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Evolution of the bonding mechanism of ZnO under isotropic compression: A first-principles study

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Abstract

The electronic structure and the bonding mechanism of ZnO under isotropic pressure have been studied by using the full-potential linear augmented plane wave (FP-LAPW) method within the density-functional theory (DFT) based on LDA + U exchange correlation (EXC) potential. We used the theory of Atoms in Molecules (AIM) method to analyze the change of the charge transfer and the bonding strength under isotropic pressure. The results of the theoretical analysis show that charge transfer between Zn and O atomic basins nearly linearly increases with the increasing pressure. Charge density along the Zn–O bond increases under the high pressure. The bonding strength and the ionicity of Zn–O bond also increase with the increasing pressure. The linear evolution process of the bonding mechanism under isotropic pressure was shown clearly in the present paper.

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Keywords: ZnO; LDA + U; Isotropic pressure; Bonding mechanism

1. Introduction

ZnO is a wide-band-gap semiconductor with large exciton binding energy (60 meV). It has many applications in optoelectronic devices, such as transparent field-effect transistors, light-emitting diodes (LED), ultraviolet nanolasers, photodetectors, solar cells, surface acoustic wave devices and so on. At ambient conditions, the thermodynamically stable phase of ZnO is wurtzite (B4) with tetrahedral coordination with typical sp^3 covalent bonding. Bates et al. [1] firstly reported that the structure of ZnO transforms from the B4 to the rocksalt (B1) phase under approximate 10 GPa pressure and the volume decreases by about 17%. Due to the necessity for the design of semiconductor apparatus, the behaviors of material under high pressure were studied thoroughly. Recently, energy-dispersive X-ray diffraction (EDXD) [2] had been employed to prove Bates' result. Using *in situ* X-ray diffraction and EDXD, Jamieson [3] and Desgreniers [4] found that the transition is reversible at room temperature. They clarified that the phase transition from B4 to B1 starts at 9.1 ± 0.2 GPa by increasing pressure. The two phases coexist over a range of 9.1–9.6 GPa and the phase transition completes at 9.6 GPa. The phase transition results in about 16.7% decrease of the unit-cell volume. Under decompression, they observed that ZnO reverts to B4 phase at 1.9 ± 0.2 GPa. There have been several first-principles studies on the structural transition of ZnO under high pressure using different approaches, including the linear combination of Gaussian-type orbital (LCGTO) HF method [5], the full-potential linear muffin-tin orbital (FP-LMTO) approach with the LDA and GGA [6], LAPW [7] and correlated HF perturbed ion (HF-PI) model [2,8]. The internal structural parameter μ [9], shear modes [10,11],

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electronic structure [5], lattice dynamics [12] and optical properties [13] of ZnO under hydrostatic pressure have also been reported systematically. However, to our knowledge, the evolution of the bonding nature of ZnO under the high pressure has not been reported yet.

There is an important connection between the structure of materials and the nature of chemical bond [14]. For example, the highly ionic materials favor the highly symmetrical structure, such as rocksalt and CsCl structure. Whereas the highly covalent materials favor the lowly symmetrical structure such as zinc-blends and wurtzite. Under high pressure, a covalent material is apt to transform into the higher symmetrical structure. Meanwhile, the degree of ionicity is an important factor for determining the transforming pressure. For example, the highly covalent material SiC starts to transform into rocksalt at a pressure about 100 GPa. Whereas the less covalent material GaN starts phase transition at a much lower pressure of about 50 GPa [15,16]. The highly ionic materials such as MgO and CdO even take on rocksalt phase at atmospheric pressure. So the study on the evolution of the bonding mechanism under high pressure is an important issue for both theory and experiment.

In our present paper, the evolution of the bonding mechanism of ZnO under isotropic pressure was studied by using the FP-LAPW method within the DFT based on LDA + U EXC. The FP-LAPW method is one of the most accurate methods for performing electronic structure calculations. LDA + U correction is very important in studying the electronic structure of ZnO as mentioned in Ref. [17]. Due to the calculations based on LDA and GGA [5,7] overestimated the hybridization between the Zn-3d and O-2p states, the energy locality of Zn-3d state was around −4.5 eV below the Fermi energy, which is discrepant from the experimental result (−7.5 eV below the Fermi energy [18]). LDA + U has been proved to amend the deficiency of LDA and effectively correct the energy level of Zn-3d state [19]. Meanwhile, we adopted the theory of Bader's Atom in Molecules (AIM) [20] to quantitatively analyze the bonding mechanism, the change of the ionicity, bonding strength and the charge transfer of Zn–O bond under pressure.

2. Computational detail

DFT calculations were performed by employing the FP-LAPW method implemented in the WIEN2K package [21]. The spin–orbit interaction was considered in the present computational process. To ensure the well convergence and the accuracy of calculations, the muffin-tin radii and the number of k-points to generate the final results were carefully chosen after optimization. The value of $R_{\mathrm{MT}}K_{\max}$ was set to be 10.0, where $K_{\max}$ is the maximum value of the plane-wave vector which determines the energy cut-off for the plane-wave expansion, and the R_{MT} is the smallest muffin tin radii. The valence wave functions inside the sphere were expanded up to $l_{\max} = 10.0$ and the basis function was composed of 3727 plane waves. $15 \times 15 \times 8$ k-points in the irreducible Brillouin zone were chosen in the calculations. The self-consistent iteration was considered to be converged when the total energy and total charges in the atomic sphere were stable within 10^{-4} eV per unit cell and 10^{-4} electron charges per atom, respectively.

The LDA + U method was used to correct the local energy of Zn-3d states in our present work. LDA + U method is based on the framework of the local density functional and combined with the Model Hamilton to improve the descriptions of the system coexisting delocalized and local states. The electrons in the system are divided into two types: (i) delocalized states (such as s and p states), which are treated with LDA [22] ; (ii) local states (such as d states in ZnO), which are treated with +U. On the basis of the LDA method, the energy of local state electrons are treated as orbital dependent and the energy of d–d interaction in LDA is subtracted, i.e.

$$E_{\mathrm{LDA+U}} = E_{\mathrm{LDA}} + U \sum_{i \neq j} n_i n_j - UN(N-1)/2, \tag{1}$$

where n_i is the occupancy for the localized states, N is the total number of electrons, U is the Hubbard parameter, defined as

$$U = E(d^{n+1}) + E(d^{n-1}) - 2E(d^n) \tag{2}$$

i.e. the needed Coulomb potential energy to place two electrons at the same site.

The LDA + U method has been applied in a great many of complex systems with local states [19,23,24]. Among the three existing LDA + U methods, the schemes introduced by Anisimov et al. has been used in the present paper. An effective U_{eff} was used instead of the independent parameters U and J, where J is the average exchange interaction in the considered shell. The optimized U_{eff} for LDA + U and GGA + U were 8.5 and 7.1 eV, respectively, in our present paper. The details of the determination of the U_{eff} can be found in our previous work [17]. Although the value of U_{eff} will be a function of the unit-cell volume under different pressures to simplify the calculations, we used U_{eff} of equilibrium structure for the compressed systems. The results were in reasonable agreement with experiments. Photoemission spectroscopy of rocksalt phase would be of use to determine the value of U_{eff} best describing the electronic structure, which could make our present results more accurate.

3. Result and discussion

3.1. Equilibrium structure

Because the LDA + U and GGA + U EXC have been proved to be effective to calculate the equilibrium volume, we used LDA, LDA + U, GGA [25] and GGA + U [26] EXC to optimize the equilibrium, respectively. The results were listed in Table 1. The results show that the unit cell volume decreases by about 18% as the phase transforms