrc='tinisn222.fc'
 /

# filedyn ⇒ file where the dynamical matrix is written
# zasr ⇒ Indicates the type of Acoustic Sum Rules used for the
Born
effective charges.
# flfrc ⇒ Output file containing the IFC in real space (must be
specified)
```

13. Execute the below code for the calculation of IFCs

```
q2r.x < q2r.in > q2r.out
```

14. For further information, refer to q2r.x: input description
15. **matdyn.x** : produces phonon frequencies at a generic wave vector using the IFC file calculated by **q2r.x**; may also calculate phonon DOS, the electron-phonon coefficient λ, and the function $\alpha^2F(\omega)$
16. Calculate the phonon band structure along the path of interest (given in the paper or in the reference file). Create the 'matdyn.in' and Edit the path according to paper

```
&input
      asr='simple',  amass(1)=47.867 , amass(2)=58.69354  ,
amass(3)=118.71
# asr ⇒ Indicates the type of the Acoustic Sum Rule imposed
      flfrc='tinisn222.fc', flfrq='tinisn.freq',
q_in_band_form=.true.,
```

```
 /
 5
  gG  51
  X   51
  W   51
  L   51
  gG  51

# flfrc ⇒ File produced by q2r containing force constants
# flfrq ⇒ output file for frequencies
# q_in_band_form ⇒ if .true. The q points are given in band
form: only the first and last point of one or more lines
are given.
```

17. Execute the below code for calculations along the path of interest

```
matdyn.x < matdyn.in > matdyn.out
```

18. For further information, refer to [matdyn.x: input description]
19. To plot the band structure, create the file 'plotband.in'

```
tinisn.freq # Frequency data file
0 310       # Minimum and maximum energies on the plot (y-axis)
freq.plot
freq.ps     # Output files
0.0         # fermi energy
50.0 0.0    # Smallest step in energy (y-axis)
```

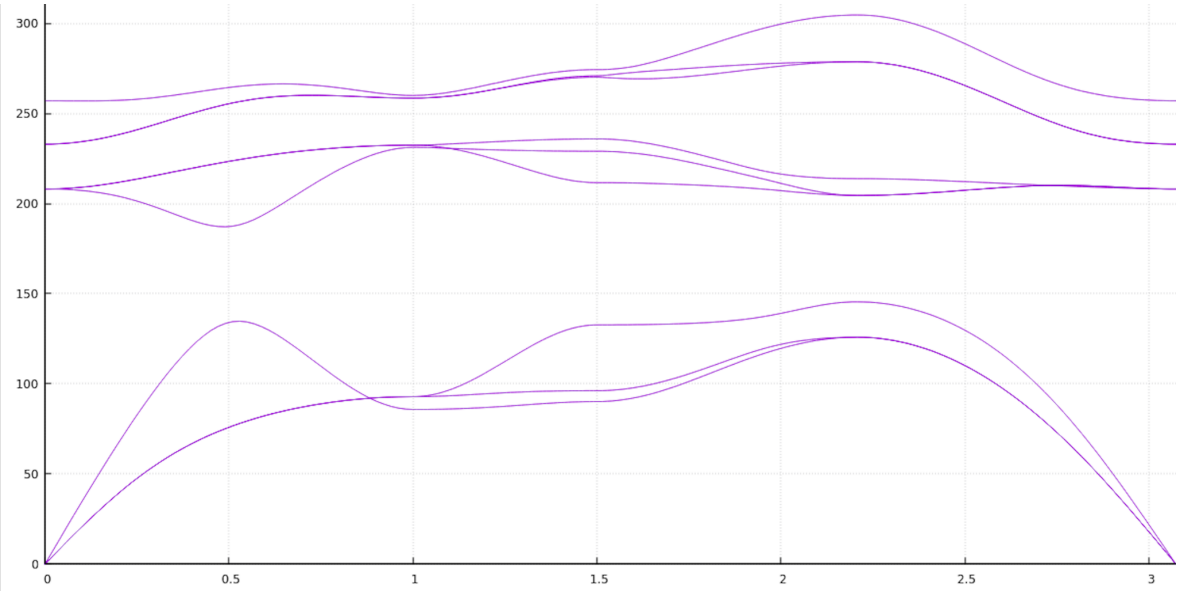
20. Execute the below code for calculations along the path of interest

```
plotband.x < plotband.in > plotband.out
```

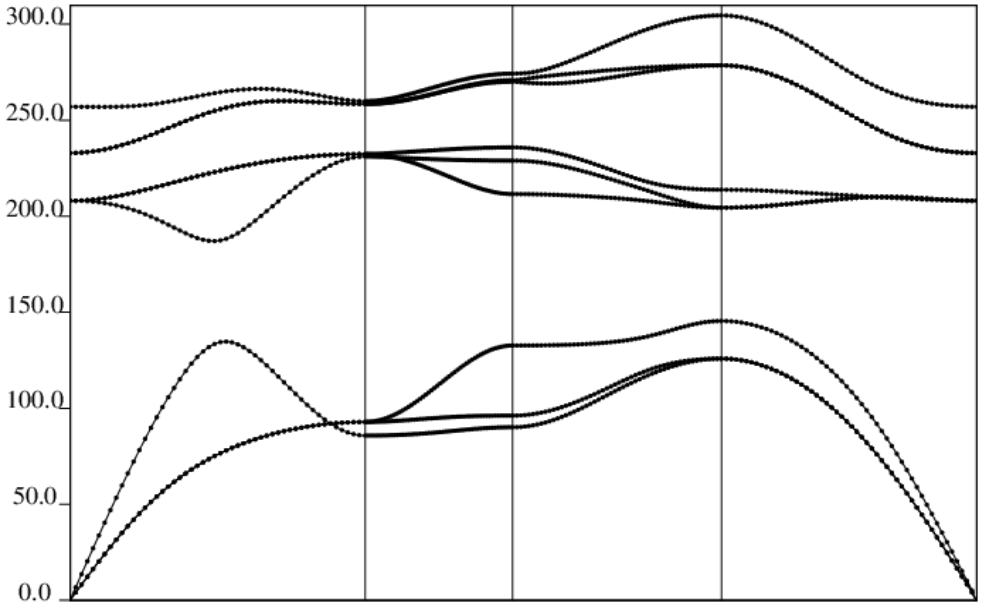
21. For further information, refer to [How to make input file for "plotband.x" in QUANTUM ESPRESSO? | ResearchGate]

❖ Observations :

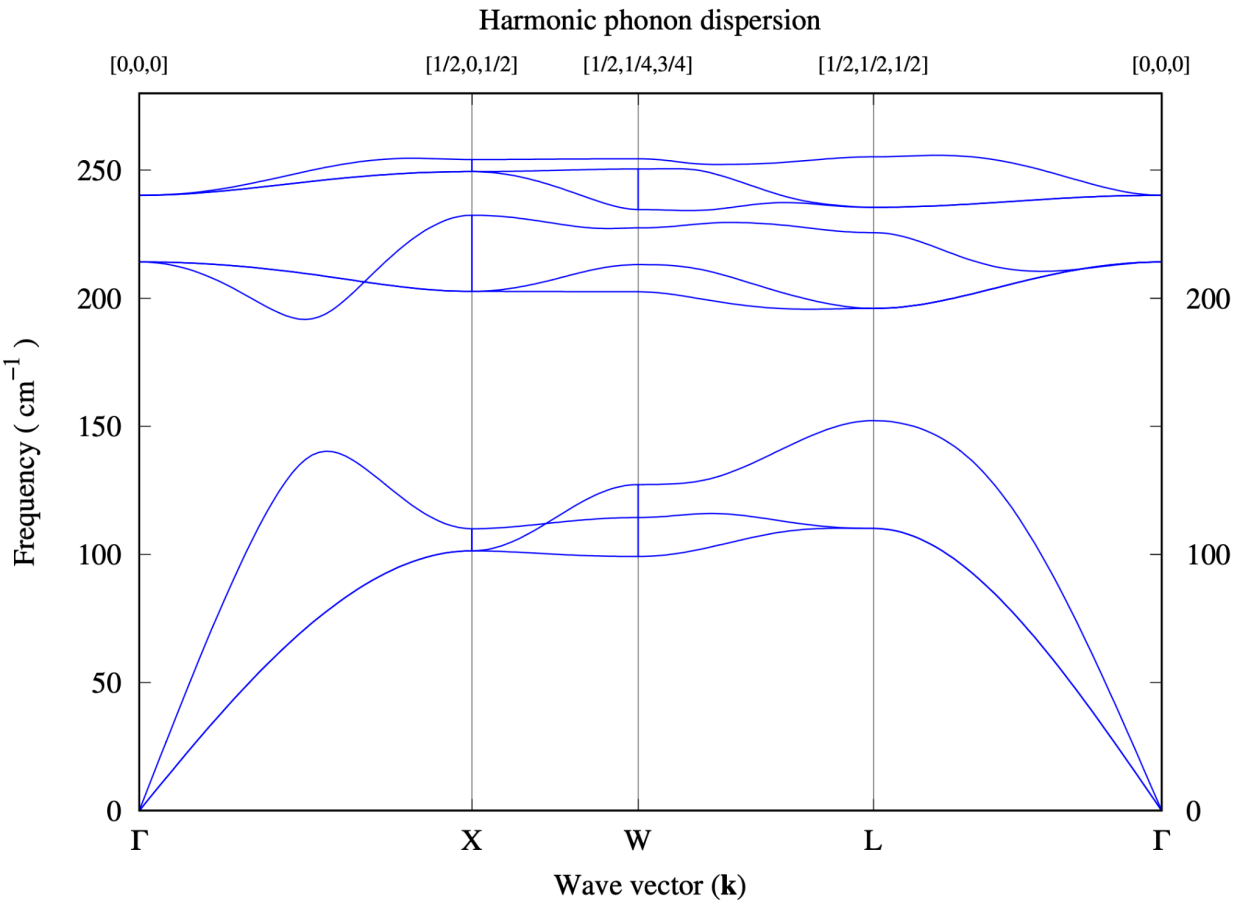
There are three band structures attached below, one of which is reference structure and the others are calculated from the above procedure (***Path is same in all the cases***)



(*The above band structure is drawn with GNUPLOT.*)



(*The above band structure is drawn using 'plotband.x'.*)



(*The reference band structure provided with the exercise.*)

- From the above schematics, it is clear that the calculated and reference band structures are similar (*Minor difference in the structure is due to the parameters used*)

❖ Purpose :

Use of the Phonon Band Structure Calculations:

Phonon band structure computations are essential for analysing crystalline materials' vibrational properties, especially in condensed matter physics and materials science. Phonons, quantized vibrational modes in a crystal lattice, reveal material behaviour through their band structure. Phonon band structure computations serve these tasks and provide these insights

- ***Vibrational Properties:*** Phonon band structures characterise crystal vibrations. The frequency, amplitude, and polarisation of vibrations at different places in the Brillouin zone (the reciprocal lattice's basic unit) are included.
- Predicting material ***thermal conductivity*** requires understanding phonon dispersion relations. Designing thermally efficient materials requires knowledge of phonon dispersion behavior.
- ***Thermal Expansion:*** Phonon band topologies affect material thermal expansion. Phonon frequencies and dispersion relations reveal how a material expands or contracts when heated or cooled.
- ***Phonon-Phonon Interactions:*** Phonon band structures explain phonon interactions. This is crucial for studying phonon scattering, which is crucial for understanding material heat transport.
- ***Anharmonicity:*** Phonon band topologies reveal crystal anharmonic effects. knowing thermal characteristics requires knowing anharmonicity, which affects phonon-phonon scattering and thermal transport.
- ***Electronic-Phonon Interactions:*** Superconductivity and other physical processes depend on electron-phonon coupling. Phonon band structures help predict and understand these interactions.
- ***Crystal stability*** can be assessed using phonon calculations. Phonon modes with imaginary frequencies indicate instability, suggesting a phase change in the crystal structure.
- ***Materials development:*** phonon band structures help develop and discover materials. Researchers can adapt materials for high-temperature superconductors or thermoelectrics by studying their vibrational properties.

❖ Conclusion :

- We successfully calculated the phonon band structure of the TiNiSn system, which is quite similar to the reference phonon band structure.
- Further, this band structure can be used to get insightful information about the properties and structure of the TiNiSn system.

❖ References :

- Quantum Espresso
- Electron dominated thermoelectric response in MNiSn (M: Ti, Zr, Hf) half-Heusler alloys
- Materials Cloud
- ResearchGate

Thank You !!! 🙏🏽

The End