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A role of Eu-doping on Electronic Structure and Optical Properties of ZnO from First-principles

Lanli Chen [1, 2], Hongduo Hu [1, 2], Zhihua Xiong [1#]

1. Key Laboratory for Optoelectronics and Communication of Jiangxi Province, Jiangxi Science & Technology Normal University, Nanchang 330013, China

2. Department of Electronics and Information Engineering, Huangshi Polytechnic College, Huangshi 435003, China

#E-mail: xiong_zhihua@126.com

Abstract

Based on the first principles, the electronic and optical properties of Eu-doped ZnO have been investigated. The calculated results indicate that the Fermi level moves to the conduction band, and highly localized Eu-4f states exist near the Fermi level after Eu-doping into ZnO. It is also found that the optical properties are changed greatly in the low-energy region after doping. However, there is almost no effect in the high-energy region. The changes of optical properties are explained in connection with the calculated electronic properties.

Keywords: ZnO; Optical Properties; Electronic Structure; First-principle Calculation

1 INTRODUCTION

ZnO has the attribute of a wide direct band gap of 3.4 eV and the excited energy as large as 60 meV at room temperature. Because ZnO has a great advantage for applications in optical devices, doping ZnO with various elements has been a popular technique to gain the extrinsic properties for device applications, such as p-type doping [1-3] and n-type doping [4, 5]. Specially, the researchers found that rare earth doping exhibits special optical properties [6] that two strong blue emissions are observed in the system after earth doping, which is absent in pure-ZnO. Therefore, many study groups have begun to investigate the system for rare earth doping. Our group [7] have found that Y doping in ZnO can improve the conductivity. Later, in experiment, Q.Q.Dai et al [8] have reported that Eu-doped ZnO thin films present UV emission and red emission from Eu^{3+} ions, demonstrating efficient energy transfer from the host to Eu^{3+} ions. Simultaneously, they found that Eu-doped ZnO can gain high luminous efficiency, indicating that Eu-doped ZnO is a promising material for lighting and flat panel display application. S.Bachir et al [9] found that Eu-doping ZnO has a good luminescent property as a green colored phosphor. A.Ishizumi et al [10] has reported that undoped and Eu-doped ZnO nanocrystals have the rod-like shape. Afterward, R.Krishna et al [11] has investigated ZnO doped with Eu by means of high temperature calcination method. They found that it produces a sharp and intense red signal which is a signature of Eu^{3+}. Meanwhile, they observed the characteristic of red emission at 607 nm using high-energy excitation along with the native deep centre emission of ZnO peaking around 525 nm. Yet there are few reports on the theoretical studies on Eu-doped ZnO. Therefore, this paper mainly calculates the electronic and optical properties of Eu-doped ZnO through the first-principles. Simultaneously, the theory results agree well with the experiment results [12, 13].

2 CALCULATION METHODS

All calculations are carried out using the first-principles pseudopotential method based on the density functional theory (DFT) with the generalized gradient approximation (GGA), as implemented in the Vienna ab initio Simulation Package (VASP)[14, 15]. The energy cut-off for the plane wave expansion is set to be 450 eV. A gamma centred 5×5×3 k-point mesh has been employed for the Brillouin zone. All atoms have been fully relaxed until the force on each atom is below 0.01 eV/Å. In addition, a 2×2×2 supercell has been constructed for pure ZnO, consisting of 32 atoms. For the doping model, the supercell containing 32 atoms were in use, where one Zn atoms are

substituted by the Eu atom. Experimentally, Y.S.Tan et al.[16] have reported that Eu atom substitutes Zn atom in the lattice. So, in the doped system, the calculation models were constructed with Eu atom substituting Zn atom. By optimizing the pure-ZnO systems, they are consistent with experimental results [17]: a= 3.24 Å, c= 5.19 Å, c/a= 1.602, which implies that our calculation methods and results are reasonable.

3 RESULTS AND DISCUSSION

Firstly, the electronic structure of the pure-ZnO has been calculated. Fig.1 shows the DOS and band structure of pure-ZnO. The valence band of pure-ZnO can be divided into three regions: the upper part from -2.2 to 0 eV is mainly contributed by 2p states of O; the lower part from -6.5 to -2.2 eV comes mainly from 3d states of Zn. Moreover, Zn-3d and O-2p states have the role of orbital hybrization, and the electron states have a certain overlap between each other, indicating that ZnO has a covalent bond, and a strong role of ionic bond. The conduction band is primarily contributed by the Zn-4s states and the O-2p states. From the DOS, it can be seen that the band gap is determined by O-2p states and Zn-4s states. As shown in Fig.1b, the band gap of pure-ZnO is 0.76 eV, which had been discussed in Ref. [7]. The value is less than the experimental value of 3.4 eV due to the limitation of DFT in GGA. The discontinuity in the exchange-correlation potential is not taken into account with the framework of DFT [18].

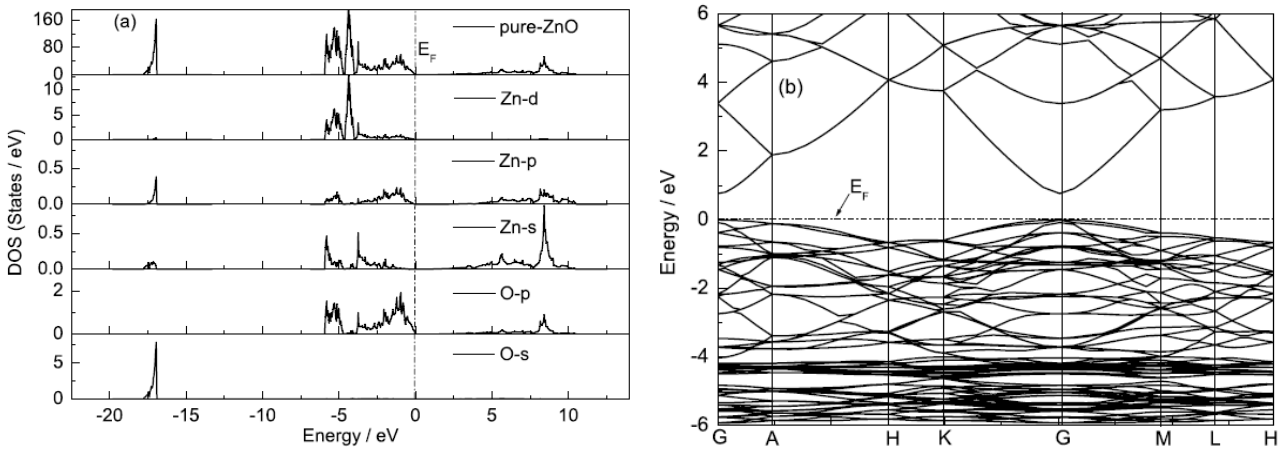


FIG. 1 (A) DOS OF PURE-ZNO AND (B) BAND STRUCTURE OF PURE-ZNO.

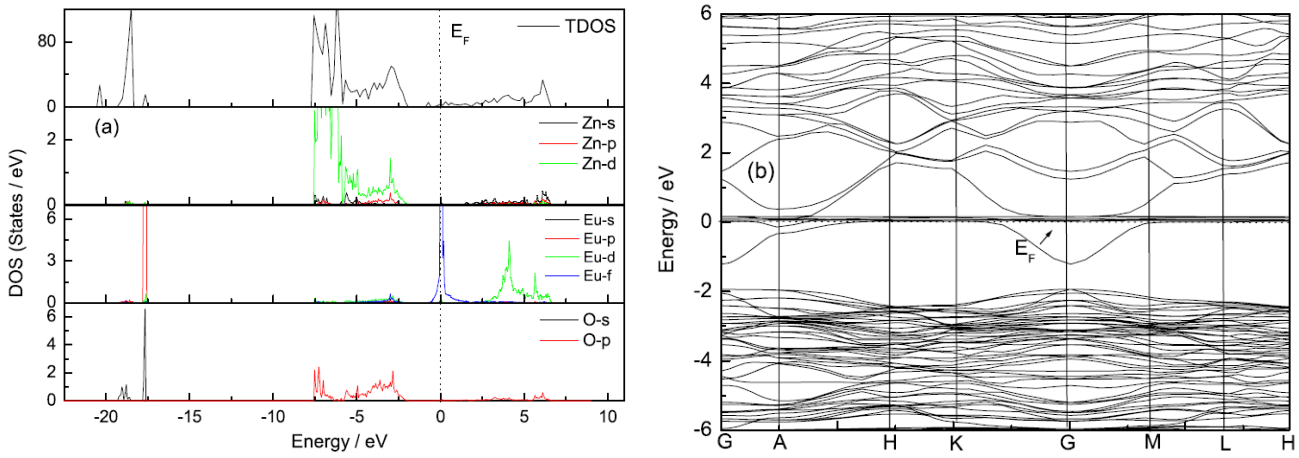
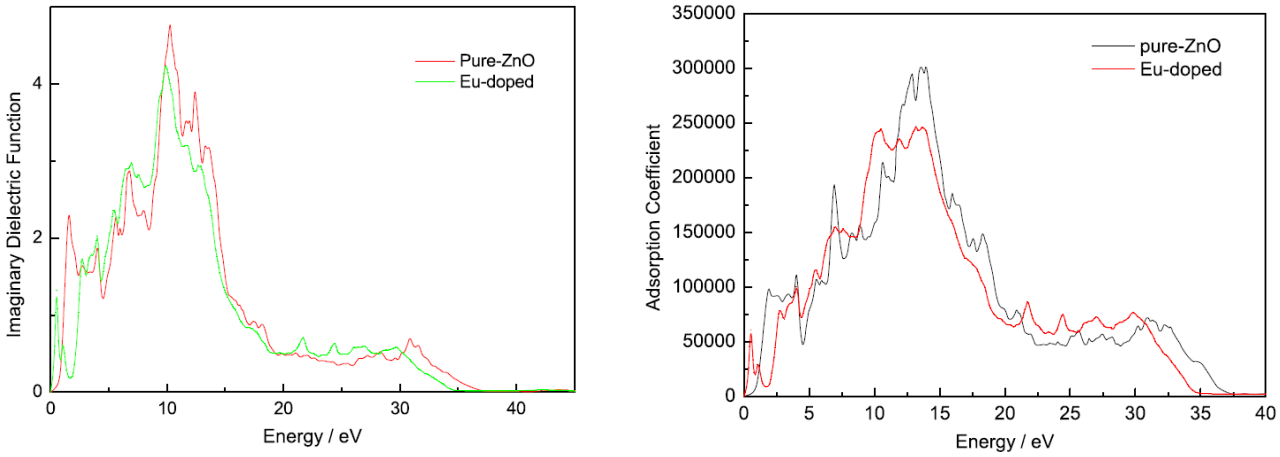


FIG. 2 (COLOR ONLINE) (A)DOS OF EU-DOPED ZNO AND (B) BAND STRUCTURE OF EU-DOPED ZNO.

Then, the electronic structure of Eu-doped ZnO has been discussed. As shown in Fig.2, the band gap of Eu-doped ZnO is smaller than that of pure-ZnO, which is consistent with the experimental results reported in Ref. [11, 12]. It is noted that, in the valence band part, the valence band within -19.24 to -18.64 eV is mainly introduced by the O-2s

states. While the valence band within -17.86 to -17.52 eV is chiefly contributed by Eu-5p states and O-2s states, and that between -7.61 eV and -2.1 eV is mainly contributed by the Zn-3d states and the O-2p states. In the conduction band part, it is noted that the Eu-4f states are localized in a narrow impurity band within 0.5 eV near the Fermi level. The conduction band within -1.21 to 1.23 eV is chiefly contributes by the Zn-4s states. The result is consistent with the experiment results [19, 20].



(a) (b)

FIG. 3 (COLOR ONLINE) (A) IMAGINARY PART OF THE DIELECTRIC FUNCTION AND (B) ADSORPTION COEFFICIENT

Sequentially, the optical properties of Eu-doped ZnO have been calculated. In the range of the linear response, solid macro-optical response function can be depicted by the light of the complex dielectric constant which is listed as follows [21]:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \tag{1}$$

However, the interaction of a phonon with the electrons can be described in terms of time dependent perturbations of ground-state electronic states in crystal. Phonon field disturbance caused the changes between the electron wave function in the occupied and unoccupied state. According to the definition and Kramers-Kroning relationship, the real part of dielectric function and absorption coefficient can be derived. The imaginary part $\varepsilon_2(\omega)$ of dielectric function can be obtained form the momentum matrix elements between the occupied and unoccupied wave functions. The calculation methods can be listed as follows [21]:

$$\varepsilon_2 = \frac{4\pi^2}{m^2\omega^2}\sum_{v,c}\int_{BZ} d^3k \frac{2}{2\pi}\left|e \bullet M_{cv}(K)\right|^2 \times \delta[E_c(k) - E_v(k) - \hbar\omega] \tag{2}$$

$$\varepsilon_1 = 1 + \frac{2}{\pi}\rho_0\int_0^{\infty}\frac{\omega'\varepsilon_2(\omega)}{\omega'^2 - \omega^2}d\omega \tag{3}$$

$$I(\omega) = \sqrt{2}\omega[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega)]^{1/2} \tag{4}$$

Where m is the free electron mass, e is the free electronic. v and c represent the valence and conduction bands, respectively. k represents the k point, ω is frequency of the incident light. BZ is first Brillouin zone, $M_{cv}(K)$ is momentum matrix element, $E_c(k)$ and $E_v(k)$ is intrinsic energy level.

Fig.3a is the imaginary part of the dielectric function of pure and Eu-doped ZnO. We distinguish the different polarization directions are distinguishable and only the ordinary light polarization (E ⊥ c-axis) in the calculations is in consideration. From the figure, it can be observed that pure-ZnO has five main peaks, corresponding to 1.55, 4.01, 6.75, 10.23 and 12.36 eV. The first peak at about 1.55 eV is originated from the transition between O-2p and Zn-4s orbital; the second peak comes from the transition between O-2p and Zn-3d orbital, and the third peak is coming from the transition between O-2p and Zn-3d orbital; the fourth peak is due to the transition between O-2p and Zn-3d orbital, and the last peak at about 12.36eV is due to the transition between Zn-3d and O-2s orbital.

However, after Eu-doped in ZnO, it is found that one new peak exists near 0.419 eV, derived from the transition

between O-2p and Eu-4f orbital. The peak at about 5.462 eV comes from the transition between Eu-4d and O-2p orbital, while the peak at about 9.736 eV is due to the transition between Zn-3d and O-2s orbital. It is noted that the peak intensity almost remained unchanged in the high-energy region. The results show that Eu-doped ZnO has interesting features in the low-energy region.

Fig.3b is the adsorption coefficient of pure and Eu-doped ZnO. For the pure-ZnO, the optical adsorption edge is about 0.71 eV, which fits well with the preceding calculated result. For Eu-doped ZnO, the adsorption peaks shift to the low energy range relative to that of pure ZnO and the pronounced absorption at lower energies due to the electron transition from impurity band, which is consistent with the experiment result [16, 22].

4 CONCLUSIONS

In conclusion, we have presented a study on the electronic and optical properties of Eu-doped ZnO from the first-principles. After doping, the Fermi level goes into the conduction band, which is demonstrated as n-type semiconductor. Moreover, it is found that highly localized Eu-4f states exist near the Fermi level after Eu-doping into ZnO. Furthermore, it also revealed that the optical properties of Eu-doped ZnO are almost consistent with that of pure-ZnO in the high-energy region, while there is a significant change in the low-energy region.

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AUTHORS



[1]**Lanli Chen**(1984-) female, the Han nationality; Graduated from the Key Laboratory for Optoelectronics and Communication of Jiangxi Province; the master graduate.

Ms. Chen was a master graduate student and worked on the laboratory. The current job is a university teacher. The research direction is the light emitting materials. She has published about 15 papers SCI & EI on the international journals of SCI & EI.



[2]**Hongduo Hu**(1983-) male, the Han nationality; the master graduate.

He is interested in the application areas for photoelectron technology, as well as theoretical materials physics and chemistry, including semiconductor.

His current job is university teacher. The research direction is the light emitting materials. He has published about 6 papers on the international journals of SCI & EI, such as Advanced Materials Research, and J. Phys. Chem. Solids. He has held three subjects.

[3]**Zhihua Xiong**(1974-) the Han nationality, Professor, Doctor, Graduate tutor, Physics director of Jiangxi Province, leader of young academic of Jiangxi Province.

Dr. Xiong, with a broad research background in theoretical materials physics and chemistry, has investigated in ZnO for many years. He well knows properties of defects/impurities in a wide range of semiconductors.

Dr. Xiong held the subjects about a dozen, such as National Natural Science Foundation of China, Natural Science Foundation of Jiangxi Province and Science & Technology Support Program of Jiangxi Province, and Young Scientist Program of Jiangxi Province. Dr. Xiong has published more than 60 SCI & EI papers in the international journals such as Phys. Rev. B, Scripta Mate., Phys. Lett. A, Chem. Phys. Lett., Opti. Mate., J. Phys. Chem. Solids, and so on.