



Communication

Study on Co-doped ZnO comparatively by first-principles calculations and relevant experiments



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ABSTRACT

Co-doped ZnO was studied using first-principles methods with comparison to experimental results taken from epitaxial $\text{Zn}_{1-x}\text{Co}_x\text{O}$ ($x \sim 0.05$) films. Density of Co^{2+} ions was determined using absorption spectra for the first time, and then a definite correlation between metallic Co clusters and the magnetism of the ZnCoO films was proved and the average number of Co atoms in the metallic Co clusters was estimated to be less than 200 using a superparamagnetic model. First-principles calculations of ZnCoO alloys and the relevant problems were discussed by comparing the electronic structures with absorption spectra and the results calculated by Tanabe-Sugano theory. U correction was proved to be necessary for calculating the band-gap energy of ZnCoO alloys, but other optical properties related to Co^{2+} ions are incorrect and the conclusion for magnetic properties is ambiguous due to uncertainty of the calculated highly localized states, which are in pressing for solution in study of material properties relevant to electronic structure.

1. Introduction

ZnO is one of important II-VI semiconductors receiving much attention in the past decades [1–4]. Since Dietl et al.'s [5] evaluation of high Curie temperature by mean-field theory, ZnO was extensively studied as a candidate of dilute magnetic semiconductor (DMS) with wide band gap. In 2001, Ueda et al. [6] reported the first observation of room-temperature ferromagnetism in Co-doped ZnO films, thus much efforts were paid to the study of ZnO doped by Co or other transition-metal elements. Unfortunately, no definite conclusion has been drawn experimentally and theoretically for ZnO as a DMS candidate with room-temperature ferromagnetism up to now. For example, the nature of magnetic interaction was found changed when correlations on transition-metal ions were treated using different methods for the first-principles calculations [7]. On the other hand, Co-doped ZnO materials with and without ferromagnetism were both reported in experiment [6,8–12], and then the carriers and defects were suggested to be the crucial reasons responsible for ferromagnetic formation [13,14] because they are very sensitive to synthesis technology of ZnO materials. In addition, metallic Co clusters were demonstrated to be the possible origin of ferromagnetic Co-doped ZnO [15].

In this work, Co-doped ZnO was studied using first-principles calculations with comparison to the experimental results obtained from $\text{Zn}_{1-x}\text{Co}_x\text{O}$ films grown on sapphire (001) substrates by a

pulsed-laser deposition (PLD) method. The article is organized as below. The methods for the first-principles calculations and experiments were detailed in section II. In section III, the absorption spectra were used to determine the density of Co^{2+} ions first, and then a correlation between the saturated magnetization moment and metallic Co clusters was given. Furthermore, the magnetization loops were used to estimate the average number of Co atoms in metallic Co clusters using a paramagnetic model. In comparison with experimental results, validity of first-principles calculations was discussed, and then the physical parameters of ZnCoO alloys calculated using U correction were compared with experimental results.

2. Computational and experimental details

The first-principles calculations were performed using the code CASTEP [16] based on density functional theory. Ultra-soft pseudo-potential [17] and plane-wave expansion of the wave functions were used for the calculations. Generalized gradient approximation (GGA) in the Perdew–Burke–Erzerhof scheme [18] was used for description of the exchange and correlation potential. The interaction between ions and valence electrons was described by the projector-augmented wave potential method. Electron configurations were set to be $3d^{10}4s^2$ for Zn, $2s^22p^4$ for O, and $3d^74s^2$ for Co atoms with consideration of electron spin polarization. The wurtzite $2 \times 2 \times 1$ supercells, as shown in

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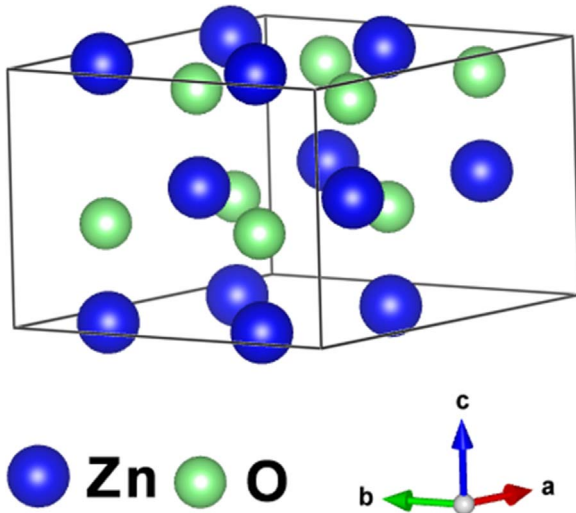


Fig. 1. (Color online) $2 \times 2 \times 1$ supercells of ZnO used for calculations, in which 1 to 3 Zn atoms are substituted by Co atoms for calculations of ZnCoO alloys.

Fig. 1, were optimized by the method proposed by Broyden et al. [19]. By carefully testing, the cutoff energy was set to 540 eV and the k -point set mesh was chosen to be $4 \times 4 \times 4$. The optimization was stopped at a force less than 0.01 eV/atom, leading to a self-consistent field tolerance of $\sim 5 \times 10^{-7}$ eV/atom. The first-principles calculations were compared with and without correction by Hubbard U .

Epitaxial $\text{Zn}_{1-x}\text{Co}_x\text{O}$ films were grown on c -plane sapphire substrates at 750 °C using a PLD system by ablating $\text{Zn}_{0.95}\text{Co}_{0.05}\text{O}$ ceramic target, which was made of ZnO and CoO powders with purities of 99.999% and 99.95%, respectively. The film deposition was carried out in an atmosphere of O_2 at $\sim 1 \times 10^{-4}$, 1.0×10^{-2} , 0.1, 1.0, and 5.0 Pa, respectively, for study of the film properties in dependence on deposition condition. More details for film preparation please refer to our previous study [20–22]. For convenience, the samples deposited at $\sim 1 \times 10^{-4}$, 1.0×10^{-2} , 0.1, 1.0, and 5.0 Pa are referred to as A, B, C, D, and E, respectively. X-ray diffraction (XRD, Bruker D8) analysis showed that all of the as-grown films exhibited good crystallinity with epitaxial relationship of ZnO [10 $\bar{1}$ 0] // Sapphire [11 $\bar{2}$ 0] and ZnO (0001) // Sapphire (0001) [23]. Quantitative analysis by electron probe mass analyzer (EPMA) showed that Co content in the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ films is dependent on the deposition pressure. For the samples A to E, the percentages of Co atoms are 7.7%, 6.5%, 5.8%, 4.7%, and 3.5%, respectively. Ultraviolet-to-near-infrared (UV-to-NIR) spectroscopy (Maya 2000 Pro) was used for measurement of the film transmittance, with which the band-gap energy (E_g) and the content of Co^{2+} ions in the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ films were determined. Measurement of magnetic properties was carried on a physical property measurement system (PPMS-9T) at room temperature and 10 K.

3. Results and discussion

3.1. Characterization of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ films

Quantitative determination of Co^{2+} ions substituting to Zn^{2+} ions is a problem that was not well issued in the study of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ films. Co content in ZnCoO films, or even in the targets for film deposition, was usually used as the content of Co^{2+} ions, thus leading to the confusion in the study of magnetic origin. As a matter of fact, Co atoms substituting to Zn^{2+} ions and clustering into metallic Co nanoparticles are both possible during film deposition and alloying. To avoid confusion, the total Co content determined by EPMA in this work is referred to as content of Co atoms (X) for distinguishing from content of Co^{2+} ions (x), which was estimated using the optical absorption cross section of Co^{2+} ions. Fig. 2 shows the absorption spectra of $\text{Zn}_{1-x}\text{Co}_x\text{O}$

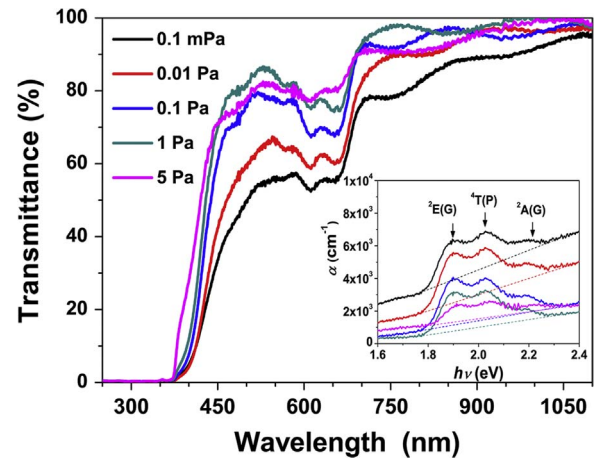


Fig. 2. (Color online) Absorption spectra of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ films deposited at the atmospheres with the given O_2 pressures. The inset shows the absorption coefficients calculated using the transmittance spectra of the samples.

films deposited at the atmospheres with the given O_2 pressures. With the increase in the deposition pressure, the absorption edge shifted toward the side of short wavelength, indicating an increase in the band-gap energy. The optical band-gap energies (E_g) of samples A to E were determined by plotting absorption coefficient (α) as a function of photon energy ($h\nu$) using equation of $\alpha = (h\nu - E_g)^{0.5}$ for an allowed direct semiconductor, and are listed in Table 1.

As shown in Fig. 2, absorption band of Co^{2+} ions is visible in the spectral range of 550–750 nm, upon excitation into the broad and structured ${}^4\text{A}_2({}^4\text{F}) \rightarrow {}^4\text{T}_1({}^4\text{P})$ d - d band centered at ~ 2.0 eV [24]. As the absorbance of Co^{2+} ions consists of nonzero unsaturable loss and saturable absorber [25] contributing to the optical absorptions of background and the structured band, respectively, the area of absorption peak (S_a) could be used to determine the density of Co^{2+} ions ($n_{\text{Co}^{2+}}$) by

$$n_{\text{Co}^{2+}} = \frac{S_a}{\sigma}, \quad (1)$$

if the ground-state absorption cross section (σ) is known for Co^{2+} ions in a crystal field with tetrahedral coordination. Based on theory of linear absorption, Denisov et al. [26] estimated $\sigma_{1.54} = 2.0 - 2.2 \times 10^{-19} \text{ cm}^2$ for ${}^4\text{A}_2({}^4\text{F}) \rightarrow {}^4\text{T}_1({}^4\text{F})$ transition of Co^{2+} ions at $\lambda = 1.54 \mu\text{m}$ in zinc aluminosilicate transparent glass ceramics (ZnAl_2O_4). According to the spectra of absorption coefficient presented in their article, the ground-state absorption cross section of Co^{2+} ions could be estimated to be $\sigma_{0.6} \approx 1.0 \pm 0.1 \times 10^{-18} \text{ cm}^2$ for ${}^4\text{A}_2({}^4\text{F}) \rightarrow {}^4\text{T}_1({}^4\text{P})$ transition of Co^{2+} ions at $\lambda \approx 0.6 \mu\text{m}$. As such, the contents of Co^{2+} ions in the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ films could be estimated using the absorption coefficients in the inset in Fig. 2. The determined contents of Co^{2+} ions are essentially in association with the contents of Co atoms determined by EPMA, but slightly smaller; thus the discrepancy ($\Delta x = X - x$) was used as an estimation of Co content in metallic Co clusters, as listed in Table 1.

Measurement of magnetization loop showed that the saturated

Table 1

Content of Co atoms (X) and Co^{2+} ions (x), content discrepancy ($\Delta x = X - x$), optical band gap (E_g) and saturated magnetic moment (M_s).

	X	x	Δx	E_g (eV)	M_s (μ_B /Co)
A	0.077 ± 0.005	0.049 ± 0.010	0.028 ± 0.015	3.16 ± 0.02	0.049
B	0.065 ± 0.005	0.062 ± 0.010	0.003 ± 0.015	3.15 ± 0.02	0.005
C	0.058 ± 0.005	0.056 ± 0.010	0.002 ± 0.015	3.18 ± 0.02	0.006
D	0.047 ± 0.005	0.051 ± 0.010	-0.004 ± 0.015	3.21 ± 0.02	0.005
E	0.035 ± 0.005	0.021 ± 0.010	0.014 ± 0.015	3.26 ± 0.02	0.038

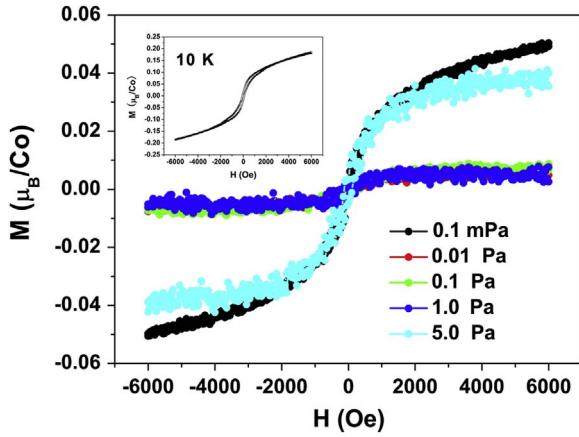


Fig. 3. (Color online) Magnetization loops of the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ films at room temperature. The inset is the magnetization loop taken at 10 K from sample A.

magnetic moment (M_S) is different sample to sample, as shown in Fig. 3, but all of the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ films exhibited weak ferromagnetism at room temperature as well as low temperature. The determined M_S values were found strongly dependent on Δx , rather than the contents of Co^{2+} ions, as shown in Table 1. Therefore, we have a definite conclusion that Co^{2+} ions substituted to Zn^{2+} in the ZnO matrix are paramagnetic and metallic Co clusters are the origin of the ferromagnetism observed in these $\text{Zn}_{1-x}\text{Co}_x\text{O}$ films. This conclusion is highly in consistent with Rode et al.'s demonstration of paramagnetic Co^{2+} ions coexisting with ferromagnetic metallic states [15]. Similar to other reports, the coercive fields (H_c) in magnetization loops were so small that the magnetization loops look like highly overlapping. Such magnetization loops are very similar to those frequently observed in superparamagnetic powders consisting of ferromagnetic nanoparticles [27].

Ferromagnetic powders exhibit superparamagnetic behaviors strongly dependent on their sizes. Under assumption of single domain in the metallic Co clusters, the dependence of moment on magnetic field (H) could be described by Langevin function [27], i.e.,

$$\frac{M}{M_S} = L(\beta) = \coth \beta - \frac{1}{\beta} \quad (2)$$

$$\beta = \mu_0 \frac{NM_S H}{kT} \quad (3)$$

where μ_0 is magnetic permeability in vacuum, N is the average number of Co atoms in metallic Co clusters, k is the Boltzmann constant, and T is temperature. Taking $M_S = 1.72 \mu_B$ for a Co atom [27] and $T = 10$ K, the magnetization loops were calculated using Eq. (2) for metallic Co clusters containing the given numbers of Co atoms. The calculated magnetization loops have similarity to those observed in our experiment, as shown in Fig. 4. Our calculations showed that the magnetic moments of metallic Co clusters are easier to reach saturation with the increase in the number of Co atoms, and then the average number of Co atoms in the metallic Co clusters could be further estimated with comparison to the results obtained in experiment. In comparison to the experiment results, the average number of Co atoms in the metallic Co clusters could be estimated to be less than 200, which leads to the small metallic Co clusters in the scale less than 1 nm, and thus was not easily to be observed in experiment; thus, the superparamagnetic loops could be regarded as the solid evidence of metallic Co clusters in the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ films indeed.

3.2. Electronic structures of ZnO, CoO, and $\text{Zn}_{1-x}\text{Co}_x\text{O}$

In the previous study, first-principles calculations were commonly accepted to discuss the possibility of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ alloys used as a DMS

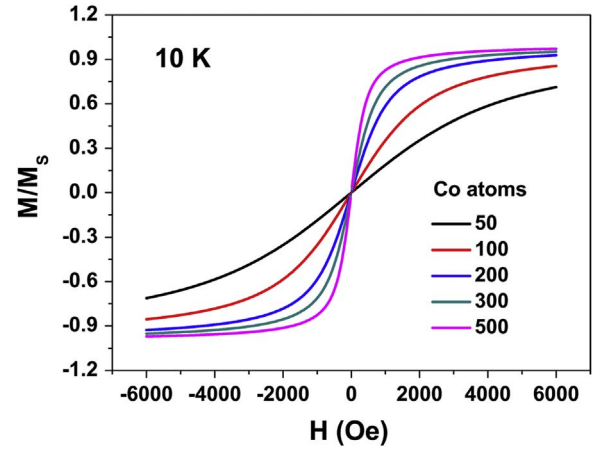


Fig. 4. (Color online) Magnetization loops calculated using Eq. (2) by taking $M_S = 1.72 \mu_B$ for a Co atom and $T = 10$ K for metallic Co clusters containing the given numbers of Co atoms.

candidate. However, the first-principles calculations did not make the issue more perspicuous. Conversely, contradictory conclusions were reported by different authors, but the reasons leading to the contradiction are ambiguous up to now. It is well-known that first-principles calculations usually produce a band-gap energy underestimated, and then Hubbard U is often adopted for correction. As a matter of fact, we have no knowledge if the calculated electronic structure is correct or not no matter whether U correction is used, because no feasible data has been used for comparison. For this purpose, we have a discussion for the electronic structures calculated by first-principles methods in comparison with the spectral data.

Fig. 5 shows the electronic structures of ZnO calculated before and after U correction, in which U value was set to be 10 eV for Zn and 7 eV for O after Sheetz et al.'s study of ZnO [28] in using CASTEP. The U correction made the band gap broadened to 3.37 eV, which is consistent with the experimental results determined at low temperature [4]. Along with elevation of the conduction band, the change in the valence band is also visible. As shown in Fig. 4, a narrow 3d band was separated from the valence band after U correction, forming a highly localized band below the valence band. On the basis of U correction to ZnO, $U = 2.4$ eV was found adequate for Co^{2+} ions because the calculated band-gap energy of CoO with rocksalt structure is ~ 2.4 eV, which is in good agreement with the experimental result [29], as shown in Fig. 6. The electronic structure indicates that rocksalt CoO is a paramagnetic indirect semiconductor. In addition, two highly localized bands are observed at the energy levels close to the conduction band minimum (CBM) and the valence band maximum (VBM), respectively. The former is assigned to the anti-binding state (t_{2g}) of Co^{2+} ions and

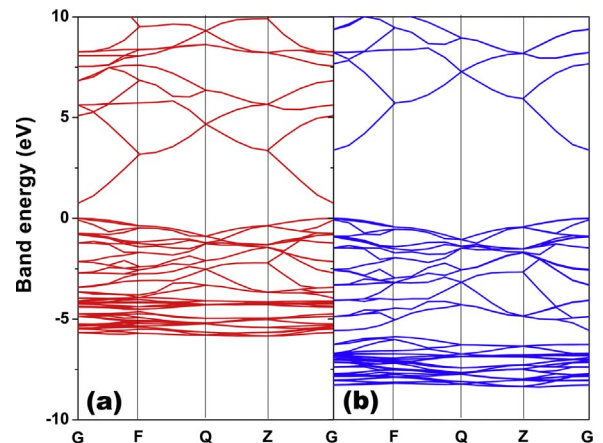


Fig. 5. (Color online) Electronic structures of ZnO with and without U correction.

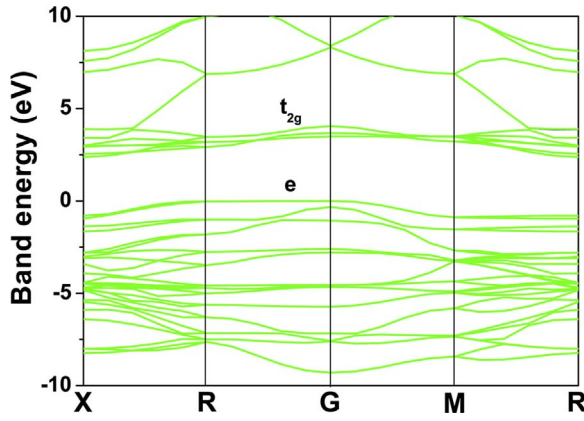


Fig. 6. (Color online) Electronic structures of CoO with $U = 2.4$ eV.

the latter is the non-binding state (e).

When a Co atom was doped in ZnO, the energy level of highly localized t_{2g} band was found not consistent with the results obtained in experiment or calculated using Tanabe-Sugano theory [30], as shown in Fig. 7. Taking $10 Dq/B \sim 5.0$ in $Zn_{1-x}Co_xO$, the t_{2g} band or ${}^4T_1(P)$ band calculated using Tanabe-Sugano theory is centered at ~ 2.0 eV [24], which is in good agreement with our observation in the absorption spectra. In addition, Tanabe-Sugano theory predicted metal-to-ligand charge transfer (ML_{CBCT}) and ligand-to-metal charge transfer ($L_{VB}MCT$) transitions between the t_{2g} and conduction bands. Such kinds of charge transfer transitions were demonstrated existence in Co-doped ZnO by our measurement of photoluminescence [19]. However, the first-principles calculations suggested the t_{2g} band located in the conduction bands. Therefore, we conclude that first-principles calculations are deficient in some details of electronic structure, at least for the highly localized states. This deficiency is likely to be the major reason leading to confusion in the calculations of magnetic properties. In comparison with the results calculated without U correction, U correction is able to separate the localized band consisting of some Zn 3d electrons from the valence band (Fig. 5). Therefore, U correction seems to be necessary for study of ZnCoO alloys because the electronic density of states (DOS) will change if these localized electrons are located in the valence band. On the other hand, the incorrect t_{2g} band

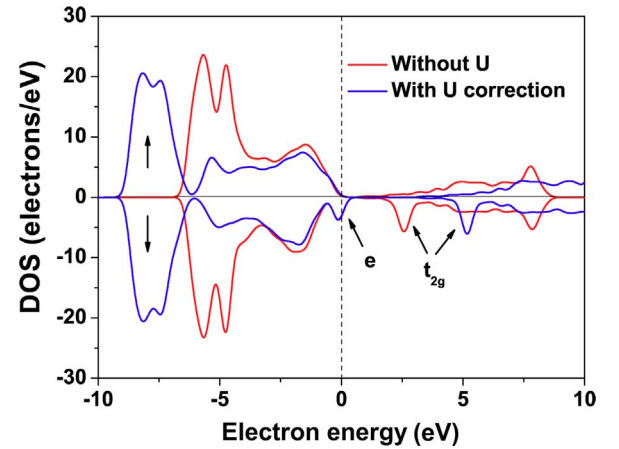


Fig. 8. (Color online) DOS of $Zn_{0.875}Co_{0.125}O$ alloy with and without U correction.

mainly influences the optical properties related to Co^{2+} ions, but has few effects on the magnetic properties.

Fig. 8 shows the DOS of $Zn_{0.875}Co_{0.125}O$ alloy before and after U correction. Similar to ZnO, U correction made localized 3d states separated from the valence band. Quantitative analysis showed that the ferromagnetic phase is favorable with a moment of $\sim 3 \mu_B/Co$ before U correction and paramagnetic phase is favorable with a moment $\sim 0.1 \mu_B/Co$ after U correction. Our results are highly in accordance with Gopal and Spaldin's conclusion that ferromagnetic coupling is favorable for single-type substitutional transition-metal ions within local density approximation (LDA) and unfavorable within LDA + U [7]. However, if more Co atoms were doped, for example, $Zn_{0.75}Co_{0.25}O$ and $Zn_{0.625}Co_{0.375}O$, our calculations with U correction showed that ferromagnetic phase is favorable with a moment of $\sim 3 \mu_B/Co$, which is contradictory to Hu et al.'s [31] conclusion obtained using LDA+ U . Due to the deficiency in calculation of electronic structure using first-principles methods, we are unable to have a definite judgment for the favorable phase. Conversely, a more realistic conclusion is that the formation energies of the paramagnetic and ferromagnetic phases are very close. Hu et al.'s calculations also showed that the discrepancy in the formation energy of the two phases is as low as ~ 5 meV/atom, which is about one thousandth of the formation energy of ZnO [4]. We

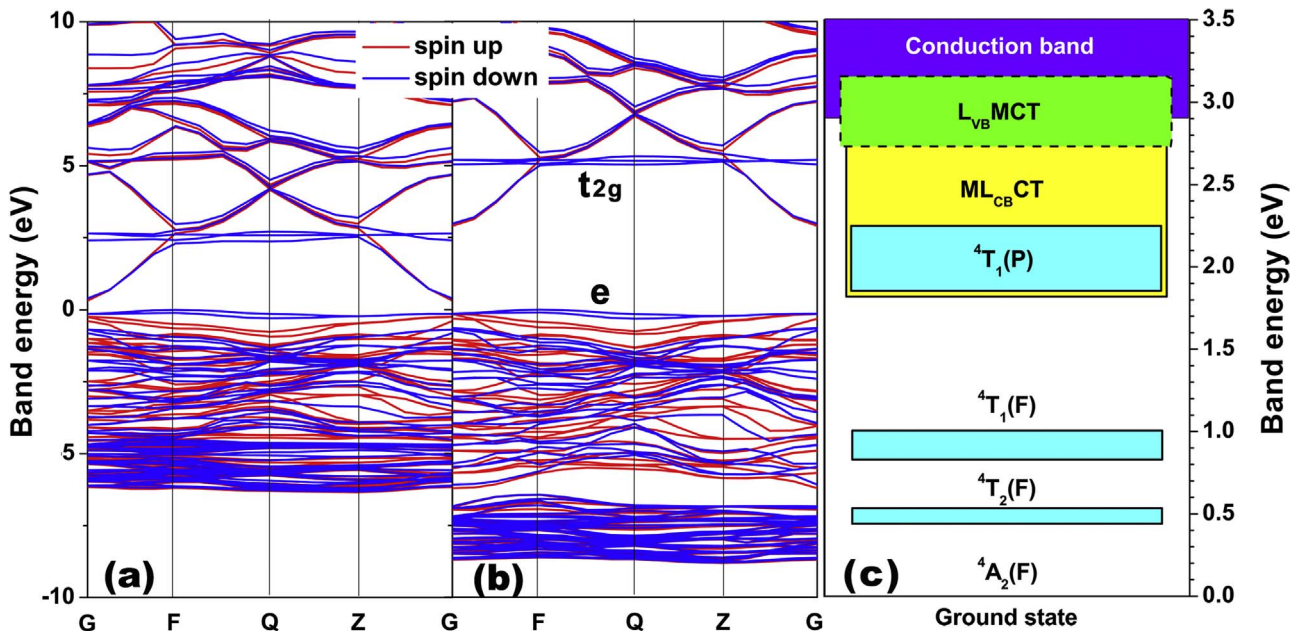


Fig. 7. (Color online) (a) and (b) Electronic structures of $Zn_{0.875}Co_{0.125}O$ alloy before and after U correction, respectively, and (c) Excited states of Co^{2+} ions in $Zn_{1-x}Co_xO$ alloy calculated using Tanabe-Sugano theory.

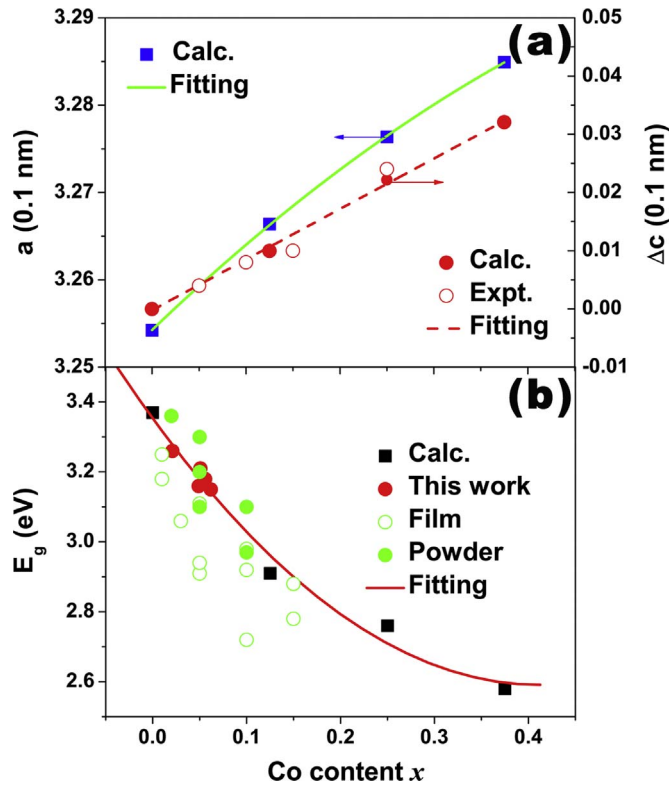


Fig. 9. (Color online) Lattice parameters a and c (a) and band-gap energy (b) plotted as a function of Co content. The experimental data in Fig. 8a was taken from Ref. [6]. The experimental data in Fig. 8b was taken from Refs. [32,33] for powder samples and from Refs. [11,34,35] for film samples.

are convinced that the two phases are both possible if the interactions between Co^{2+} ions are enhanced with the increase in Co content and/or the Ruderman-Kittler-Kasuya-Yosida (RKKY) interactions are enhanced due to an increase in carrier density. Therefore, we suggest that high Co content and/or high carrier density is more favorable for preparation of a ferromagnetic ZnCoO film. This suggestion is consistent with the fact that strong ferromagnetism is usually observed in the samples with high Co contents and paramagnetism or weak ferromagnetism is often reported in the samples with relatively low Co contents. As a consequence, deposition conditions may play a crucial role in formation of ferromagnetic ZnCoO films.

3.3. Material parameters of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ alloys

Though the first-principles calculations leave the favorable phase in $\text{Zn}_{1-x}\text{Co}_x\text{O}$ alloys ambiguous, the material parameters, such as lattice parameters and band-gap energy, were found reasonable after U correction. Fig. 9a shows the calculated lattice parameters a and c in comparison with the experimental data, in which the shifts in lattice parameter c with respect to ZnO are plotted for comparison with experimental data. Using the calculated results of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ alloys with $x=0.125, 0.25$, and 0.375 , the lattice parameters a and c of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ alloys can be fitted by

$$a = 3.254 + 0.103x - 0.058x^2 \quad (4a)$$

$$c = 5.218 + 0.087x - 0.001x^2 \quad (4b)$$

where a and c are in angstrom. With the increase in Co content, a is increasing with a small bowing coefficient (< 0.06) and c is increasing almost linearly, in good agreement with the results determined in experiment [6].

Fig. 9b shows the band-gap energy calculated by the first-principles method with U correction and plotted as a function of Co content with

comparison to the results reported by different groups. The band-gap energy can be fitted by

$$E_g(\text{eV}) = 3.37 - 3.70x + 3.48x^2 \quad (5)$$

This equation is highly in consistent with the data obtained in this work, in which the contents of Co^{2+} ions are used as x . As for the experimental results from other groups [11,32–35], Eq. (5) fits the data determined from powder samples [32,33] better than that from the film samples [11,34,35] because the Co contents in the targets other than the realistic Co contents in the films were used as x in some film samples. On the other hand, the contents of Co^{2+} ions in these $\text{Zn}_{1-x}\text{Co}_x\text{O}$ powder and film samples were not determined, thus leading to the discrepancy relatively larger than our data.

Above results demonstrated the first-principles calculations with U correction are capable of approaching to some realistic results of ZnCoO alloys better than that without U correction. However, the results are still incorrect for optical absorption related to Co^{2+} ions, or other transition-metal element doped. On the other hand, the conclusion is ambiguous for the ferromagnetic properties. These uncertainties are probably in association with the deficiency of pseudo-potentials, which are unable to produce accurate energy levels for some electronic orbits, especially for the highly localized states, even if U correction is used.

4. Conclusions

In conclusion, we studied magnetic properties of Co-doped ZnO using the first-principles methods with comparison to experimental results of epitaxial ZnCoO films. Metallic Co clusters were definitely proved to be responsible for the magnetic properties of the $\text{Zn}_{1-x}\text{Co}_x\text{O}$ films with $x \sim 0.05$, and Co^{2+} ions substituting to Zn^{2+} ions produced paramagnetism. The average number of Co atoms was estimated to be less than 200 in the metallic Co clusters. The first-principles calculations showed that U correction is necessary for study of $\text{Zn}_{1-x}\text{Co}_x\text{O}$ alloys, but the results are still incorrect for optical absorption related to the highly localized states, which are in pressing for solution in study of material properties relevant to electronic structure. On the other hand, the conclusion is ambiguous for the ferromagnetic properties, possibly due to the ferromagnetic and paramagnetic phases having very close formation energy. We suggest that high Co content and/or high carrier density is more favorable for preparation of a ferromagnetic ZnCoO film due to the enhancement in the interactions between Co^{2+} ions and in the RKKY interactions.

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