Journal of Physics and Chemistry of Solids 116 (2018) 131–136

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs

One- and two-dimensional search of an equation of state using a newly released 2DRoptimize package

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ARTICLE INFO

Keywords:
Crystal structure
Electronic material
Electronic structure
Equation of state
Inorganic compound

ABSTRACT

A new package called 2DRoptimize has been released for performing two-dimensional searches of the equation of state (EOS) for rhombohedral, tetragonal, and hexagonal compounds. The package is compatible and available with the WIEN2k package. The 2DRoptimize package performs a convenient volume and **c/a** structure optimization. First, the package finds the best value for **c/a** and the associated energy for each volume. In the second step, it calculates the EoS. The package then finds the equation of the **c/a** ratio vs. volume to calculate the **c/a** ratio at the optimized volume. In the last stage, by using the optimized volume and **c/a** ratio, the 2DRoptimize package calculates **a** and **c** lattice constants for tetragonal and hexagonal compounds, as well as the **a** lattice constant with the **α** angle for rhombohedral compounds. We tested our new package based on several hexagonal, tetragonal, and rhombohedral structures, and the 2D search results for the EOS showed that this method is more accurate than 1D search. Our results agreed very well with the experimental data and they were better than previous theoretical calculations.

1. Introduction

The rapid increase in computational power motivated us to improve the method used for obtaining the equation of state (EOS) for compounds with two degrees of freedom, i.e., tetragonal, hexagonal, and rhombohedral (THR) symmetries (changes in volume and **c/a** ratio). One of the methods for obtaining the EOS for THR compounds involves calculating the EOS based on changes in volume at a constant **c/a** ratio (one-dimensional (1D) search of the EOS). However, the accuracy of the results obtained is inadequate if we do not find the minimum of the **c/a** and the associated energy for each volume in order to obtain the correct EOS. Using the new 2DRoptimize package [1], we aim to perform structural optimization by changing both the volume and **c/a**, i.e., our package first finds the minimum values of **c/a** and the associated energy for each volume, which are then used for obtaining the EOS. Thus, if we try to improve the method for obtaining the EOS for compounds with more than one degree of freedom, such as THR symmetries, we can improve the determination of the lattice parameters, which is a first step toward predicting important properties such as the electronic, optical, and magnetic properties according to the theoretical framework employed (density functional theory (DFT) in this case) [2,3]. It has been proved that DFT is one of the most accurate methods for computing the electronic structures of solids [4–6], especially when using the highly accurate all-electron full-potential (linearized) augmented plane-wave plus local orbital [FP-(L)APW+lo] method. We refer to the new package for two-dimensional (2D) search of the EOS as 2DRoptimize. The results obtained by 2D search of the EOS are better than those produced by 1D search of the EOS. In addition, the accuracy of the calculation is increased compared with 1D search. In our previous study [7], we calculated the cell parameters and bulk modulus (B) for hexagonal MnAs and Mg structure compounds using the old version of this package (2Doptimize) [8], which only supports hexagonal and tetragonal structures. In this study, we performed a detailed comparison of the results obtained based on 1D and 2D searches of the EOS for THR compounds.

2. 2D search

The 2DRoptimize [1] package performs a convenient volume and **c/a** structure optimization for THR compounds. Therefore, several self-consistent calculations are required to obtain the optimized lattice parameters (**a** and **c**). In this package, for each volume, we first select different sets of **c/a** and using the following equation:

$$E = E_0 + a_1 x + \ldots\ldots + a_n x^n \quad n = 2, 3, 4, \tag{1}$$

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https://doi.org/10.1016/j.jpcs.2018.01.034
Received 21 September 2017; Received in revised form 16 January 2018; Accepted 17 January 2018

where n and x represent the order of fitting and the c/a ratio, respectively, the package finds the best **c/a** ratio for each corresponding volume such that the energy has the minimum value and the best order of fitting. In the next step, we have a set of energies and volumes at the optimized **c/a** ratios, and by using the EOSs supported in the package, i.e., EOS2, Murnaghan, and Brich–Murnaghan, the minimum of the total energy and the equilibrium volume are calculated. Next, in order to find the **c/a** ratio at the equilibrium volume, the 2DRoptimize package fits the optimized **c/a** ratios for each volume according to the polynomial:

$$coa(v) = b_0 + b_1 v + \ldots\ldots + b_n v^n \; n = 2,\ 3,\ 4, \tag{2}$$

where coa and v denote the optimized **c/a** ratio for the volume used and the optimized volume, respectively. Using the resulting fit based on equation (2), the 2DRoptimize package calculates the optimized **c/a** ratio at the optimized volume.

In the last stage, using the optimized volume and **c/a** ratio, the 2DRoptimize package calculates the lattice constants **a** and **c** for tetragonal and hexagonal compounds, and the lattice constant **a** with the **α** angle for rhombohedral compounds. The package then checks the sensitivity of the results to the order of fitting by obtaining the equation of **c/a** vs. volume. The 2DRoptimize package converts the calculated **a** and **c** lattice parameters into rhombohedral specifications using the following equations.

$$\alpha_r = 2\mathrm{Arcsin}(9a^2/(4c^2 + 12a^2))^{0.5} \tag{3}$$

$$a_r = (a/2)\sin(\alpha_r/2) \tag{4}$$

The best strategy involves selecting only 3 × 3 points and more points can be added in the next step if necessary to check the sensitivity of the results to the order of fitting in equations (1) and (2). If we need to specify the old volume and **c/a** ratio, then these results will be considered automatically without recalculation. Moreover, the 2DRoptimize package allows us to leave out the points that are very far from the minimum (i.e., a volume with different values of **c/a**).

It should be noted that during the calculation of the EOS for THR compounds using 1D search (changes the volume at a constant **c/a** ratio), we must use the same **c/a** ratio for all of the volume changes, whereas the 2D search of the EOS finds the best value of the **c/a** ratio for each value of the volume changes. This is one of the most important features of the new package.

We performed several calculations to test the results obtained by 2D search of the EOS using the 2DRoptimize package. Table 1 shows the relative errors (as percentages) for the c/**a** ratio used in 2D and 1D searches of the EOS. These relative errors with respect to the **c/a** ratio were used in 1D search of the EOS for different percentage volume changes by the tetragonal MnO_2 and SnO_2 compounds using the 2DRoptimize package within Perdew, Burke and Ernzerhof Generalized gradient approximation (PBE) [9]. According to Table 1, the results obtained by 2D search of the EOS using the 2DRoptimize package could be important, and they may be a source of error between the 1D and 2D searches of the EOS. However, these errors may be negligible in some cases, so we performed several tests to assess this hypothesis. For example, we performed 1D and 2D searches of the EOS for Y and Sc within the PBE functional. The results and the experimental data [10] are presented in Table 2. Table 2 shows that the effect of 2D search of the EOS using the 2DRoptimize package is important, where the accuracy of this method is better than that of 1D search of the EOS. Furthermore, we

Table 1
Relative error (percentage) in the c/a ratio when used in 2D and 1D searches of the EOS relative to the c/a ratio used for 1D search of EOS for different percentage volume changes for tetragonal MnO_2 and SnO_2 within the PBE.

Volume change, percentage	−10	−5	0	5	10
MnO_2	0.63	0.08	−0.63	−1.41	−2.37
SnO_2	2.75	1.55	0.40	−0.86	−2.35

Table 2
Effects of 1D and 2D searches of EOS on the optimized values of hexagonal Y and Sc compounds within the PBE.

	V (bohr^3)	B (GPa)	B′	E (Ryd)
Y_{1D}	443.6371	40.73	2.90	−13542.8590
Y_{2D}	443.6268	40.93	3.00	−13542.8591
Exp[a]	446.4639	37		
Sc_{1D}	332.3874	55.20	2.48	−3056.9046
Sc_{2D}	332.2953	54.45	2.05	−3056.9047
Exp[a]	337.8289	44		

[a] Ref. [10].

Table 3
Effects of 1D and 2D searches of EOS on the optimized values and pressure of the induced-phase transition for the CdTe compound within the PBE.

CdTe	V (bohr^3/atom)	B (GPa)	B′	E (Ryd/atom)	P (GPa)
1D search	245.6168	35.21	4.41	−12392.896945	11.4
2D search	245.6107	35.25	4.36	−12392.896949	10.6

performed another test related to the pressure of the induced phase transition of the CdTe compound from cubic to hexagonal phases within the PBE, and the results are given in Table 3. According to Table 3, the effect of 2D search of the EOS for the hexagonal phase of the CdTe compound is negligible, but the 2D search of the EOS predicts that the pressure of the induced phase transition is around 0.8 (GPa) lower than that obtained by the 1D search of the EOS for the CdTe compound. Finally, we calculated the EOS for the rhombohedral-Bi within the PBE exchange-correlation based on 2D and 1D searches of the EOS. As shown in Fig. 1, when we changed the search method from 2D to 1D, the effect of 2D search caused the value of the optimized volume to change from 496.96 to 494.96 (*Bohr*^{3}), and from 463.69 to 465.62 within PBE-sol. Moreover, for Bi, the 2D search predicted a lower bulk modulus (B) and a higher pressure derivative (B′) than those obtained using 1D search. Therefore, these results show clearly that if we can improve the method used to search for the EOS for compounds with more than one degree of freedom, such as THR symmetries, then the accuracy of the calculation method (DFT in this study) will be better than that obtained using 1D search.

3. Details of the calculations

A new and more accurate package called 2DRoptimize has been released for 2D search of the EOS for THR compounds. The old version of this package called 2Doptimize [8] only supports hexagonal and tetragonal structures, whereas the new 2DRoptimize package also supports rhombohedral structure in addition to hexagonal and tetragonal structures. The new package is compatible with the FPLAPW+lo method, as implemented in the WIEN2k package [11]. It should be noted that when using the 2DRoptimize package for calculations, switch 5 is generally used for calculating the volume changes and switch 7 for calculating the **c/a** changes. Therefore, in these calculations, at least 35 self-consistent calculations are needed in order to find the optimized lattice parameters **a** and **c** for each symmetry. Table 4 shows the other critical parameters comprising the **k**-points mesh, number of times of the smallest atomic muffin-tin sphere radius, and the largest K vector ($R_{min\ MT} \times K_{max}$) as a cutoff parameter to check the convergence of the basis set and the maximum angular momentum (l_{max}) for WIEN2k calculations. For compounds with internal coordinates, we minimized the forces (1 mRy/au) acting on each atom.

4. Results and discussion

Using the 2DRoptimize package, we calculated the cell parameters of 21 THR compounds, as shown in Tables S2 and S3 in the supplementary materials. Fig. 2 shows the differences in the optimized energy, volume,