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First-Principle Calculation of Elastic Compliance Coefficients for $BiFeO_3$

Y. L. WANG,* Z. H. WU, Z. C. DENG, L. Z. CHU, B. T. LIU, W. H. LIANG, AND G. S. FU

College of Physics Science and Technology, Hebei University, Baoding 071002, China

The elastic compliance coefficients of $PbTiO_3$ with/without geometric optimization are firstly calculated by using density-functional theory (DFT) under different exchange correlation functions. It is found that the best results are not obtained by LDA/CA-PZ and optimized structure although these induce the nearest lattice constants to experimental ones, however, the results of $PbTiO_3$ without geometry optimization under GGA/PW91 function are in great consistent with the experimental data. Based on the same calculating method of $PbTiO_3$, the elastic compliance coefficients for $BiFeO_3$ are obtained. And the data are compared with previous results predicted by fitting experimental data to Landau-type phenomenological theory, which possessing the difference of an order of magnitude with our data.

Keywords $BiFeO_3$; elastic compliance coefficients; first-principle theory

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1. Introduction

As a kind of important functional material, ferroelectrics [1–5], especially multiferroic material [6–10], simultaneously possessing ferroelectric, ferromagnetic, and/or ferroelastic properties, has attracted more and more attention for potential applications in transducers, actuators, sensors and improved data-storage media. These applications are based on some interesting phenomena brought forth by multiferroic materials. For example, a strong coupling between ferroelectric and antiferromagnetic domain walls has been found in $YMnO_3$ [7], in orthorhombic $TbMnO_3$ and $TbMn_2O_4$ the ferroelectric polarization can be reoriented by a magnetic field [8, 9], and ferromagnetic ordering can be "switched on" by an electric field in hexagonal $HoMnO_3$ [10]. They further intrigue scientists world-wide to study the physics behind the phenomena.

$BiFeO_3$, one of the most popular multiferroic materials, has simultaneously demonstrated strong ferroelectricity and ferromagnetism at room temperature [6], with Curie temperature of 830°C and Neél temperature of 370°C. In order to better study the physics behind the phenomena referred to $BiFeO_3$, it is fundamental and necessary to determine the basic parameters that affect properties of $BiFeO_3$. However, to date not enough information

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*Corresponding author. E-mail: hdwangyl@hbu.edu.cn

has been known about these parameters for $BiFeO_3$ both from the experimental measurement and theoretical calculation. Facing with these difficulties, Jiang et al. estimated its parameters including elastic compliance coefficients (ECCs) by fitting experimental data to Landau-type phenomenological theory, and using these parameters, they discussed the influence of the thickness of epitaxial $BiFeO_3$ thin film on ferroelectric/ferromagnetic properties [11].

As was already known, the first-principle calculation can predict some basic parameters of a novel material with known structure. Using this method, some materials such as $BaTiO_3$, $CaTiO_3$, $PbTiO_3$ and $KNbO_3$ [12–16] have been investigated. From our best knowledge, however, no results have been reported on the ECCs of $BiFeO_3$ with *R3C* rhombohedral structure calculated by first-principles. The calculation of elastic constants is potentially very useful, since the full tensor has only been measured experimentally for a very small percentage of all known solids. This is primarily because the practical determination typically requires single crystals with a size of a few micrometres at least. In this paper, we carry out the calculation by using CASTEP software package based on density functional theory (DFT), and the results are compared with previous data predicted by Landau-type phenomenological theory [11].

2. Model and Method

The choice of exchange correlation functions (ECFs) is crucial for precision in CASTEP calculation. For $BiFeO_3$, no experimental data can be used for comparison with our calculation results. In order to search appropriate ECF in the calculation, ECCs of $PbTiO_3$ are firstly calculated. Here, crystal lattice parameters of tetragonal $PbTiO_3$ which belongs to *P4mm* space group are taken as $a = 3.904$ Å, $c = 4.152$ Å [17], and crystal lattice parameters of rhombohedral $BiFeO_3$ which belongs to *R3C* space group are $\alpha = 59.35°$, $a = c = 5.616$ Å [18].

Before calculating ECCs of $PbTiO_3$, Geometry optimization was carried out using the Broyden–Fletcher–Goldfarb–Shannon algorithm (BFGS), enabling us to obtain the best unit-cell parameters (lattice parameters, unitcell angles, internal atomic coordinates). The electron-ion interactions were described by ultrasoft pseudopotentials, and electron exchange and correlation energies were calculated with the generalized gradient approximation (GGA) and the local density approximation (LDA) respectively. In which four various ECFs, *i.e.*, GGA/PW91, GGA/PBE, GGA/RPBE and LDA/CA-PZ are chosen, respectively. Then, the ECCs are calculated based on the same ECFs. The parameters used in geometric optimization are as follows: for GGA/PW91, the cut-off energy is 380 eV and Monkhorst-pack k-point meshes are $7 \times 7 \times 5$; for GGA/PBE, the cut-off energy is 380 eV and the Monkhorst-pack k-point meshes are $7 \times 7 \times 5$; for LDA/CA-PZ, the cut-off energy is 380 eV and the Monkhorst-pack k-point meshes are $6 \times 6 \times 6$; The energy tolerance was 1.0×10^{-6} eV/atom, the force tolerance was 0.002 eV/Å, and the displacement tolerance was 1.0×10^{-4} Å. But for GGA/RPBE, the cut-off energy and Monkhorst-pack k-point meshes are taken as 340 eV and $6 \times 6 \times 5$, and the energy tolerance was 2.0×10^{-6} eV/atom, the force tolerance was 0.006 eV/Å, and the displacement tolerance was 2.0×10^{-4} Å.

For examining the impact of lattice constants on ECCs of $PbTiO_3$, the experimental structure without geometric optimization is also calculated with cut-off energy of 340 eV and k-point set mesh of $6 \times 6 \times 6$ under the four ECFs. At last, the different calculated

Table 1
Optimized lattice constants of $PbTiO_3$ calculated with different exchange correlation functions (ECFs)

		Lattice constants	
Pseudopotential	ECF	a/Å	c/Å
ultrasoft	GGA/PW91	3.8249	4.7922
ultrasoft	GGA/PBE	3.8347	4.7817
ultrasoft	GGA/RPBE	3.8605	5.1318
ultrasoft	LDA/CA-PZ	3.8670	4.0473

ECCs are compared with the experimental ones, and the ECF which induces the best result is used to calculate the ECCs of $BiFeO_3$.

3. Results and Discussion

3.1. Analysis on Calculated Results of Elastic Compliance Constant of $PbTiO_3$

The optimized lattice constants of $PbTiO_3$ under various ECFs are listed in Table 1. Obviously, the calculation value with LDA/CA-PZ is the nearest to experimental data (a = 3.904 Å, c = 4.152 Å) among the four ECFs.

Table 2 shows theoretical and experimental ECCs (Label C) of $PbTiO_3$ with (Label A)/without (Label B) geometric optimization under ECFs of GGA/PW91 (Label 1), GGA/PBE (Label 2), GGA/RPBE (Label 3) and LDA/CA-PZ (Label 4). It is obvious that various ECFs, especially lattice constants result in different ECCs, which indicates various discrepancies with experimental values. EEC is composed of six independent values,

Table 2
Comparably analysis on theoretical and experimental data of elastic compliance coefficients of $PbTiO_3$

		Elastic compliance coefficients/$(GPa)^{-1}$					
Lable	ECF	S_{11}	S_{12}	S_{33}	S_{44}	S_{66}	RMSE
A1	GGA/PW91	0.0060388	−0.0011905	0.0303474	0.0144596	0.0101213	0.001836
B1	GGA/PW91	0.0082858	−0.0018087	0.0359725	0.0235413	0.0116430	0.005585
A2	GGA/PBE	0.0060685	−0.0011028	0.0284642	0.0159731	0 .0101548	0.002753
B2	GGA/PBE	0.0078727	−0.001923	0.0262836	0.0214423	0.0114601	0.005239
A3	GGA/RPBE	0.0059939	−0.0012195	0.0237283	0.0142719	0.0100898	0.004201
B3	GGA/RPBE	0.0086455	−0.0034862	0.0038783	0.0280910	0.0133833	0.014871
A4	LDA/CA-PZ	0.0070721	−0.0003146	0.0712281	0.0156354	0.0103958	0.017442
B4	LDA/CA-PZ	0.0053047	−0.0002975	0.0211624	0.0111256	0.0095515	0.005278
C		0.0072	−0.0021	0.0325	0.0122	0.0079	

Notion: From A1 to A4, the results is calculated with experimental lattice constants.From B1 to B4, the results is calculated with optimized lattice constants. C is experimental data of elastic compliance coefficients of $PbTiO_3$.

namely, S_{11}, S_{12}, S_{13}, S_{33}, S_{44} and S_{66} due to its symmetry. These values possess different errors, compared with the corresponding experimental data [20]. For example, regarding group B2 obtained using GGA/PBE function, S_{11}, S_{12} and S_{33} better agree with experimental data, but, S_{44} and S_{66} is not satisfied; for group B4 calculated by using the LDA/CA-PZ function, S_{11}, S_{44} and S_{66} are consistent with experimental values, nevertheless, S_{12} and S_{33} are not satisfied. The root of mean square error (RMSE), shown in the last column in Table 2, is used to scale the calculation precision. It can be seen that RMSE of group A1 is the smallest, implying that EECs calculated under GGA/PW91 with experimental lattice constants (without geometric optimization) are in best agreement with experimental values among these six groups. It should be emphasized that the best results are not obtained by LDA/CA-PZ and optimized structure although these induce the nearest lattice constants to experimental ones. Lattice constants (with or without geometric optimization), merged with ECF, determine the ECCs.

In CASTEP calculation, ECCs are obtained by linearly fitting the stress tensor inducing a given strain series according to Hooke's law. Note that maximum strain cannot exceed the scope of flexibility, and at the same time, it cannot be too small so that change of the corresponding stress is bigger than the error of stress settled in the calculation. Therefore the "amplitude of maximum of strain" should be appropriately chosen. In above calculation, the "amplitude of maximum strain" is chosen as 0.004. To examine if it is in the scope of flexibility, altering the "amplitude of maximum strain" ranging from 0.004 to 0.008 with the same calculated process as A1, ECCs of $PbTiO_3$ are listed in Table 3. We find that the numerical values hardly vary, which indicates the "amplitude of maximum strain" of 0.004 is appropriate for the deformation of $PbTiO_3$.

It is noted that although geometric optimization can ensures the structure to be in a stable state, it induces lattice constants deviating from the experimental data. Thus, some times, In the first-principle calculation of some properties of the material, experimental lattice constants can be directly used in order to the consistency of calculated and experimental data [21].

3.2. *Analysis on Calculated Results of Elastic Compliance Coefficients of $BiFeO_3$*

Similar to $PbTiO_3$, experimental lattice constants without geometric optimization and ECF of GGA/PW91 are used for ECCs calculation of $BiFeO_3$. The calculated data are shown in Table 4. Due to the symmetry difference, for $BiFeO_3$, there are seven independent ECC elements, S_{11}, S_{12}, S_{13}, S_{14}, S_{33}, S_{44} and S_{66}. In order to test if the strain is in its scope of flexibility, the ECCs corresponding to the "amplitude of maximum strain" of 0.004, 0.006

Table 3

Elastic compliance coefficients of $PbTiO_3$ with different amplitudes of max strain

Amplitude of max strain	Elastic compliance coefficients/$(GPa)^{-1}$					
	S_{11}	S_{12}	S_{13}	S_{33}	S_{44}	S_{66}
0.004	0.0060388	−0.0011905	−0.0053987	0.0303474	0.0144596	0.0101213
0.006	0.0064923	−0.0003668	−0.0073083	0.0315096	0.0144935	0.0101730
0.008	0.0064540	−0.0002445	−0.0077827	0.0350734	0.0153807	0.0100023

Table 4
Elastic compliance coefficients of $BiFeO_3$ with different amplitudes of max strain

Max strain	Elastic compliance coefficients/$(GPa)^{-1}$						
	S_{11}	S_{12}	S_{13}	S_{14}	S_{33}	S_{44}	S_{66}
0.004	0.0182167	−0.0006753	−0.0179691	0.0011707	0.0492076	0.0192123	0.0377839
0.006	0.018479	−0.0004835	−0.0019521	0.0010689	0.0472036	0.0192456	0.0384576
0.008	0.018571	−0.0005638	−0.0018379	0.0012712	0.0476491	0.0188542	0.0349572

and 0.008 are calculated, respectively. The data of different groups are almost the same, which indicates our calculation is appropriate for the deformation of $BiFeO_3$.

To discuss the thickness dependence of ferroelectric and magnetic properties in epitaxial $BiFeO_3$ thin films, Jiang et al roughly estimated a few of elastic compliance coefficients of $BiFeO_3$ by fitting experimental data to Landau-type phenomenological theory [11], which gave $S_{11} = 0.00425\ (GP)^{-1}$, $S_{12} = -0.004\ (GP)^{-1}$, $S_{13} = -0.00155\ (GP)^{-1}$, possessing the difference of an order of magnitude with our data.

4. Conclusions

In conclusion, we use CASTEP package based upon density-functional theory to calculate elastic compliance coefficients of $BiFeO_3$. To choose the crucial factors impacting precision, *i.e.*, lattice constants and exchange correlation functions, elastic compliance coefficients of $PbTiO_3$, with known experimental data and similar structure as $BiFeO_3$, are firstly calculated. For $BiFeO_3$, the calculation with experimental lattice constants and GGA/PW91 function shows $S_{11} = 0.0182167$, $S_{12} = -0.0006753$, $S_{13} = -0.0179691$, $S_{14} = 0.0011707$, $S_{33} = 0.0492076$, $S_{44} = 0.0192123$ and $S_{66} = 0.0377839$ with unit of $(GP)^{-1}$.

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