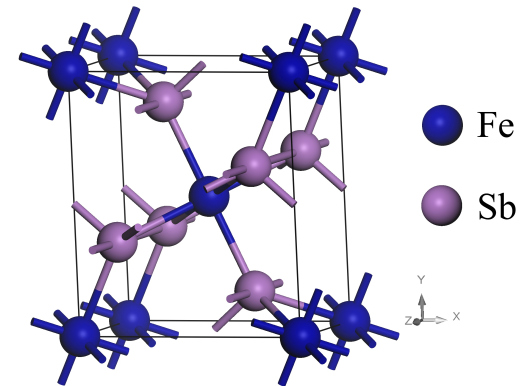
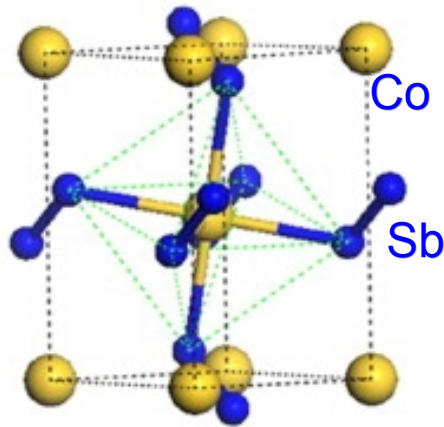


Electronic Structure and Lattice Dynamics Calculations of FeSb_2 and CoSb_2

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Introduction

- Basic ideas of Density Functional Theory (*DFT*)
- Approximations and implementation
- *DFT* in crystals, method of pseudopotentials
- Limitations of *DFT*
- *Quantum Espresso* package
- Electronic calculations on cobalt and iron antimony
- Density functional perturbation theory (crystal lattice dynamics)
- Phonon calculations of *CoSb₂* and *FeSb₂*

Quantum mechanics

$$\hat{H} \Psi = E \Psi$$

$\Psi = \Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ Many-electron wave function

$$\hat{H} = \sum_{\mu=1}^N \hat{H}_{\mu} + \frac{1}{2} \sum_{\mu=1}^N \sum_{\substack{\nu=1 \\ \nu \neq \mu}}^N \frac{e^2}{|\mathbf{x}_{\mu} - \mathbf{x}_{\nu}|}$$

Single electron term
(kinetic energy, nuclear
charge attractive energy)

Many-electron term
(Coulomb interaction)

3N-body problem



Density functional theory



The Nobel Prize in Chemistry 1998

"for his development of the density-functional theory"

"for his development of computational methods in quantum chemistry"



Walter Kohn

🏆 1/2 of the prize

USA

University of California
Santa Barbara, CA, USA

b. 1923
(in Vienna, Austria)



John A. Pople

🏆 1/2 of the prize

United Kingdom

Northwestern University
Evanston, IL, USA

b. 1925
d. 2004

Density functional theory

Hohenberg, Kohn:

- Universal energy functional of the electron density exists and it has a global minimum in the ground state of the system

$$E[n] = T[n] + \int d\mathbf{r} n(\mathbf{r}) V_{ext}(\mathbf{r}) + E_{int}[n]$$

- All properties can be expressed as a functional of electron density
- Functional $T[n] + E_{int}[n]$ is universal for for all systems of interacting particles

Difficulties:

- The form of universal functional is unknown
- It can not be minimized in terms of electron density

Kohn-Sham approach

1. Replacing difficult interacting many-electron system with an auxiliary system which is easy to solve
2. Problem of finding the universal functional reduce to finding of exchange-correlation functional

$$n(\mathbf{r}) \equiv n_{KS}(\mathbf{r})$$

Kohn-Sham orbitals

$$E_{KS}[n] = \sum_l \int d\mathbf{r} \psi_l^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 \right) \psi_l(\mathbf{r}) + \int d\mathbf{r} \rho(\mathbf{r}) V_{ext}(\mathbf{r}) + E_H[n] + E_{xc}[n]$$

$$n(\mathbf{r}) = \sum_{l \in occ} |\psi_l(\mathbf{r})|^2$$

$$E_{xc}[n] = ???$$

$$E_H[n] = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}$$

Approximations of exchange-correlation functional

1. Local density approximation (*LDA*), easy to generalize for spin systems (*LSDA*)

$$E_{xc}^{LSDA}[\rho] = \int \rho(\mathbf{r}) \varepsilon_{xc}^{unif}(\rho^\uparrow(\mathbf{r}), \rho^\downarrow(\mathbf{r})) d\mathbf{r}$$

2. Generalized gradient approximation (*GGA*)

$$E_{xc}^{GGA}[n] = \int d\mathbf{r} f(n^\uparrow, n^\downarrow, \nabla n^\uparrow, \nabla n^\downarrow)$$

Example of E_{xc} (LDA)

- It is calculated from the homogeneous electron gas using Monte-Carlo methods (in principle functional is universal)
- Most of the time problem is reduced to calculation of the potential

$$V_{KS} = V_{ext}(\mathbf{r}) + V_H + V_x + V_c = V_{ext}(\mathbf{r}) + \frac{\delta E_H[n]}{\delta n(\mathbf{r}, \sigma)} + \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r}, \sigma)}$$

$$\varepsilon_c = \frac{A}{2} \left\{ \log \left(\frac{x^2}{X(x)} \right) + 2 \frac{b}{Q} \arctan \left(\frac{Q}{2x+b} \right) - \frac{bx_0}{X(x_0)} \left[\log \left(\frac{(x-x_0)^2}{X(x)} \right) + \frac{2(b+2x_0)}{Q} \arctan \left(\frac{Q}{2x+b} \right) \right] \right\}$$

$$V_c = \varepsilon_c - \frac{1}{6} A \frac{c(x-x_0) - bxx_0}{(x-x_0)(x^2+bx+c)}$$

$$\varepsilon_x = -\frac{3}{4} \left(\frac{3}{\pi} (n_\uparrow + n_\downarrow) \right)^{1/3} = -\frac{3}{4} \left(\frac{3}{2\pi} \right)^{2/3} \frac{1}{r_s}$$

$$V_x = \frac{4}{3} \varepsilon_x = - \left(\frac{3}{2\pi} \right)^{2/3} \frac{1}{r_s}$$

Algorithm

1. We start from the initial electron density and calculate the Kohn-Sham potential

$$n^{in}(\mathbf{r}) \Rightarrow V_{KS}$$

2. Solve the Schrodinger equation

$$\left[-\frac{1}{2}\nabla^2 + V_{KS}\right]\psi_i(\mathbf{r}) = \epsilon_i\psi_i(\mathbf{r})$$

3. Calculate new electron density and start from the beginning

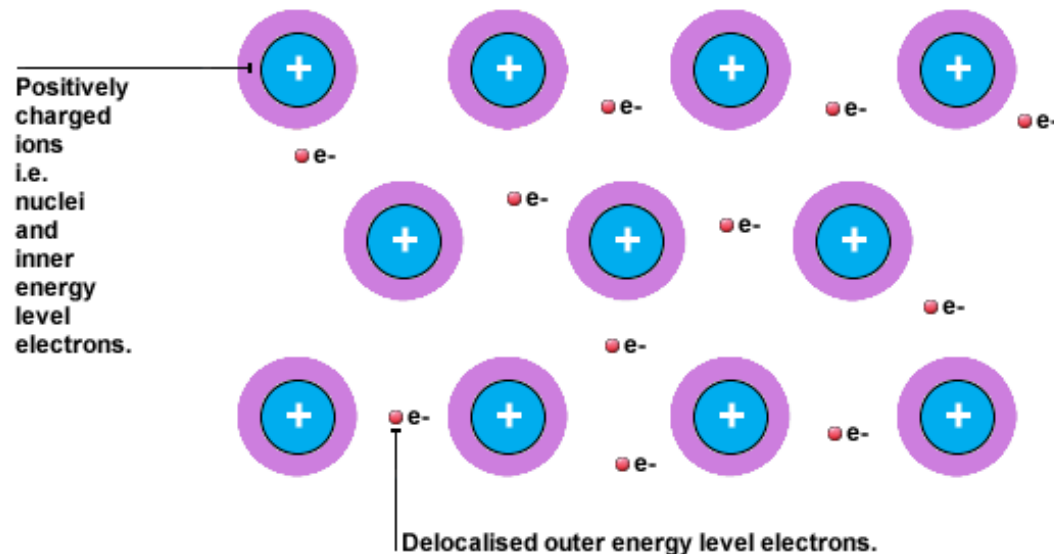
$$n^{out}(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2$$

Convergence condition:

$$\int d\mathbf{r}(\rho_{out}(\mathbf{r}) - \rho_{in}(\mathbf{r}))^2 < \varepsilon$$

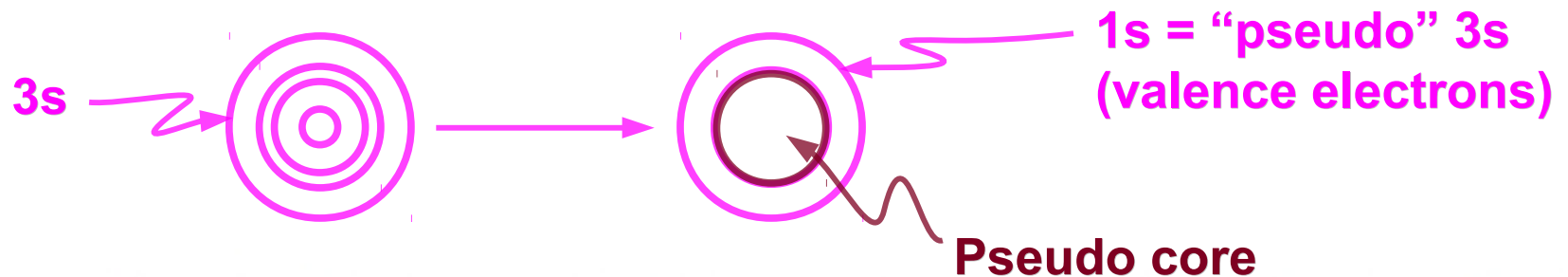
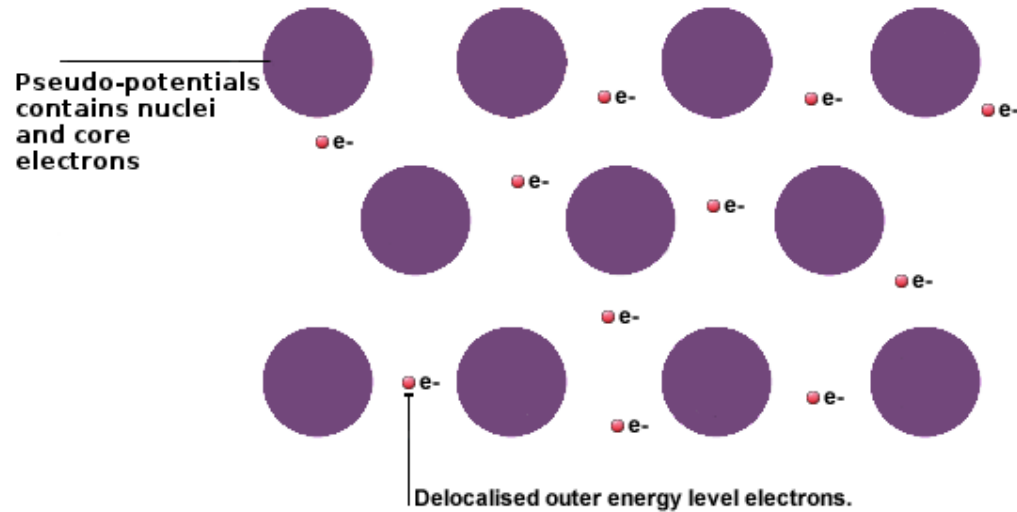
Density functional theory in crystals

- **Main problem** – large number of electrons around the nuclei
- **Inner electrons** – strongly coupled to the nuclei – well described with atomic-like orbitals
- **Valence electrons** – weakly coupled to the nuclei, determine bounds between molecules, electronic, optical and magnetic properties, etc. – well described with plane waves



Pseudo-potentials

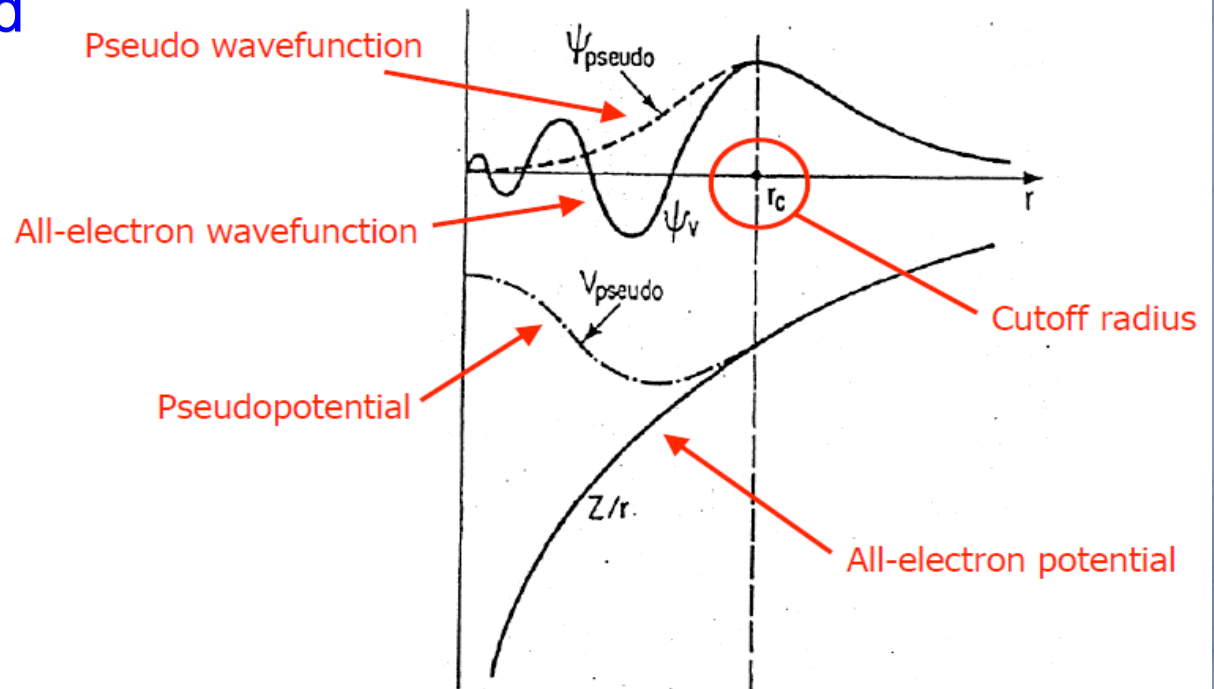
- Influence of all core electrons replace with pseudo-potential.
- Valence electrons are treated exactly.



Pseudo-potentials

Conditions for pseudo-potential to satisfy:

- All-electron potential and pseudo-potential must coincide outside radius of core electrons r_c
- All-electron wave function and pseudo wave function must coincide outside r_c
- Pseudo-potentials and pseudo wave functions are smooth



When DFT “works”

- It works excellent for metals and band insulators
- It works very well for semiconductors (with minor adjustments of pseudo-potentials even excellent)
- It does not describe Mott insulators and physics near the Mott metal-insulator transition (relevant for materials with partially filled f and d orbitals: cuprates, rare earth intermetallics and actinide, numerous transition metal oxides, iron based superconductors(?))

Quantum Espresso

<http://www.quantum-espresso.org/>

*Quantum opEn-Source Package for Research in
Electronic Structure, Simulation, and Optimization*

- Ground state calculations
 - Structural optimization
 - Ab-initio molecular dynamics
 - Response functions, e.g. lattice dynamics
 - Certain spectroscopic properties
 - Quantum ballistic transport
-
- Runs on all major operating systems (*Linux, MacOS, Windows*)
 - Runs on all architectures

Input parameters for CoSb₂

Self-consistent calculation (*pw.x*):

```
&control  
  calculation = 'scf',  
  prefix = 'CoSb2',  
  wf_collect = .true.,  
  pseudo_dir = './',  
  outdir = './out_bare',  
/
```

```
&system  
 ibrav = 12,  
celldm(1) = 12.3607,  
celldm(2) = 0.99451,  
celldm(3) = 0.97589,  
celldm(4) = -0.464069,  
nat = 12,  
ntyp = 2,  
occupations='smearing',  
smearing='mv',  
degauss=0.01,  
ecutwfc = 50,  
ecutrho = 500,  
/  
&electrons  
  conv_thr = 1.0d-10  
  mixing_beta = 0.7  
/
```

Input parameters

ATOMIC_SPECIES

Co 58.93320 Co.pz-nd-rrkjus.UPF

Sb 121.76000 Sb.pz-bhs.UPF

ATOMIC_POSITIONS crystal

Co 0.2183 0.2299 0.0005

Co 0.2817 -0.2299 0.5005

Co -0.2183 -0.2299 -0.0005

Co 0.7183 0.2299 0.4995

Sb 0.3325 0.1534 0.6431

Sb 0.1675 -0.1534 1.1431

Sb -0.3325 -0.1534 -0.6431

Sb 0.8325 0.1534 -0.1431

Sb 0.1329 0.3511 0.3607

Sb 0.3671 -0.3511 0.8607

Sb -0.1329 -0.3511 -0.3607

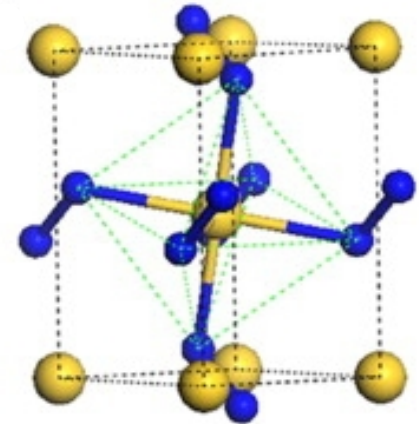
Sb 0.6329 0.3511 0.1393

K_POINTS automatic

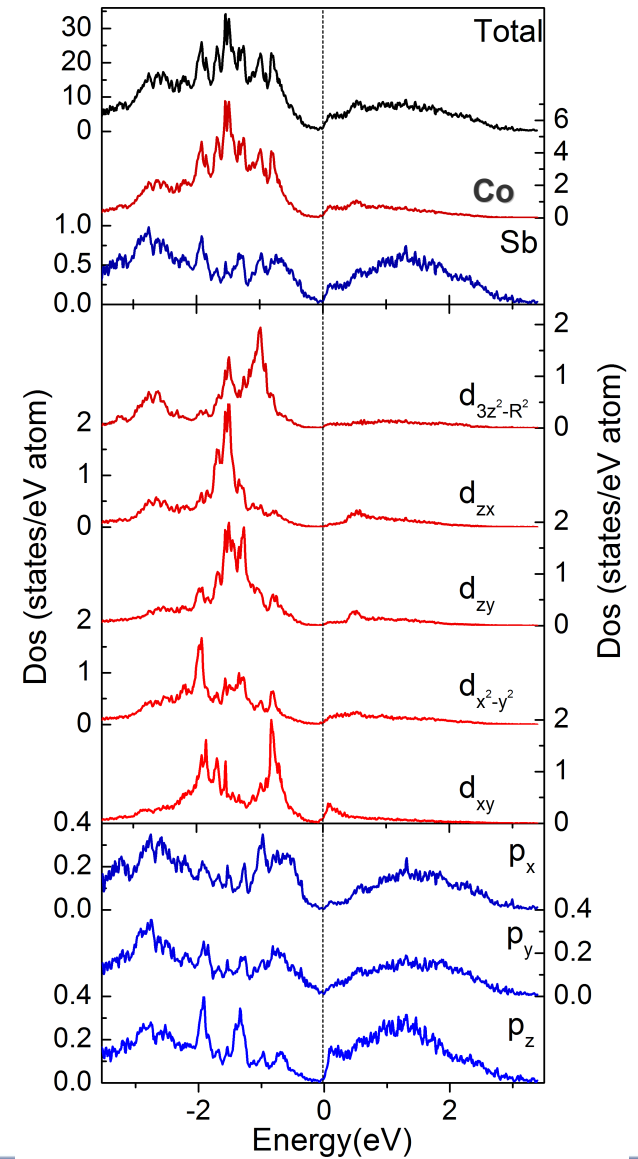
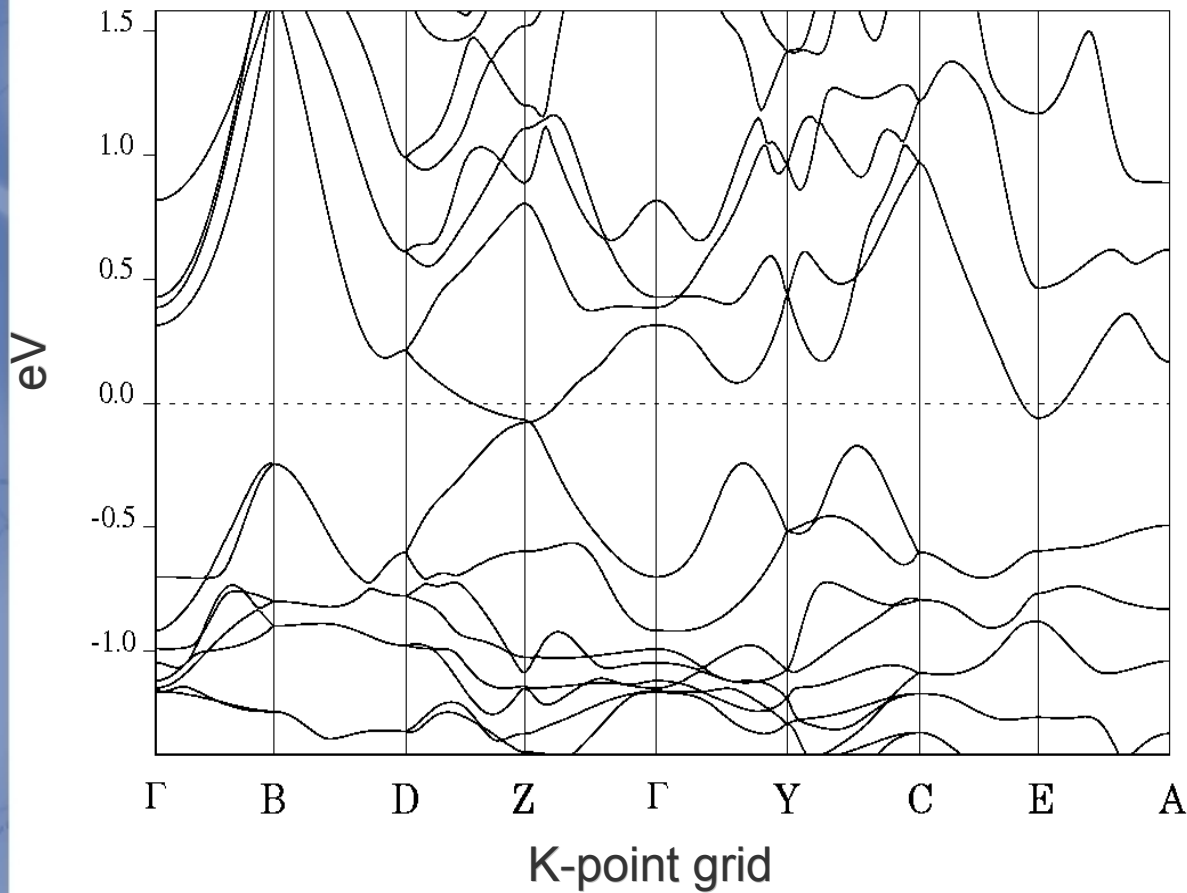
16 16 16 0 0 0

Lattice parameters of CoSb_2

Symmetry: $P2_1/c$
Wyckoff positions: $\text{Co}, 4e (x,y,z)$
 $\text{Sb}(1), 4e (x,y,z)$
 $\text{Sb}(2), 4e (x,y,z)$
Lattice parameters: $a=6.5051 \text{ \AA}$
 $b=6.3833 \text{ \AA}$
 $c=6.5410 \text{ \AA}$
 $\beta=117.65^\circ$
Pseudo-potentials: *ultrasoft GGA*
 $\text{Co}, 4s^1 3d^8 4p^0$
 $\text{Sb}, 5s^2 5p^3$

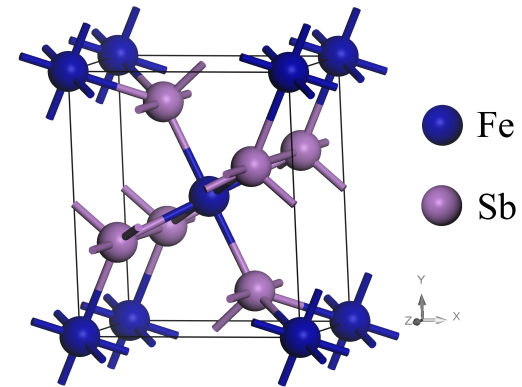


Electronic structure of CoSb_2

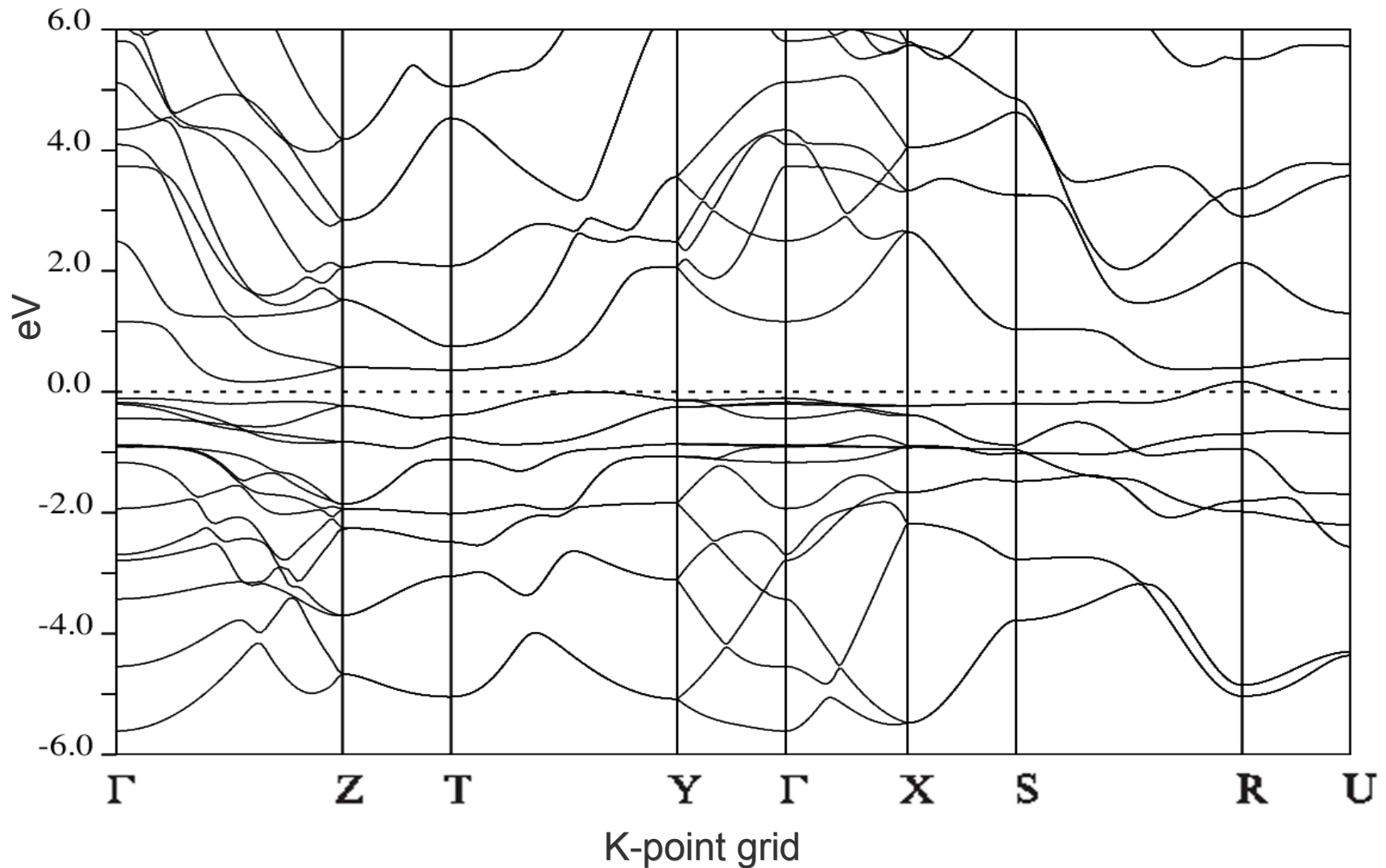


Relaxed parameters $FeSb_2$

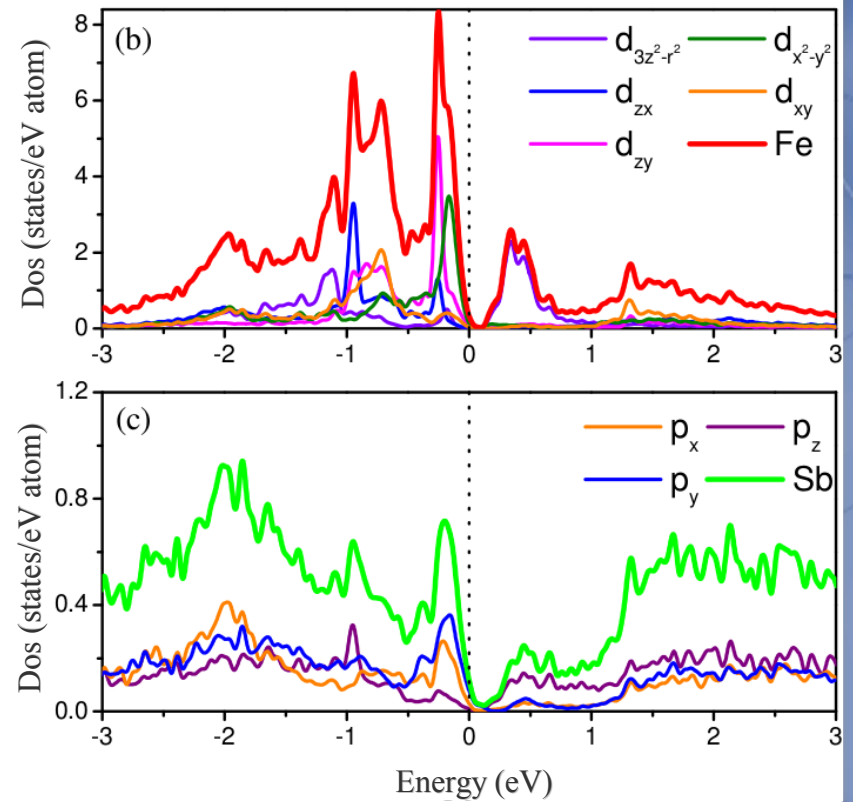
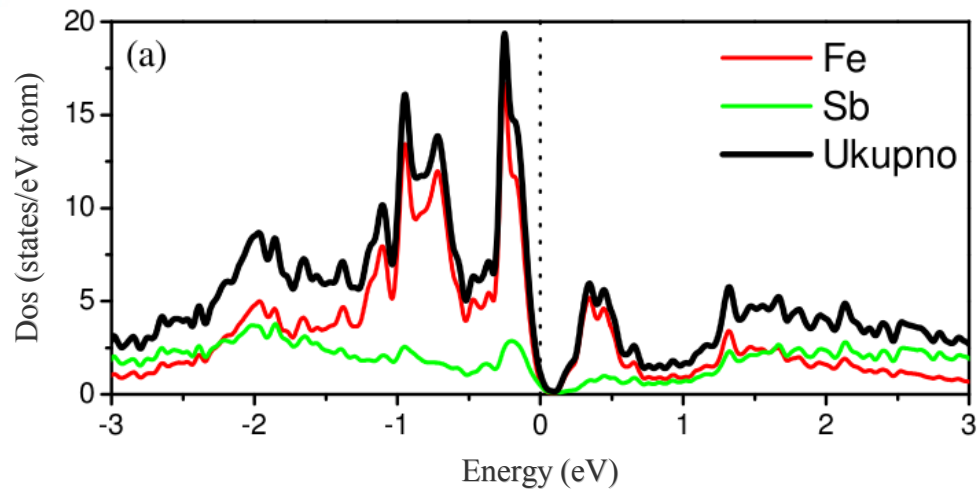
Symmetry: $Pnmm$
Wyckoff positions: $Fe, 2a (0,0,0)$
 $Sb, 4g (0,u,v)$
Lattice parameters: $a=5.859 \text{ \AA}$
 $b=6.583 \text{ \AA}$
 $c=3.812 \text{ \AA}$
 $u=0.1882$
 $v=0.3554$
Pseudo-potentials: *ultrasoft GGA*
 $Fe, 3s^2 3p^6 4s^2 3d^6$
 $Sb, 4d^{10} 5s^2 5p^3$



Electronic structure of FeSb₂



Electron density of states of FeSb_2



Density functional perturbation theory (DFPT)

$$i\hbar \frac{\partial \hat{\Phi}(\mathbf{r}, \mathbf{R}; t)}{\partial t} = \left(- \sum_I \frac{\hbar^2}{2M_I} \frac{\partial^2}{\partial \mathbf{R}_I^2} - \sum_i \frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}_i^2} + V(\mathbf{r}, \mathbf{R}) \right) \hat{\Phi}(\mathbf{r}, \mathbf{R}; t)$$

$$V(\mathbf{r}, \mathbf{R}) = \sum_{I>J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|} - \sum_{i,I} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \sum_{i>j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$
$$\equiv V_{nn}(\mathbf{R}) + V_{ne}(\mathbf{r}, \mathbf{R}) + V_{ee}(\mathbf{r})$$

Born-Oppenheimer:

$$\hat{\Phi}(\mathbf{r}, \mathbf{R}; t) \simeq \Phi(\mathbf{R}) \Psi(\mathbf{r}|\mathbf{R}) e^{-i\hat{E}t/\hbar}$$

Problem can be reduced to:

- Solving of electronic system which depends on positions of nuclei
- Considering system of nuclei in effective inter-atomic potential determined by the electrons

DFPT

$$\left(-\sum_i \frac{\hbar^2}{2m} \frac{\partial^2}{\partial \mathbf{r}_i^2} + V(\mathbf{r}, \mathbf{R}) \right) \Psi(\mathbf{r}|\mathbf{R}) = E(\mathbf{R})\Psi(\mathbf{r}|\mathbf{R})$$

$$\left(-\sum_I \frac{\hbar^2}{2M_I} \frac{\partial^2}{\partial \mathbf{R}_I^2} + E(\mathbf{R}) \right) \Phi(\mathbf{R}) = \hat{E}\Phi(\mathbf{R})$$

$$\mathbf{F}_I = -\frac{\partial E(\mathbf{R})}{\partial \mathbf{R}_I} = 0$$

Normal modes in crystals

Harmonic approximation: second order expansion of interatomic potential energy (independent LHOs).

Normal modes (frequencies and elongations) are determined from secular equation

$$\sum_{t,\beta} \left(\tilde{C}_{st}^{\alpha\beta}(\mathbf{q}) - M_s \omega^2(\mathbf{q}) \delta_{st} \delta_{\alpha\beta} \right) U_t^\beta(\mathbf{q}) = 0$$

Dynamical matrix:

$$\tilde{C}_{st}^{\alpha\beta}(\mathbf{q}) \equiv \sum_{\mathbf{R}} e^{-i\mathbf{q}\cdot\mathbf{R}} C_{st}^{\alpha\beta}(\mathbf{R}) = \frac{1}{N_c} \frac{\partial^2 E}{\partial u_s^{*\alpha}(\mathbf{q}) \partial u_t^\beta(\mathbf{q})}$$

$$\mathbf{R}_I[\mathbf{u}_s(\mathbf{q})] = \mathbf{R}_l + \boldsymbol{\tau}_s + \mathbf{u}_s(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{R}_l}$$

Raman active normal modes CoSb₂

IOP PUBLISHING

JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **24** (2012) 135402 (5pp)

doi:10.1088/0953-8984/24/13/135402

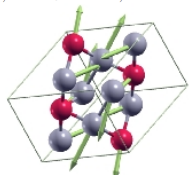
Phonon properties of CoSb₂ single crystals

N Lazarević¹, M M Radonjić², Rongwei Hu^{3,4}, D Tanasković²,
C Petrović³ and Z V Popović¹

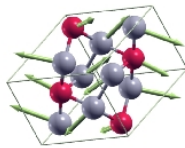
¹ Center for Solid State Physics and New Materials, Institute of Physics Belgrade, University of Belgrade, Pregrevice 118, 11080 Belgrade, Serbia

² Scientific Computing Laboratory, Institute of Physics Belgrade, University of Belgrade, Pregrevice 118, 11080 Belgrade, Serbia

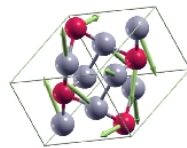
³ Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, NY 11973-5000, USA



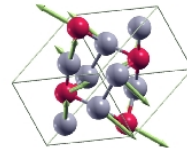
$$A_g^1 = 68.7 \text{ cm}^{-1}$$



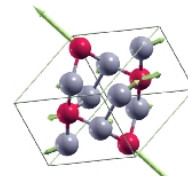
$$B_g^1 = 70.5 \text{ cm}^{-1}$$



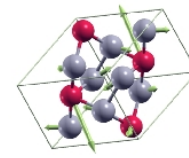
$$A_g^2 = 97.7 \text{ cm}^{-1}$$



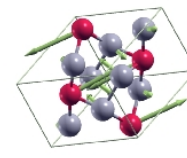
$$B_g^2 = 98.9 \text{ cm}^{-1}$$



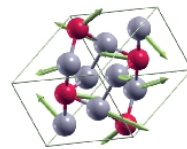
$$A_g^3 = 104.1 \text{ cm}^{-1}$$



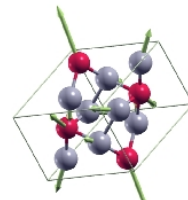
$$B_g^3 = 111.5 \text{ cm}^{-1}$$



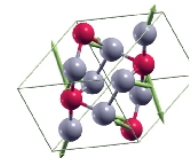
$$B_g^4 = 140.3 \text{ cm}^{-1}$$



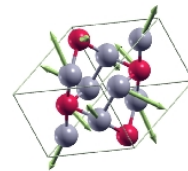
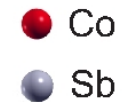
$$A_g^4 = 141.5 \text{ cm}^{-1}$$



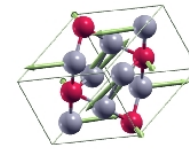
$$B_g^5 = 252.6 \text{ cm}^{-1}$$



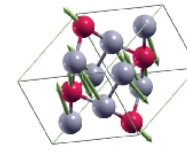
$$A_g^5 = 253.5 \text{ cm}^{-1}$$



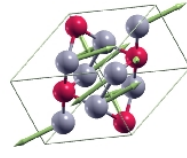
$$A_g^5 = 154.3 \text{ cm}^{-1}$$



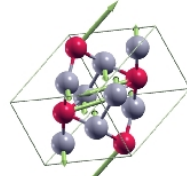
$$A_g^6 = 171.8 \text{ cm}^{-1}$$



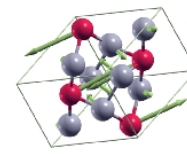
$$B_g^5 = 187.6 \text{ cm}^{-1}$$



$$B_g^6 = 190.5 \text{ cm}^{-1}$$



$$A_g^8 = 238.3 \text{ cm}^{-1}$$



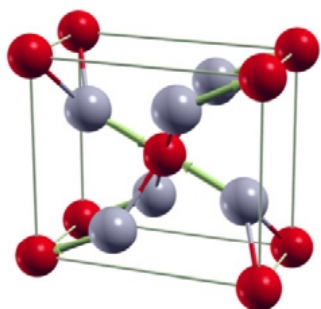
$$B_g^8 = 235.5 \text{ cm}^{-1}$$

Raman active normal modes CoSb₂

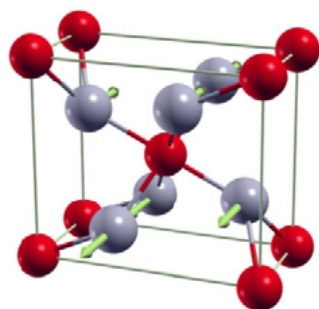
Table 1. Raman tensors for monoclinic crystal structure and selection rules for the (1 $\bar{1}$ 0) plane of CoSb₂ single crystal together with Raman mode energies (in cm⁻¹) of CoSb₂ single crystal.

Raman tensors						Selection rules for the (1 $\bar{1}$ 0) plane of CoSb ₂			
$A_g = \begin{pmatrix} a & d & 0 \\ d & b & 0 \\ 0 & 0 & c \end{pmatrix}$			$B_g = \begin{pmatrix} 0 & 0 & e \\ 0 & 0 & f \\ e & f & 0 \end{pmatrix}$			(c, c)	→	A_g	
						(⊥c, c)	→	$A_g + B_g$	
						(⊥c, ⊥c)	→	$A_g + B_g$	
Raman active modes						Infrared active modes			
Symmetry	Exp.	Calculations	Symmetry	Exp.	Calculations	Symmetry	Calculations	Symmetry	Calculations
$A_{g\sigma}^1$	63.8	68.7	$B_{g\sigma}^1$	80.9	70.5	A_u^1	99.7	B_u^1	133.3
$A_{g\sigma}^2$	93.7	97.7	$B_{g\sigma}^2$	91.1	98.9	A_u^2	108.3	B_u^2	144.2
$A_{g\sigma}^3$	102.5	104.1	$B_{g\sigma}^3$	109.7	111.5	A_u^3	142.7	B_u^3	166.6
$A_{g\sigma}^4$	136.5	141.5	$B_{g\sigma}^4$	134.4	140.3	A_u^4	167.4	B_u^4	174.4
$A_{g\sigma}^5$	153.9	154.3	$B_{g\sigma}^5$	179.6	187.6	A_u^5	174.6	B_u^5	214.6
$A_{g\sigma}^6$	168.0	171.8	$B_{g\sigma}^6$	187.3	190.5	A_u^5	205.5	B_u^5	235.9
$A_{g\sigma}^7$	221.2	220.3	$B_{g\sigma}^7$	217.6	221.8	A_u^7	224.8	B_u^7	249.4
$A_{g\sigma}^8$	239.6	238.3	$B_{g\sigma}^8$		235.5	A_u^8	265.7		
$A_{g\sigma}^9$	256.6	253.5	$B_{g\sigma}^9$		252.6				

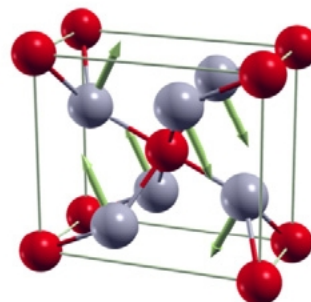
Raman active normal modes FeSb₂



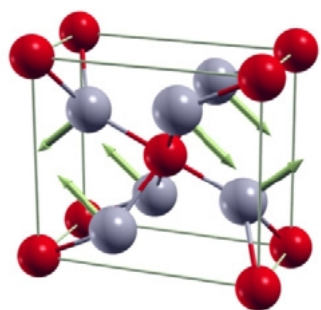
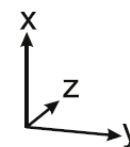
$$A_g^1 = 146.8 \text{ cm}^{-1}$$



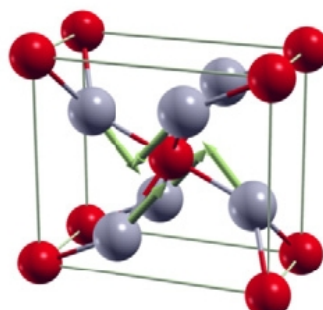
$$B_{3g} = 95.6 \text{ cm}^{-1}$$



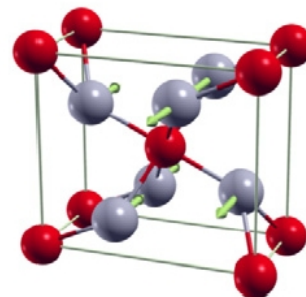
$$A_g^2 = 161.2 \text{ cm}^{-1}$$



$$B_{1g}^1 = 173.3 \text{ cm}^{-1}$$



$$B_{1g}^2 = 184.3 \text{ cm}^{-1}$$



$$B_{2g} = 89.4 \text{ cm}^{-1}$$



Phonon frequencies in the center of Brillouin zone FeSb₂

Table 1. Raman- and infrared-active mode energies (in cm⁻¹) of FeSb₂ single crystal.

Symmetry	Exp. [14]	$\Omega(0)$	Calculation	Activity	Symmetry	Exp. [11, 25]	Calculation	Activity
A _g ¹	150.7	160.3	146.8	R	B _{1u}	195	177.4	IR
A _g ²	153.6	164.4	161.2	R	B _{2u} ¹	106.4	108.1	IR
B _{1g} ¹	154.3	164.6	173.3	R	B _{2u} ²	231.0	210.7	IR
B _{1g} ²	173.9	190.4	184.3	R	B _{2u} ³	257.0	259.6	IR
B _{2g}	90.4		89.4	R		271.0		IR
B _{3g}	151.7		95.6	R	B _{3u} ¹	121.0	122.8	IR
					B _{3u} ²	216.0	219.2	IR
					B _{3u} ³	261.4	236.6	IR
					A _u ¹		84.9	Silent
					A _u ²		195.2	Silent

Phonon dispersion and density of states

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Lattice dynamics of FeSb₂

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