Ab initio calculation of the ground-state properties of CoSi$_2$

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G Uğur[1], **F Soyalp**[1], **H M Tütüncü**[2], **S Duman**[2] **and G P Srivastava**[3]

[1] Gazi Üniversitesi Fen-Edebiyat Fakültesi Fizik Bölümü, 06500, Ankara, Turkey
[2] Sakarya Üniversitesi Fen-Edebiyat Fakültesi Fizik Bölümü, 54100, Adapazari, Turkey
[3] University of Exeter, School of Physics, Stocker Road, Exeter EX4 4QL, UK

Abstract
We have investigated the structural and electronic properties of CoSi₂ by using
a generalized gradient approximation of the density functional theory and
ab initio pseudopotentials. The calculated lattice constant and electronic band
structure have been used in the application of a linear response approach based
on density functional perturbation theory for phonon studies. The structural
results are in good agreement with previous works. The calculated phonon
spectra are in good agreement with available experimental data. A detailed
discussion of atomic displacement pattern is provided corresponding to the two
sets of LO and TO phonon modes.

1. Introduction

In recent years, considerable experimental and theoretical works have been done on the
structural and electronic properties of transition metal silicides. In particular, the CoSi₂ crystal
is currently being actively investigated in view of its larger scattering lengths in electrical
transport, which allowed the creation of the first semiconductor–metal–semiconductor
transistor [1, 2]. Moreover, this material can be used in microelectronics technology as
Schottky barriers and gate electrodes [3, 4]. In order to design electronic and microelectronic
devices related to this material properly, experimental and theoretical research on the electronic
properties of these materials is also needed. On the experimental side, electronic band
structure of CoSi₂ has been measured using angle-resolved photoemission [5] and x-ray
spectroscopy methods [6–10]. In addition to these experimental studies, considerable progress
has been made in theoretical description of the structural and electronic properties of CoSi₂.
A semiempirical tight-binding scheme [10, 11], a linear muffin-tin-orbital method [12] and
an *ab initio* pseudopotential method [13, 14] have been used to investigate the structural and
electronic properties of this material.

Although considerable progress has been made in theoretical description of the structural
and electronic properties of CoSi₂, many of its vibrational properties are still not well
established. However, it is well known that a wide variety of physical properties of solids

depend on their phonon properties: specific heats, thermal expansion, and heat conduction; the electron–phonon interaction plays an important role in the resistivity of metals and superconductivity. Up to now, the acoustical phonon dispersion curves of CoSi$_2$ along the main symmetry directions ([100], [110] and [111] directions) have been measured by means of coherent one-phonon scattering of thermal neutrons [15]. On the theoretical side, acoustic phonon frequencies for CoSi$_2$ along the [100] direction have been calculated by using the Vienna *ab initio* molecular-dynamics method [14]. To the best of our knowledge, the full phonon spectrum of CoSi$_2$ has not been investigated by using any theoretical or experimental method. Thus, we have carried out a study of the structural, electronic and dynamical properties of CoSi$_2$, in order to provide a sounder basis for further experimental and theoretical investigations. The calculated structural parameters are compared with available experimental [15, 16] and theoretical results [11, 13, 14]. In particular, the calculated electronic band structure for CoSi$_2$ shows reasonable agreement with angle-resolved photoemission experiment data [5] along the [111] symmetry direction. In addition to the structural and electronic properties, the density functional perturbation method as suggested by Baroni and coworkers [17] has been used to calculate the phonon dispersion curves and density of states for CoSi$_2$. Our calculated acoustic phonon spectrum shows very good agreement with thermal neutron scattering experiments [15] along the main symmetry directions.

2. Theory

The calculations have been performed using a first-principles pseudopotential method based on the density functional theory. Ultrasoft pseudopotentials [18] for Co and Si have been generated according to a modified Rappa–Rabe–Kaxiras–Joannopoulos (RRKJ) scheme [19]. Besides the valence electrons, the semi-core Co 3d states are treated following a non-linear core correction scheme. The density functional theory has been implemented within a generalized gradient approximation, using the Perdew–Burke–Ernzerhof method [20]. The Kohn–Sham single-particle functions were expanded in a basis of plane waves. Self-consistent solutions of the Kohn–Sham equations were obtained by sampling the irreducible part of the Brillouin zone by employing special **k**-points. A kinetic energy cut-off of 50 Ryd is used while the **k**-space integrals are approximated by sums over 120 special points of the Chadi–Cohen type [21]. Integration up to the Fermi surface is done with a smearing technique [22] with the smearing parameter $\sigma = 0.05$ Ryd. In order to obtain the phonon spectrum of CoSi$_2$, we have used a linear response scheme to the *ab initio* pseudopotential method. The dynamical matrices have been computed on a $4 \times 4 \times 4$ **q**-point mesh, and a Fourier interpolation has been used to obtain complete phonon dispersion curves.

3. Results

CoSi$_2$ crystallizes with the well known calcium fluorite structure, with three atoms per unit cell. The three atoms have coordinates $\tau_{Co} = (0, 0, 0)$, $\tau_{Si} = (0.25, 0.25, 0.25)$ and $\tau_{Si} = (-0.25, -0.25, -0.25)$. The equilibrium lattice parameter has been determined by minimizing the crystal total energy calculated for different values of the lattice parameter. Then, these energy values have been fitted to Murnaghan equation of state [23] in order to obtain the lattice constant, the static bulk modulus at zero pressure B, and the first-order pressure derivative of the bulk modulus B'. The calculated values for a, B and B' are listed in table 1. Our calculated lattice constant is in good agreement with an experimental value [15] to within 0.2%. The calculated bulk modulus agrees with the measured value of 1.715 ± 0.034 Mbar [16] to within 0.9%. Moreover, the calculated values for a, B and B' compare very well with
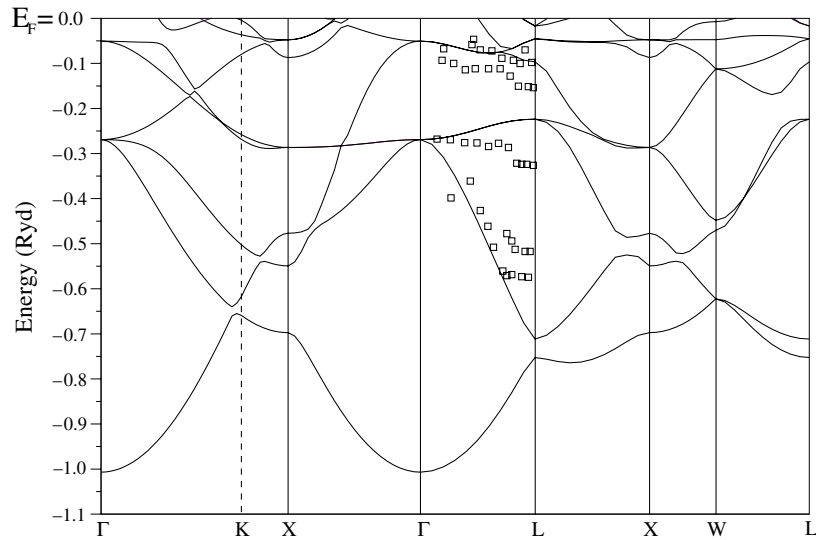
Figure 1. The calculated electronic band structure of CoSi$_2$ along the main symmetry directions in the fcc Brillouin zone. Experimental results are denoted by open squares [5] along the $\Gamma-L$ symmetry direction.

Table 1. Calculated structural lattice constant a, bulk modulus B and the pressure derivative of bulk modulus B' of CoSi$_2$ compared with previous theoretical [11, 13, 14] and experimental [15, 16] results.

Reference	a (Å)	B (Mbar)	dB/dP
This work	5.376	1.731	4.180
Tight binding [11]		1.90	
LDA [13]	5.344	1.820	4.400
GGA [14]	5.350	1.715	
LDA [14]	5.292	2.018	
Experimental [15]		1.870	
Experimental [16]	5.365	1.715 ± 0.034	

previous theoretical results [11, 13, 14]. The electronic band structure of CoSi$_2$ is displayed in figure 1 along several symmetry directions. The currently calculated electronic band structure shows reasonable agreement with angle-resolved photoemission experiment data [5] along the [111] symmetry direction. Due to the 17 valence electrons per primitive unit cell, the system is metallic.

The calculated phonon spectrum dispersions of CoSi$_2$ in the cubic calcium fluorite structure are plotted in figure 2 along several high symmetry lines in the Brillouin zone of the fcc lattice. In this figure, our results are compared with experimental thermal neutron scattering data [15]. The agreement between our results and experimental is very good. In particular, the agreement is excellent for the acoustic branches along the $\Gamma-L$ direction. The density of states curve in the right-hand panel in figure 2 shows a broad feature centred at 4 THz due to the transverse acoustic (TA) branches.

The six optical branches are grouped into two triplets at the zone centre. The triple degeneracies are maintained due to negligible ionicity of the CoSi$_2$ crystal [24]. The frequencies of these phonon modes calculated in our work are 9.45 and 9.75 THz. These modes
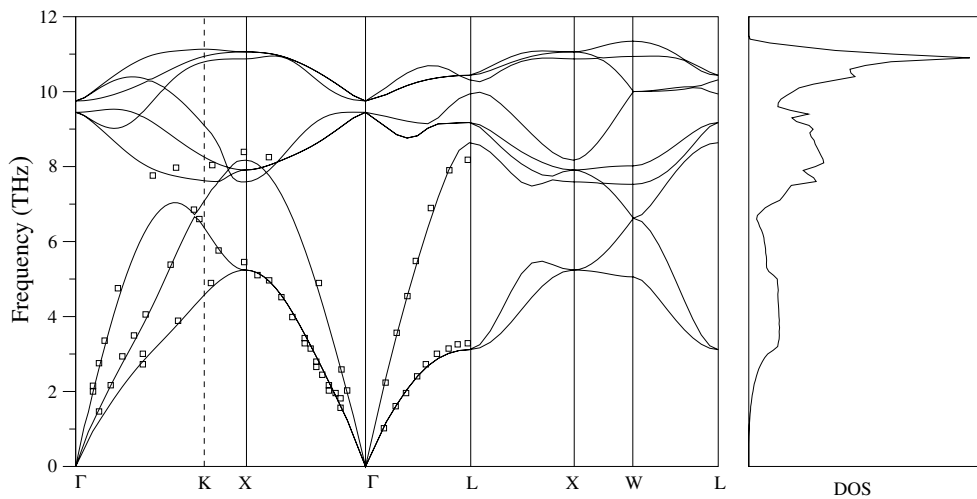
Figure 2. *Ab initio* phonon dispersions and density of states for CoSi$_2$ in the cubic calcium fluorite structure. Experimental data (open squares) are taken from [15].
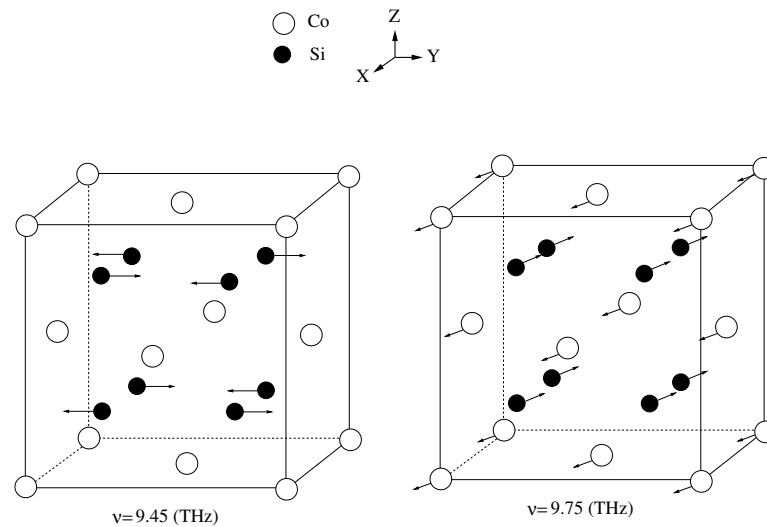

Figure 3. Schematic eigendisplacements of two optical zone-centre phonon modes in CoSi$_2$. The mode with the lower frequency (shown in the left panel) is Raman active, and the mode with the higher frequency (shown in the right panel) is infra-red active.

are Raman and infra-red active, respectively [25]. The displacement patterns corresponding to these are shown in figure 3. The Raman active mode is characterized by vibrations of Si atoms against each other, given by the expression $\nu_R = \sqrt{2K_R/m_{Si}}$. For the infra-red mode in-phase vibrations of the two Si atoms take place against the vibration of the Co atom, given by the expression $\nu_{IR} = \sqrt{K_{IR}\frac{2m_{Si}+m_{Co}}{2m_{Si}m_{Co}}}$. For our numerical results we estimate the ratio of $K_{IR}/K_R = 2.18$. This suggests that the effective force constant governing the infra-red mode is approximately twice as large the force constant governing the Raman mode. The degeneracy and splitting of zone-centre optical phonons in CaF$_2$, with identical crystal structure, is different
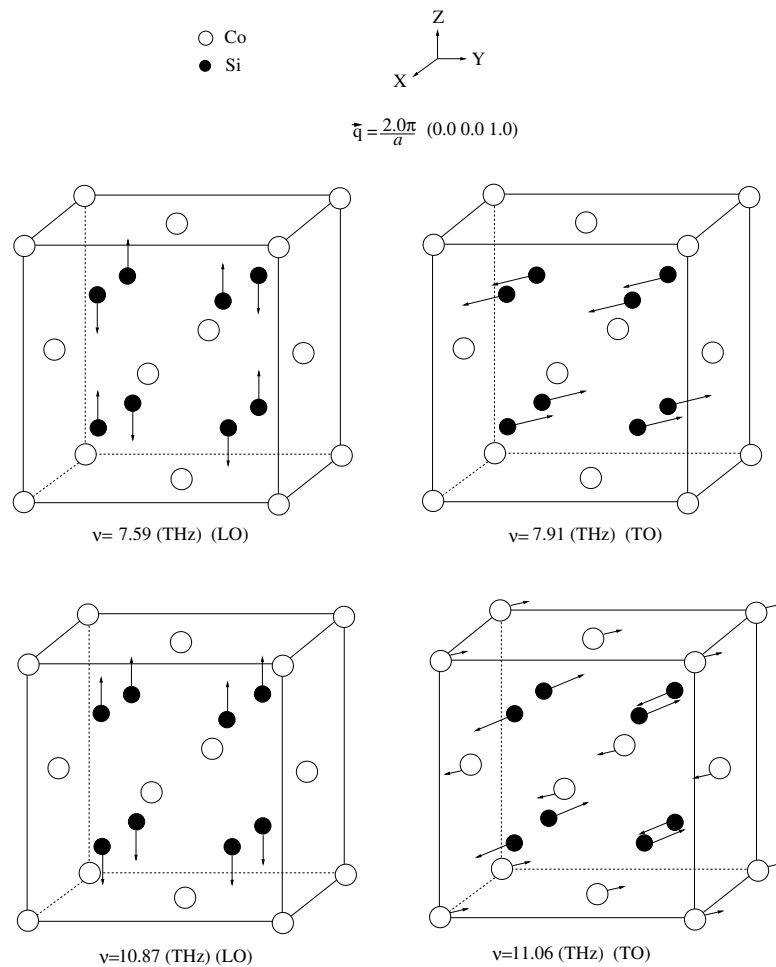
Figure 4. Atomic displacement patterns of optical phonon modes at the *X* point.

from the results obtained here for CoSi$_2$. The work carried out by Verstraete and Gonze [26] suggests that instead of two triplets, the six zone-centre optical modes in CaF$_2$ are distributed, in increasing energy order, as non-degenerate (T$_{1u}$-TO), triply degenerate (T$_{2g}$) and doubly degenerate (T$_{1u}$-LO) modes [26]. The huge difference between the (T$_{1u}$-TO) and (T$_{1u}$-LO) modes arises due to the extremely high ionicity of this material [27].

A large amount of dispersion has been observed for six optical phonon modes along the main symmetry directions ([100], [110] and [111]). On the other hand, the flatness of some optical phonon modes close to the zone edge *X* (along the *L–X* direction) and *W* (along the *X–W* direction) creates a very sharp peak with frequency of 11.0 THz in the phonon density of states. Another interesting feature in the phonon spectra is that when the *q* wavevector increases along the [100] direction, the LA phonon branch lies higher in frequency than the lowest TO and LO phonon branches. At the zone edge *X*, the frequencies of six distinct phonon modes are found to be 5.24 THz (TA), 7.59 THz (LO$_1$), 7.91 THz (TO$_1$), 8.17 THz (LA), 10.87 THz (LO$_2$) and 11.06 THz (TO$_2$). Due to the mass difference between Co and Si atoms, the optic phonon modes include large atomic vibrations from Si atoms. Figure 4 shows

the eigendisplacement patterns of all optic phonon modes at the X point. Only the highest optical phonon mode includes atomic vibrations from both Co and Si atoms while other optical phonon modes are localized on the Si atoms.

4. Summary

In this work, we have presented a complete theoretical analysis of the structure and electronic states of $CoSi_2$ by using the generalized gradient approximation of the density functional theory and *ab initio* pseudopotentials. Our calculated lattice constant and bulk moduli for $CoSi_2$ agree quite well with previous experimental and theoretical results. Moreover, the calculated electronic structure for $CoSi_2$ is in reasonable agreement with angle-resolved photoemission experiment data along the [111] symmetry direction. Using our calculated lattice constant and electronic structure, lattice dynamics of this material has been studied by employing a linear response approach based on density functional perturbation theory. Agreement of phonon dispersion curves with experimental data is very good along the main symmetry directions. In addition to phonon dispersion curves, density of phonon states for $CoSi_2$ has been presented and discussed. Finally, the eigendisplacement patterns of the optical phonon modes at the zone centre and the zone edge X have been analysed.

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