

# THE INFLUENCE OF PRESSURE ON THE STRUCTURAL AND ELECTRONIC PROPERTIES OF Bi

## INFLUENCIA DE LA PRESIÓN SOBRE LAS PROPIEDADES ESTRUCTURALES Y ELECTRÓNICAS DE Bi

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### ABSTRACT

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Calculation of the structural and electronic properties of Bi was carried out in the framework of density functional theory (DFT). The graphs of energy vs. volume for some possible structures show that the most stable one is the rhombohedral; the others are metastable. We also found two phase transitions induced by pressure. The most important result of this research is the prediction about the existence of FCC structure of Bi at higher pressures than ~3GPa. The electronic properties for the rhombohedral structure show that our calculations are in overall good agreement with other calculations. This agreement serves to validate the pseudo Bi.pbe-dn-kjpaw.UPF. Therefore, the above-mentioned is suitable for use in future calculations.

**Key words:** Bismuth, structural and electronic properties, wien2k, quantum-espreso, rhombohedral structure

### RESUMEN

Se realizaron cálculos acerca de las propiedades estructurales y electrónicas del Bi en el marco de la teoría DFT. De los gráficos de energía contra volumen se halló que la estructura más estable es la romboedra; las demás son meta estables. También encontramos dos transiciones de fase provocadas por presión. Nuestro principal hallazgo es la existencia del Bi en la fase FCC para presiones superiores a 3GPa aproximadamente. Nuestros resultados de las propiedades calculadas están en muy buen acuerdo con otros cálculos y con mediciones experimentales. Esta concordancia nos sirve para validar el pseudopotencial Bi.pbe-dn-kjpaw.UPF para otros cálculos futuros.

**Palabras clave:** Bismuto, propiedades estructurales y electrónicas, wien2K, quantum-espreso, estructura romboedra.

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## Introduction

Bi is interesting because its surfaces, such as Bi(111), Bi(110), and Bi(100), are an open door for use in nanotechnology. Because Bi's surfaces are quasi-two-dimensional metals with peculiar spin properties, Bi could be used in both spintronics and quantum computing as a spin source or a spin filter [1]. Due to the fact that its importance in nanotechnology is rising [2], here we present the first step of a wider investigation that comprises volume, surfaces, absorption of atoms, and interfaces with other materials such as graphene or MgO. Bi has been studied in thin films, nanowires and clusters [3]. In the present paper, we carried out calculations of energy as a function of volume for several structures such as diamond (#227), NiAs-like (#194), FCC-like (#225), Cubic Simple-like (CS, #221), and rhombohedral (R-structure, #166). From these graphs, we deduce that the most stable one is the R-structure and that the others are metastable, and finally there are two phase transitions induced by pressure. After that, we present the electronic properties.

Bi is semi-metallic and has an R-structure with  $a=4.746 \text{ \AA}$ ,  $\alpha=57.23^\circ$  (300K) [1]. Because  $\alpha \approx 60^\circ$ , and this value defines the cubic structure, other cubic and hexagonal phases such as the NiAs-like were included, because they are close to it. Taking into account that at room-temperature Bi exhibits a phase transition toward monoclinic at about 2.55 GPa and after that it changes, at about 2.7GPa, to tetragonal and finally reaches a body-centered cubic structure, at  $\sim 7.7$  GPa, we searched for other phase transitions and in fact found some of them. The study of this had not been done before our research. All calculations were carried out in the framework of DFT, with spin polarization using W2k [5] and QE [6]. This task was also done in order to validate the pseudo Bi.pbe-dn-kjpaw.UPF, which we obtained from Theos-Theory and Simulation of Materials's pseudo library [7]. The results show that this pseudo is suitable for use in QE-calculations, because

**Table 1.** Cell parameters for Bi in hexagonal structure space-group #166, \*the method used in [1] is tight-binding and in [4], [8] and [10] is interaction of X-Ray with matter.

Bismuth	a (Å)	c(Å)	c/a
Ph. Hofmann [1]	4.5332	11.7967	
C. Laulhé, et al. [4]	4.546	11.862	
P. Cucka and C. S. Barrett [8]	4.546 (298°K)	11.862 (298°K)	
	4.535 (78°K)	11.814 (78°K)	
T.N. Kolobyanina, et al. [10]	4.5452 (298°K)	11.860 (298°K)	2.609 (298°K)

se the results are in a good agreement with those obtained with the all-electron full-potential (linearized) augmented plane-wave ((L)APW) + local orbitals (lo) method, which is implemented in the W2k code and other calculations. Table 1 shows some parameters found in the scientific literature which served us for the sake of comparison.

## Calculation details: Parameters used in wien2k and quantum-espresso

In calculations with W2k, we used the GGA approx. in the parametrization of Perdew, Burke y Ernzerhof (PBE) [11]. Muffin-tin radius was  $R_{MT} = 2.65$  a.u., and  $R_{MT} \times K_{max} = 8.0$ , where  $K_{max}$  limits the maximum kinetic energy for plane wave base. For the base of spherical harmonics  $Y_{lm}$ , we used  $l_{max} = 10$ . The convergence criterion for the energy was 0.0001 Ry. In QE-calculations, we also used GGA-PBE approx. with 45 Ry as the energy cutoff, and the charge density cutoff was 450 Ry. The convergence was 0.0001 Ry.

## Results

Fig. 1 shows the dependence of cohesion energy as a function of volume for several structures. These results are very similar for calculations carried out with W2k and QE. All phases are metastable because they all have a minimum, and the most stable one is the R-structure. The values of a and c are in a good agreement with those in [1] ( $\sim 1\%$  for a and  $\sim 2\%$  for c). Fig. 2 shows the enthalpy calculated from the data of energy vs. volume. One can observe that there are interceptions at  $\sim 3$  GPa, because there are two phase transitions induced by pressure. One is from FCC to CS, and the other is from NiAs to the CS phase. We predict a new structure for Bi: FCC; from that phase it would be possible to reach the CS phase.

In the transitions the volume reduces by about 12%, from  $67 \text{ \AA}^3$  to  $60 \text{ \AA}^3$ . The minimum of the energy of the FCC and the NiAs-like differ by only 0.11 eV and 0.18 eV by unit formula, respectively. The structural parameters obtained by means of W2k are shown in Table 2. Calculations performed with QE resulted in  $a=4.5651 \text{ \AA}$ ,  $c/a=2.5327$ , and volume  $V=52.170 \text{ \AA}^3$ . These parameters differ by only 0.7% and 2.7% from those in [1] in a and the quotient c/a, respectively. With the R-structure, we obtained  $a=4.7043 \text{ \AA}$  and  $V=70.058 \text{ \AA}^3$ . The Bi atoms were freed during the relaxation process in QE, and the final coordinates were (0.54, 0.54, 0.54) and (0.0067, 0.0067, 0.0067). Other parameters were  $\alpha=57.890^\circ$  and  $d_1/d_2=0.86$ . Comparison with [1] shows that  $\alpha$  and  $d_1/d_2$  differs by only 0.95% and 2.23%, respectively.

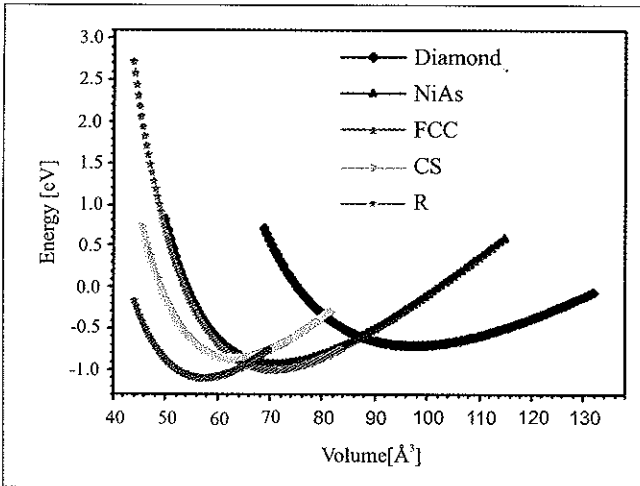


Figure 1 Energy vs. volume for several phases

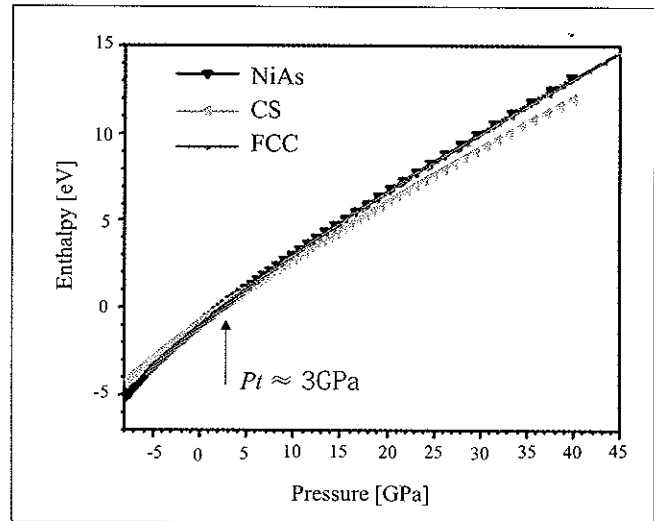


Figure 2. Enthalpy vs. pressure shows the transition phases

Table 2. Structural properties of Bi calculated with W2k.

Structural Parameter	Diamond Our results	NiAs Our results	FCC Our results	CS Our results	R-structure Our results
amin [Å]	7.300	4.515	6.565	3.983	4.6719
Volume [Å <sup>3</sup> ]	97.256	71.138	70.745	63.218	58.072
c/a	-----	1.78	-----	-----	2.6303
B [GPa]	28.24	42.19	47.04	53.14	52.50
B'	4.33	4.887	4.059	4.30	4.5198
E cohesión [eV]	-0.707	-0.9315	-1.0018	-0.859	-1055

### Electronic Properties

Fig. 3 shows the electron bands in the R-structure at the minimum of the energy, i.e. at zero pressure, and they are in a good agreement with those obtained in [1] and [3]. We note that the valence and conduction bands touch each other at the L and T high-symmetry points of the first Brillouin zone, and this fact is a sign of the semi-metallic behavior of Bi. Fig. 4 shows the bands calculated by means of QE-code, and one can observe that they are in a good agreement with those of Fig 3.

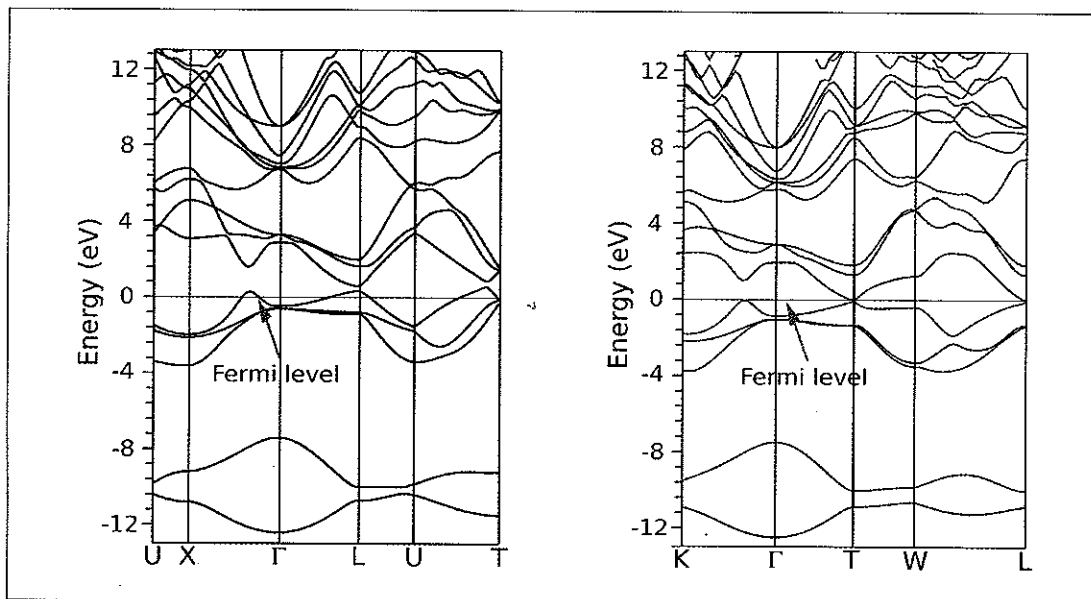


Figure 3. Bands of Bi in the R-structure calculated using W2k

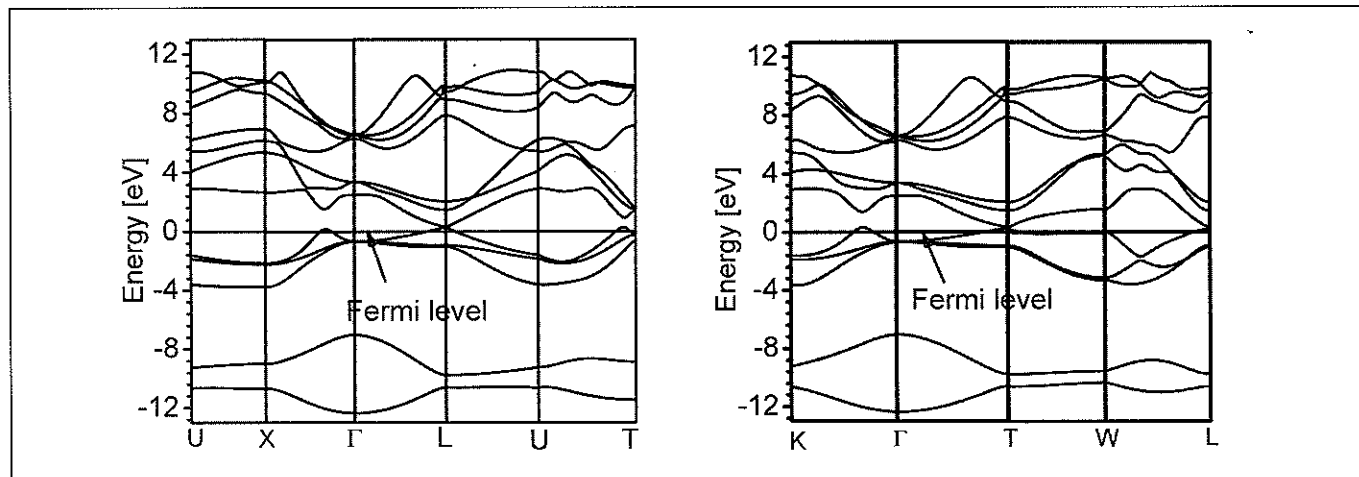


Figure 4. Bands of Bi in R-structure calculated using QE-code

### Summary and conclusions

Calculations of the structural and electronic properties of Bi were carried out in the framework of DFT using two codes: W2k and QE. From the graphs of the energy as a function of volume, in several possible structures, one finds that the most stable is the R-structure. The other structures considered are metastable, and one also finds two phase transitions induced by pressure. The first is from FCC to CS, and the other is from NiAs to the CS. Our main conclusion is about the prediction of the phase FCC of Bi at higher pressures than  $\sim 3$  GPa. The electronic properties for the R-structure show that our calculations are in overall good agreement with other calculations. This agreement serves to validate the pseudo of Bi that we obtained from the QE pseudo library. Therefore, the pseudo mentioned is suitable for use in future calculations.

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