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INFLUENCE OF EXCHANGE-CORRELATION FUNCTIONAL ON THE STRUCTURAL AND ELECTRONIC PROPERTIES OF PERIODIC STRUCTURES WITH TRANSITION METAL ATOMS

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Abstract. The influence of the exchange-correlation functional on the crystal fundamental property calculation is shown. CrGeTe₃, compound with transition metals, was used for the simulation of structural and electronic properties. The calculations were carried out using such functional classes as LDA and GGA. It has been shown that LDA exhibits 0.4 % and 5.2 % overestimations of the lattice constants for *a* and *c*, respectively. GGA (OR) overestimates *a* by 0.58 % and underestimates *c* by 4 %. The influence of the Hubbard correction on the band gap was also investigated. If U_{eff} is applied to the *d*-electrons, then the band gap will decrease. This is due to the hybridization of the *p*-electrons of the chalcogen and the *d*-electrons of the transition metal. Thus, GGA demonstrates better agreement with the experiment. The convergence of the calculation of the total energy with a change in the *k*-points and the cutoff energy were also investigated.

Keywords: exchange-correlation functional, DFT, VASP, GGA, LDA.

Conflict of interests. The author declares no conflict of interests.

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Introduction

Most quantum mechanical simulation methods are *ab initio* methods, i. e. they do not require experimental parameters to obtain results. The main source of errors and inaccuracies in calculations by DFT methods is the exchange-correlation functional (E_{ex}). The form of the exchange-correlation functional is determined by the approximation that is used to take this component into account. The local density approximation (LDA), the generalized gradient approximation (GGA), and other approaches, which are used in DFT (Density Functional Theory), have their drawbacks and are sources of errors. This leads to the need of verifying the simulation results for each specific compound.

The validity of the calculations by the DFT methods, i. e., the approximations used, can be checked by comparing the structural and electronic properties obtained in quantum mechanical calculations and the data obtained from experiments.

DFT functional for structure parameters

There are two main methods of accounting for E_{ex} such as the LDA and the GGA. The difference between the methods lies in the fact that in the second case, the dependence of the exchange and correlation energies on the gradient of the electron density is taken into account. Based on these methods, the corresponding classes of functionals have been developed.

Structural properties, in particular the parameters of the space lattice, depend on the choice of the pseudopotential. We performed the relaxation procedure for bulk CrGeTe₃ using four types of pseudopotentials (Tab. 1). In particular, from the class of GGA functionals, we used Perdew–Wang 91 (91) [1], PBE-sol (PS) [2], and optPBE [3]. The simulation results are presented in Tab. 1. All calculations were performed in the VASP software package.

Table 1. Structural properties of CrGeTe₃

Lattice constant	LDA	GGA (91)	GGA (OR)	GGA (PS)	Experiment
<i>a</i>	6.8546	6.9059	6.8660	6.7885	6.8263 [4], 6.820 [5]
<i>c</i>	21.6085	18.9652	19.7164	15.1656	20.5314 [4], 20.371 [5]

According to the results, the best agreement with experiment is obtained by the functionals GGA (OR). The LDA exhibits 0.4 % and 5.2 % overestimations of the lattice constants for *a* and *c*, respectively. GGA (OR) overestimates *a* by 0.58 % and underestimates *c* by 4 %.

DFT functional for electronic calculation

Classical LDA and GGA functionals often underestimate the band gap [6]. To overcome the difficulties that arise, new classes of functionals such as meta-GGA, hybrid, and also a method that introduces an additional correction (DFT+U) have been developed. However, hybrid functionals and functionals from the meta-GGA class require significant computing resources for all its efficiency. For example, Borlido and al. [7] provides a comparison of the average of the estimated time. Thus, meta-GGA, mBJ, and hybrid functionals are 5, 10–50, and 100 or more times slower than GGA.

DFT+U is a computationally simpler method. An additional correction for strongly correlated electrons, which takes into account the single-site Coulomb interaction, is used in framework ones. The rest of the electrons are described by the classical DFT functional. Within the framework of this method, two parameters are introduced. The first one (*U*) characterizes the local Coulomb interaction, and the second one (*J*) is a characteristic of the exchange interaction. The sum of these parameters is called “the effective Hubbard coefficient (U_{eff})”. U_{eff} can be calculated using the *ab initio* simulation [8, 9]. However, U_{eff} values are usually obtained semi-empirically by comparison with the experimental band gap [10, 11]. The semiempirical technique allows one to avoid significant computational costs for calculating U_{eff} from the first principles.

We performed calculations of electronic properties and energy band diagrams for the LDA (*U*) and GGA (*U*) functionals (Fig 1). GGA, quite expectedly, gives a larger bandgap than LDA. This amounts to 0.20 and 0.30 eV, respectively. The experimental value is 0.38 eV [12]. Both functionals underestimate the band gap.

The obtained data for functionals with Hubbard correction differs from the expected ones. We got a lower value than for classical functionals. GGA+*U* demonstrates 0.16 eV and LDA + *U* gives a completely metallic type of conductivity. The Hubbard coefficient was 5 eV and was used for *d*-electrons of chromium. The same results for CrGeTe₃ were obtained by the authors in the work [13].

Other research groups obtained similar results as well. Boukhvalov et al. [14] noted that a large Hubbard coefficient decreases *3d-2p* hybridization in BiMnO₃. Therefore, it affects the characteristics of the Mn-O chemical bond (bond length and angle). CrGeTe₃ has a similar structure to BiMnO₃. A transition metal (in our case Cr, in [14] work it is Mn) with a valence *d* shell is surrounded by six atoms with a valence *p* shell (in our work it is Te, in [14] work it is O).

All this leads to hybridization of the *p*- and *d*- orbitals and the formation of a covalent bond. Usually, the Hubbard parameter is added only for *d*- and *f*-electrons. Thus, in CrGeTe₃, the *d*-orbitals are shifted, like BiMnO₃. The energy of *p*-electrons remains unchanged. This leads to the distortion

of the octahedral environment of Cr in CrGeTe₃ or Mn in BiMnO₃. A decrease of the band gap with an increase of the Hubbard coefficient in TiO₂ [11] has been observed.

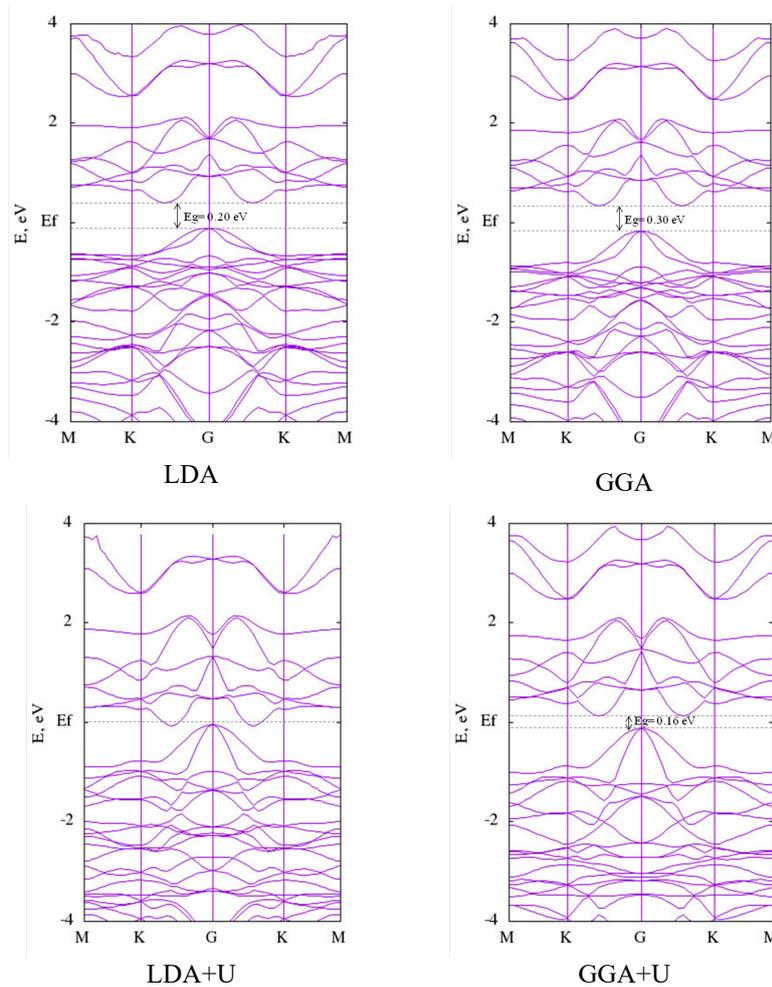


Fig. 1. Band structure of CrGeTe₃ obtained by different functionals

Cutoff energy and k -points

The exchange correlation functional is the only approximation in the DFT. However, the Kohn–Sham equations are a system of coupled, nonlinear, and partial differential equations. These equations are solved numerically using additional approximations. One of such approaches is the Born-Oppenheimer approximation, which allows to separate the electrons of an atom into core (inner electron shell) and valence electrons (outer electron shell). Thus, the inner shell can be described by an effective pseudopotential, which is calculated by the ab initio methods once and forms a database of such pseudopotentials. The effective method of plane waves is used to solve the Kohn–Sham equations describing the wave functions of valence electrons [15].

The cutoff energy (E_{cut}) controls the completeness of the base set of plane waves. An increase in the cutoff energy leads to an increase in the calculation accuracy. However, the number of plane waves can become so large as to be computationally incredibly expensive. Thus, a trade-off has to be found between the accuracy, which is influenced by the cutoff energy, and the computational cost.

We calculated the dependence of the total energy of the system on the completeness of the basis set (cutoff energy). The calculation results are shown in Fig. 2, *a*. It was found that saturation occurs at 250 eV and above, i. e. the relative error between the obtained values does not exceed 2 %.

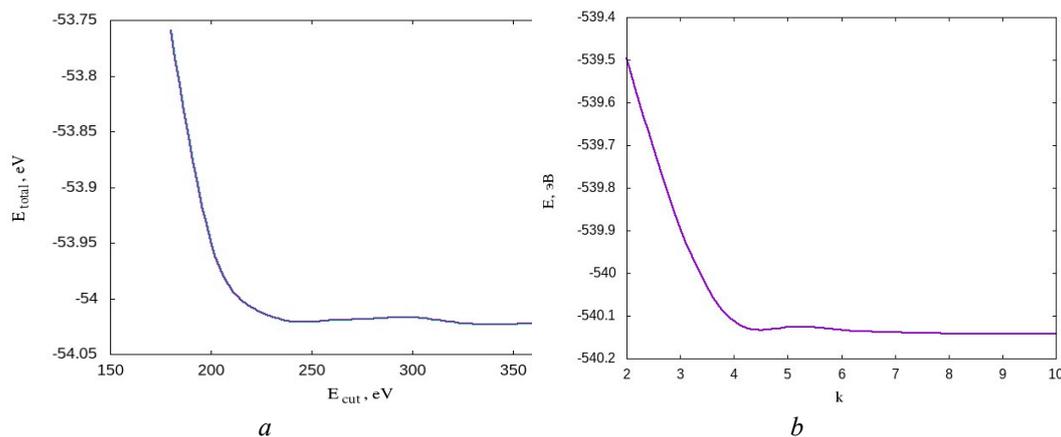


Fig. 2. The dependence of the total energy on the cutoff energy (a) and dependence of the total energy on the k -points mesh (b)

The efficiency of quantum-mechanical calculations by DFT methods is determined, among other things, as a set of special points of reciprocal space (k -points). The number of k -points strongly affects the computational resources spent. Too many can lead to the fact that the time is too large or there is not enough computing power. On the other hand, setting a small set of k -points can lead to computational errors. k -points are specified to define Bloch vectors. This should be an optimal set of interpolation points of the Fourier coefficients for the expansion of the Kohn-Sham wave functions in the basis of plane waves. The optimal number of k -points was determined by test calculations. Fig. 2, b shows the dependence of the total energy of the system on a set of $n \times n \times 2$ ($n = 1, 2 \dots 8$) k -points for the same atomic system. According to the graph shown in Fig. 2, the optimal set, i. e., which will allow obtaining sufficient accuracy with adequate computing resources, has a set of 8.

Conclusion

The article presented the investigation of quantum mechanical simulation parameter effects on the reliability of the results. The simulation results were compared with the known experimental data. The influence of the functional choice on the structural and electronic properties is established. Convergence tests were performed. This helped to determine the optimal set of k -points and establish an effective value of the cutoff energy. Thus, the reliability of the results of the CrGeTe₃ simulation of the fundamental properties in the framework of the theory of the electron density functional has been confirmed.

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