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Article

LSDA+*U* study on the electronic and anti-ferromagnetic properties of Ni-doped CuO and Cu-doped NiO

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ABSTRACT

Doping is an effective way to improve the activity of photocatalysts. The effect of doping on the magnetic properties of some photocatalysts that are easily recycled was studied using the local spin density approximation (LSDA)+*U* method on typical divalent metal oxide semiconductors CuO, NiO, Ni-doped CuO, and Cu-doped NiO. It is found that the influence of Ni doping on the spatial structure of CuO and that of Cu doping on the spatial structure of NiO are negligible because of the similar radii of Ni²⁺ and Cu²⁺. The valence band and conduction band for Ni-doped CuO are clearly spin-split, corresponding to a net effective magnetic moment of $\mu_{\text{eff}} = 1.66 \mu_B$. This may improve the photocatalytic efficiency and raise the recycle rate of photocatalysts. In the Cu-doped NiO system, the presence of Cu 3*d* states near to the Fermi level increases the width of the valence band and narrows the band gap with respect to that in pure NiO. Beyond the Cu 3*d* states, within the band gap, appear two energy levels around the Fermi level, which may effectively separate the electron-hole pair and also lead to enhanced absorption of visible light and infrared light. It can be concluded that the observed changes in the band structure may be helpful for improving the activity of photocatalysts and the doped systems have net magnetic moments, meaning that they are easily recycled and can be reused.

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1. Introduction

For many materials, density-functional theory (DFT) [1] with the local spin density approximation (LSDA) [2] provides a good description of their ground-state properties. However, problems arise when the DFT-LSDA approach is applied to materials with ions that contain incomplete *d* or *f* shells, such as transition-metal oxides or heavy fermion systems. We circumvent this problem by applying DFT+*U* calculations to study the

structural, electronic, and magnetic properties of doped metal oxides.

Most transition-metal oxides are wide-gap antiferromagnetic insulators [3–9], which are predicted to be either metals (e.g., FeO and CoO) or small-gap semiconductors (e.g., MnO and NiO) by DFT-LSDA [10]. The failure of the DFT-LSDA can be traced to the mean-field character of the Kohn-Sham equations as well as to the poor description of strong correlation effects within the homogeneous electron gas. The strong correlation

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effects are responsible for the breakdown of the DFT-LSDA description of the electronic structure of these compounds. To provide a better description of these effects, the Mott-Hubbard picture has been introduced [11].

For transition-metal oxides, *d* orbitals are well localized and have a strong atom-like character. Even though the local density approximation (LDA) provides a good approximation for the average Coulomb energy of *d-d* interactions, it fails to correctly describe the strong Coulomb and exchange interaction between electrons in the same *d* shell. The main intention of LDA+*U* is to identify these atomic orbitals and describe their electronic interactions as strongly correlated states. The other orbitals are delocalized and considered to be properly described by the LDA.

3*d* transition-metal monoxides exhibit a rich variety of electronic and magnetic phenomena, and as a result they have received much attention in the last few decades. Transition metal monoxides, MO (*M* = Mn, Co, Ni and Cu), reveal complicated magnetic as well as electronic structures. Ferromagnetic properties are observed in nano-sized MO and 3*d* metal-doped MO by modifying the original magnetic order [12]. Among the transition metal monoxides, CuO is a strongly correlated electron system that exhibits Mott insulating and antiferromagnetic (AFM) behavior. The magnetic structure of CuO consists of Cu–O parallel sheets, in which an oxygen atom is located at the center of a copper distorted tetrahedron in the (110) plane. The exchange in the Cu–O–Cu chains along the (101) direction is strongly and completely AFM. CuO (tenorite) is an antiferromagnet below ~230 K. Different authors have introduced diverse defects into the oxygen and/or cation lattices as a means of both evaluating the relationship of the dopants with the anomalous magnetic properties of CuO, and to study the kind of magnetic bonds that lead to the ordering in CuO. Doping is an effective way to improve the activity of photocatalysts [13–15]. To study the effect of doping on the magnetic properties of some photocatalysts, which are easily recycled for practical application in photocatalysis, we choose typical magnetic divalent oxide semiconductors CuO and NiO as examples. Doping with a very low concentration of impurities has been performed for the study of the intrinsic magnetic properties of the two metal oxides [16,17].

For CuO, it is concluded that, in contrast to standard DFT calculations, taking into account electronic correlations by DFT+*U* for an AFM insulator leads to an energy gap and magnetic moment values in good agreement with experimental data [18–21]. Ahmad et al. [22] applied DFT+*U* calculations with a spin polarized approach on the low-index surface of CuO, showing that CuO (111) and CuO (011) have the appropriate band edge to accomplish water splitting and CO₂ reduction. Thus, CuO is a good photocatalyst [23,24] from which to start tuning its magnetic property via doping. In this way, CuO with a low-index surface may have the appropriate band edge to encourage the reaction of water splitting and CO₂ reduction [25] and possess magnetism at the same time. This material, modified by doping for enhanced magnetic performance, will have more potential application in the field of photocatalysis than non-magnetic photocatalytic materials as a result of its

ability to recycle.

NiO is known as a p-type semiconducting material and it is widely used in the fabrication of p–n heterostructures with n-type TiO₂ because of their substantial technological potential in the area of photocatalysis [26,27]. It is a highly correlated material with insulating and AFM character [28]. In addition, it displays a simple, ordered cubic NaCl-type crystal structure. The NiO insulating state is characterized by a gap of about 4 eV and a magnetic moment of about 1.7 μ_B . In the Mott-Hubbard picture of NiO, the *d-d* Coulomb interaction splits the Ni *d* subbands into the so-called lower and upper Hubbard bands. The upper Hubbard band has mostly Ni 3*d*⁹ character, while the top of the valence band (VB) is of 3*d*⁸ character, leading to a Mott-Hubbard *d-d* type gap. However, O 1s X-ray absorption [29], X-ray photoemission, and bremsstrahlung isochromat spectroscopies [9] on Li_xNi_{1-x}O have shown that the additional hole has mainly oxygen character. In contrast to the Mott-Hubbard model, the energy-band gap caused by the Ni 3*d* correlations is, therefore, of the charge-transfer type between the occupied O 2*p* and Ni 3*d* empty states.

There are strong indications that NiO is a charge-transfer insulator and the top of its VB is primarily formed by O 2*p* states, while the bottom of its conduction band (CB) is Ni 3*d* states. Certainly, the LDA in DFT, widely used in solid-state physics, fails to describe NiO as an insulator and predicts it to be a metal [10,30]. It has been suggested that the difficulty of the LDA to properly describe narrow-band insulators is related to the insufficient cancellation of the self-interaction correction (SIC) inherent in the local exchange functional. The SIC-LDA introduces a qualitatively correct (ca. 3 eV) gap in the spectrum, and improves the magnitude of the magnetic moments and the value of the lattice constant in NiO [31,32]. Another approach, which supplements the LDA with an effective on-site repulsion *U*, has also become popular [33,34]. An additional requirement of the LDA+*U* approach is that the additional energy is applied only to the valence electrons, which are re-optimized while constrained to be orthogonal to the core states [35].

In this work, we have performed a series of DFT+*U* calculations to study the structural, electronic, and magnetic properties of CuO and NiO crystals by choosing proper Hubbard *U* parameters. These materials can be applied as photocatalysts only if their electronic structures can be tuned for appropriate VB and CB positions. It is necessary that the conduction band minimum (CBM) has to lie above the reduction reaction potential and the valence band maximum (VBM) has to lie below the oxidation reaction potential. Herein, we attempted to change the electronic structure and magnetic properties by doping to thus endow the two semiconductors with an appropriate band structure. This will be more promising than ordinary photocatalytic materials for recycling utilization in energy and environment areas.

2. Computational details

All descriptions related to geometry, electronic and magnetic structures presented here have been based on calcula-

tions using the projector augmented wave (PAW) [36,37] method implemented in the Vienna Ab-initio Simulation Package (VASP) code [38,39]. The exchange-correlation interaction was taken into account through the local density approximation as parameterized. Eleven electrons ($4s^1 3d^{10}$) for copper, ten electrons ($3d^8 4s^2$) for nickel, and six electrons ($2s^2 2p^4$) for oxygen were considered as valence electrons. Our convergence test showed that a cut-off energy of 400 eV and a $4 \times 4 \times 4$ Monkhorst-Pack k-point mesh yielded a total energy difference within 0.002 eV. The partial occupancies for each wave function were estimated by the method of Methfessel and Paxton using the smearing parameter of 0.1 eV. The self-consistent convergence of the total energy was set to be 1×10^{-4} eV and that for the maximum force on the atoms was 0.01 eV/Å.

One difficulty in the computation of material properties is that the band gaps and related properties of most materials are generally underestimated by the standard density-functional theory approximations. To avoid this, we utilized the DFT plus effective Coulomb interaction U (DFT+ U) formalism, as implemented in the VASP code. The simplified rotationally invariant Dudarev's form for the DFT+ U technique was used to correct the electron correlation effects caused by the localized Ni 3d and Cu 3d orbitals in the NiO and CuO crystals. In this approach, only the difference between the Hubbard parameter, U , and exchange parameter, J , ($U_{\text{eff}} = U - J$), is effective. Subtle differences in the effective Hubbard parameter, U_{eff} , may significantly influence the magnetic ordering and physical stability of NiO crystal. We fixed the value of the J exchange parameter to be 0.15 eV and adjusted the value of U from 0 to 8 eV to describe the real ground state of NiO with the AFM order at the absolute temperature. At $U = 8$ eV, our calculation results described the ground state and electronic structure of NiO crystal correctly, which agree well with the assessment of U_{eff} by Gryaznov et al. [40]. The LSDA+ U calculated band gap of pure NiO was 3.5 eV, which is in good agreement with experimental values. Thus, $U = 8$ eV was correct. For the CuO crystal, the Hubbard parameter, U , was set at 8 eV and an exchange parameter of $J = 0$ eV can obtain satisfactory results.

3. Results and discussion

3.1. Perfect and Ni-doped CuO crystal

To discuss the change in the electronic and magnetic structure by introducing atom impurities, we investigated the bulk structure, and the most realistic basis set of parameters (choice of basis set, ASA sphere radii, etc.) was defined, which describes the bulk electronic structure adequately and makes the doping calculations feasible at the same time.

CuO is an anti-ferromagnetic metal oxide p-type semiconductor. Its crystallographic structure is monoclinic in the $C2/c$ space group. It has eight formula units per magnetic unit cell. It is further reported to have a band gap of 1.0–1.9 eV [41–43] and local moment per Cu atom of $\sim 0.7 \mu_B$ [44,45] (μ_B , Bohr magneton). Standard DFT calculations with local exchange-correlation functionals generally predict a nonmagnetic ground state with metallic character instead of the well-known

semiconducting ground state. The failure of standard DFT to obtain the correct electronic properties of CuO might be understood from its intrinsic nature (inability to treat electron-electron interactions in correlated systems). Improvements to first-principle theories based on DFT plus screened Coulomb interactions (U) have been proposed. For the pure CuO unit cell, the calculated optimized lattice constant was 4.155 Å, which is in good agreement with the value determined by XRD data [46,47].

From the calculation results of the total spin density-of-states (DOS) for a perfect CuO magnetic unit cell shown in Fig. 1, it is found that CuO is a magnetic material with a net effective magnetic moment of about $\mu_{\text{eff}} = 0.66 \mu_B$. Additionally, the band gap for perfect CuO can be easily calculated based on the figure with an E_g of 1.568 eV, which is in accordance with the value in the range 1.0 to 1.9 eV reported experimentally at ambient temperature [42–43]. The magnetic moment per Cu atom (M_{Cu}) (in units of μ_B) was calculated as $0.68 \mu_B$, in good agreement with the reported experimental value of $\sim 0.7 \mu_B$ [44,45].

Fig. 1 shows the calculated orbital-projected DOS of the AFM phase of CuO using LSDA with $U = 8$ eV and $J = 0$. It is interesting to see from Fig. 1 that upon incorporating U into the calculations, a band gap of about 1.5 eV was opened near the Fermi level, consistent with experimental results [41–43]. The reason for the opening of the energy gap at the Fermi level can be argued on the basis of the Cu- d orbital splitting and the subsequent splitting of the highest d orbital into an up and down side, which leads to opening of the energy gap and the formation of local magnetic moments on Cu.

The local magnetic moment was calculated for the AFM phase. It was found that the obtained magnetic moment by LSDA varies greatly from the experimental value. Hence, the magnetic moment was recalculated by using $U = 8$ eV and $J = 0$. The recalculated value of the magnetic moment of Cu turned out to be $0.65 \mu_B$, in good agreement with the experimental values of 0.65 – $0.68 \mu_B$ [44,45].

To study how doping influences the electronic structure and the magnetic moment of CuO, Ni was chosen as the dopant be-

Fig. 1. LSDA+ U calculated total spin density-of-states for a perfect CuO magnetic unit cell. The vertical straight line is the position of the Fermi energy (E_F), which is set to equal zero.

cause it has a similar radius to Cu and, more importantly, it is a magnetic atom. We used our implementation of the LSDA+*U* model to determine the ground state electronic structure of Ni-doped CuO. The data are shown in Fig. 2 with $U = 8$ eV. The energy band gap was found to be 1.57 eV. The total antiferromagnetic spin moment was $1.66 \mu_B$. The DOS obtained agrees well with previous LSDA+*U* calculations. The structure and calculated total and partial spin DOS for Ni-doped CuO are presented in Fig. 2. It can be seen from Fig. 2 that the VB and CB were clearly spin-split for the Ni-doped system, corresponding to a net effective magnetic moment of about $\mu_{\text{eff}} = 1.66 \mu_B$. Additionally, there was a raised energy state in the band gap near to the VB due to the energy overlap between the Cu 3*d* state and the Ni 3*d* state. The Ni 3*d* state emerged on the bottom of the CB, which enhanced the spin down energy. It may benefit the improvement of the photocatalytic activity and recycling ability for the Ni-doped CuO photocatalyst. The above detailed discussion is about the effect of Ni on the CuO magnetic unit cell, and in the following section, we discuss the effect of Cu on the NiO magnetic cell.

3.2. Perfect and Cu-doped NiO crystal

NiO is a model of a highly correlated material that exhibits insulating character and antiferromagnetic order even at high temperatures. Calculations of the physical properties of bulk NiO were performed using the LSDA+*U* method. To determine the optimal value for the on-site Coulomb potential, U was varied between 5 and 8 eV. We found that when $U = 8$ eV and $J = 0.15$ eV, the lattice parameter, magnetic moment, and the band gap agreed well with the experimental values. The calculated results are displayed in Table 1.

We can see that NiO crystallizes in a rocksalt structure with a lattice constant of $a = 4.155 \text{ \AA}$ and the LSDA+*U* yielded a 1% deviation compared with the experimental value of $4.17 \text{ \AA}$. The calculated magnetic moment on the Ni atom was $1.70 \mu_B$, similar to other calculation and experimental results. Thus, we can conclude that all of the calculated results using LSDA+*U* are in

Table 1

Calculated lattice parameter (a), magnetic moment on Ni atoms (m), and band gap (E_g) of perfect NiO magnetic unit cell.

	Lattice parameter ($\text{\AA}$)	Ni magnetic moment (μ_B)	Band gap (eV)
This work	4.16	1.70	3.66
GGA+ <i>U</i> [48]	4.20	1.69	3.20
HSE06 [48]	4.18	1.66	4.10
Experiment	4.17 [28]	1.64 [49], 1.77 [50], 1.90 [51]	4.00 [8], 4.30 [52]

good agreement with experimental values, apart from the underestimation of the band gap by about 0.5 eV with GGA+*U*. These results are similar to those reported by the groups of Chen et al. [48,52].

Fig. 3(a) shows the band structure of NiO calculated with LDA+*U* for $U = 8$ eV and $J = 0.15$ eV along the high-symmetry directions GX, XM, MR, and RG. Fig. 3(b) displays the total spin density of states (TDOS) and partial spin density of states (PDOS) for the Ni 3*d* and O 2*p* states. The NiO insulating state is characterized by an energy band gap of about 3.6 eV and a magnetic moment of about $1.7 \mu_B$. The top of the VB is predominantly O 2*p*-like, with a small admixture of Ni-*d* states, whereas the bottom of the CB has Ni-*d* character in all of the magnetic structures, in agreement with previous LDA+*U* calculations [53]. There are strong indications that NiO is a charge-transfer insulator because the top of the VB is primarily formed by the mixture of O 2*p* and Ni 3*d* states, while the bottom of the CB is mainly composed of Ni 3*d* states. For perfect NiO, the indirect band structure shows a band gap $E_g = 3.656$ eV, which is in agreement with the experimental value of 3.6 eV. Additionally, the VB edge states for perfect NiO consist of about 50% Ni and 50% O character, consistent with the large Ni *d* spectral mass at the top of the VB obtained from LSDA+*U* calculations and from experiment.

For Cu-doped NiO, its structure is shown in Fig. 4(a). It is found that the Ni-O bond length decreased to 1.994 from 2.077 $\text{\AA}$, which reveals that the substitution of Cu has little influence

Fig. 2. Structure (blue: Cu; gray: Ni; red: O) and calculated total spin density of states for the Ni-doped CuO unit magnetic cell and partial spin DOS for Ni 3*p* and 3*d* electrons, and Cu 3*d* electrons.

Fig. 3. Calculated band structure (a) and total and projected spin density of states of the stable antiferromagnetic structure (b) of perfect NiO.

Fig. 4. Structure ((a), blue: Cu; gray: Ni; red: O), total spin density of states for Cu-doped NiO (b) and partial spin density of states for Cu 3d electrons and Ni 3d electrons (c).

on the lattice. The reason for this phenomenon may be due to the similar nature of the neighboring atoms. Fig. 4(b) shows the TDOS of Cu-doped NiO based on LSDA+*U* calculations. Fig. 4(c) presents the band structure of Cu-doped NiO from LSDA+*U* calculations. For Cu-doped NiO, doping states in NiO emerge with two peaks within the NiO band gap. They are clearly associated with the Cu 3d state, as can be seen from the band structure. Substantially, with Cu-doped NiO, the width of the VB increases and the band gap narrows with respect to that in pure NiO because of the presence of Cu 3d states near to the Fermi level, which may benefit the improvement in photocatalytic activity. Beyond that, the emergence of the Cu 3d state within the band gap may also effectively separate the electron-hole pair, and thus lead to enhanced absorption of visible light and infrared light. The doping system appears as a magnetic material with a net effective magnetic moment of about 1 μ_B . The LSDA+*U* magnetic moment on Ni varied only slightly between Cu-doped NiO and pure NiO. The magnetic moment on Ni in pure NiO was 1.70 μ_B and that in Cu-doped NiO was 1.67 μ_B . The calculated magnetic moment on Cu was 0.56 μ_B . So, it can be predicted that Cu-doped NiO may be a good candidate magnetic photocatalyst.

The above discussion is about two complementary processes. First we modified the electronic structure of NiO with es-

sential magnetic attributes for appropriate photocatalytic potential. We then modified the magnetic properties of CuO with low-index surfaces (111) and (011), and an appropriate band edge to encourage the reactions of water splitting and CO₂ reduction for recycling. By doing so, we can endow the two materials with both an appropriate redox potential and magnetism, which can be used in the field of photocatalysis for high photocatalytic activity and simultaneous recycling ability.

4. Conclusions

A new implementation of the LSDA+*U* model based on the PAW method has been presented to calculate the effect of Ni and Cu doping on the spatial structure, magnetic properties, and electronic structure of CuO and NiO, respectively. This is an all-electron method without any shape approximation for the potential or charge density. It is found that the influence on the spatial structure of CuO doped by Ni and that of NiO introduced by Cu doping are negligible. Additionally, in the Ni-doped CuO system, the VB and CB are clearly spin-split, corresponding to a net effective magnetic moment of about $\mu_{\text{eff}} = 1.66 \mu_B$. Compared to the perfect CuO system, with a net effective magnetic moment of about $\mu_{\text{eff}} = 0.66 \mu_B$, the enhanced magnetism may benefit the improvement in photocatalytic activity and recy-

Graphical Abstract

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LSDA+*U* study on the electronic and anti-ferromagnetic properties of Ni-doped CuO and Cu-doped NiO

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The clearly spin-split and observably narrowed band gap for the two doped semiconductor photocatalysts may benefit for the improvement of photocatalytic activity and simultaneously have a net magnetic moment for easy recycle and reuse.

clinging ability of these catalytic materials. Moreover, in the Cu-doped NiO system, the appearance of Cu 3d states near to the Fermi level increases the width of the VB and narrows the band gap compared with pure NiO. The emergence of the Cu 3d states within the band gap leads to the presence of two energy levels around the Fermi level, which may effectively separate the electron-hole pair and also result in enhanced absorption of visible light and infrared light. Thus, we can conclude that the change in the band structure for the two doped semiconductors may lead to improved photocatalytic activity and simultaneously have a net magnetic moment for simple recycling and reuse.

References

- [1] P. Hohenberg, W. Kohn, *Phys. Rev. B*, **1964**, 136, 864–871.
- [2] W. Kohn, L. J. Sham, *Phys. Rev.*, **1965**, 140, 1133–1138.
- [3] R. J. Powell, W. E. Spicer, *Phys. Rev. B*, **1970**, 2, 2182–2193.
- [4] L. Messick, W. C. Walker, R. Glosser, *Phys. Rev. B*, **1972**, 6, 3941–3949.
- [5] G. A. Sawatzky, J. W. Allen, *Phys. Rev. Lett.*, **1984**, 53, 2339–2342.
- [6] S. Hufner, P. Steiner, I. Sander, F. Reinert, H. Schmitt, *Z. Phys. B*, **1992**, 86, 207–215.
- [7] S. Hufner, *Solid State Commun.*, **1985**, 53, 707–710.
- [8] S. Hufner, J. Osterwalder, T. Riesterer, F. Hulliger, *Solid State Commun.*, **1984**, 52, 793–796.
- [9] J. van Elp, H. Eskes, P. Kuiper, G. A. Sawatzky, *Phys. Rev. B*, **1992**, 45, 1612–1622.
- [10] K. Terakura, T. Oguchi, A. R. Williams, J. Kübler, *Phys. Rev. B*, **1984**, 30, 4734–4741.
- [11] J. Hubbard, *Proc. R. Soc. Lond. A, Math. Phys. Sci.*, **1963**, 276, 238–259.
- [12] F. Yang, Q. Sun, L. L. Ma, Y. Jia, S. J. Luo, J. M. Liu, W. T. Geng, J. Y. Chen, S. Li, Y. Yu, *J. Phys. Chem. A*, **2010**, 114, 84178422.
- [13] Y. J. Li, F. Yang, Y. Yu, *Appl. Surf. Sci.*, **2015**, 358, 449–456.
- [14] R. J. Liu, X. S. Zhou, F. Yang, Y. Yu, *Appl. Surf. Sci.*, **2014**, 319, 50–59.
- [15] H. Wang H, Y. J. Li, X. Ba, L. Huang, Y. Yu, *Appl. Surf. Sci.*, **2015**, 345, 49–56.
- [16] C. Niedermayer, A. Golnik, E. Recknagel, M. Rossmannith, A. Weidinger, X. S. Chang, A. Kleinhammes, N. Rosov, J. Saylor, R. Schuhmann, L. Takacs, A. Teh, G. Zhang, C. Hohenemser, J. I. Budnick, *Phys. Rev. B*, **1988**, 38, 2836–2839.
- [17] S. J. Stewart, R. A. Borzi, G. Punte, R. C. Mercader, *Phys. Rev. B*, **1998**, 57, 4983–4986.
- [18] C. E. Ekuma, V. I. Anisimov, J. Moreno, M. Jarrell, *Eur. Phys. J. B*, **2014**, 87, 23/1–23/6.
- [19] M. Heinemann, B. Eifert, C. Heiliger, *Phys. Rev. B*, **2013**, 87, 115111/1–115111/5.
- [20] F. Ahmad, M. K. Agusta, H. K. Dipojono, *J. Phys. Conf. Ser.*, **2016**,

- 739, 012040/1–012040/7.
- [21] B. Himmetoglu, R. M. Wentzcovitch, M. Cococcioni, *Phys. Rev. B*, **2011**, 84, 115108/1–115108/8.
- [22] F. Ahmad, M. K. Agusta, H. K. Dipojono, *KnE Eng.*, **2016**, 2016, DOI: 10.18502/keg.v1i1.504.
- [23] X. Q. Du, J. W. Huang, Y. Y. Feng, Y. Ding, *Chin. J. Catal.*, **2016**, 37, 123–134.
- [24] H. W. Wu, S. Y. Lee, W. C. Lu, K. S. Chang, *Appl. Surf. Sci.*, **2015**, 344, 236–241.
- [25] Y. F. Li, W. P. Zhang, X. Shen, P. F. Peng, L. B. Xiong, Y. Yu, *Chin. J. Catal.*, **2015**, 36, 2229–2236.
- [26] B. Sun, G. W. Zhou, T. T. Gao, H. J. Zhang, H. H. Yu, *Appl. Surf. Sci.*, **2016**, 364, 322.
- [27] L. L. Li, B. Cheng, Y. X. Wang, J. Q. Yu, *J. Colloid Interface Sci.*, **2015**, 449, 115–121.
- [28] L. C. Bartel, B. Morosin, *Phys. Rev. B*, **1971**, 3, 1039–1043.
- [29] P. Kuiper, G. Kruizinga, J. Ghijsen, G. A. Sawatzky, H. Verweij, *Phys. Rev. Lett.*, **1989**, 62, 221–224.
- [30] Z. X. Shen, R. S. List, D. S. Dessau, B. O. Wells, O. Jepsen, A. J. Arko, R. Bartlett, C. K. Shih, F. Parmigiani, J. C. Huang, P. A. P. Lindberg, *Phys. Rev. B*, **1991**, 44, 3604–3626.
- [31] Z. Szotek, W. M. Temmerman, H. Winter, *Phys. Rev. B*, **1993**, 47, 40294032.
- [32] V. S. L. Dudarev, G. A. Botton, S. Y. Savrasov, Z. Szotek, W. M. Temmerman, A. P. Sutton, *Phys. Status Solid A*, **1998**, 166, 429–443.
- [33] V. I. Anisimov, J. Zaanen, O. K. Andersen, *Phys. Rev. B*, **1991**, 44, 943–954.
- [34] V. I. Anisimov, I. V. Solov'yev, M. A. Korotin, M. T. Czyżyk, G. A. Sawatzky, *Phys. Rev. B*, **1993**, 48, 16929–16934.
- [35] B. Himmetoglu, A. Floris, S. Gironcoli, M. Cococcioni, *Int. J. Quant. Chem.*, **2014**, 114, 14–49.
- [36] G. Kresse, D. Joubert, *Phys. Rev. B*, **1999**, 59, 1758–1775.
- [37] P. E. Blöchl, *Phys. Rev. B*, **1994**, 50, 17953–17979.
- [38] G. Kresse, J. Furthmüller, *Phys. Rev. B*, **1996**, 54, 11169–11186.
- [39] G. Kresse, J. Hafner, *Phys. Rev. B*, **1993**, 47, 558–561.
- [40] D. Gryaznov, S. Baumann, E. A. Kotomin, R. Merkle, *J. Phys. Chem. C*, **2014**, 118, 29542–29553.
- [41] S. C. Ray, *Sol. Energy Mater. Sol. Cells*, **2001**, 68, 307–312.
- [42] D. Tahir, S. Tougaard, *J. Phys. Condens. Matter.*, **2012**, 24, 175002/1–175002/8.
- [43] F. Marabelli, G. B. Parravicini, F. Salghetti-Drioli, *Phys. Rev. B*, **1995**, 52, 1433–1436.
- [44] B. X. Yang, T. R. Thurston, J. M. Tranquada, Shirane G, *Phys. Rev. B*, **1989**, 39, 4343–4349.
- [45] M. Ain, A. Menelle A, B. M. Wanklyn, E. F. Bertaut, *J. Phys. Condens. Matter*, **1992**, 4, 5327–5338.
- [46] S. Gandhi, R. H. H. Subramani, T. Ramakrishnan, A. Sivabalan, V. Dhanalakshmi, M. R. G. Nair, R. Anbarasan, *J. Mater. Sci.*, **2010**, 45, 1688–1694.
- [47] M. H. Cao, C. W. Hu, Y. H. Wang, Y. H. Guo, C. X. Guo, E. B. Wang, *Chem. Commun.*, **2003**, 1884–1885.
- [48] H. R. Chen, J. H. Harding, *Phys. Rev. B*, **2012**, 85, 115127/1–115127/5.
- [49] H. Alperin, *J. Phys. Soc. Jpn.*, **1962**, 17 (Suppl. B–III), 12–15.
- [50] B. E. F. Fender, A. J. Jacobson, F. A. Wedgwood, *J. Chem. Phys.*, **1968**, 48, 990–994.
- [51] A. K. Cheetham, D. A. O. Hope, *Phys. Rev. B*, **1983**, 27, 6964–6967.
- [52] H. R. Chen, C. L. Freeman, J. H. Harding, *Phys. Rev. B*, **2011**, 84, 085108/1–085108/7.
- [53] O. Bengone, M. Alouani, P. Blöchl, J. Hugel, *Phys. Rev. B*, **2000**, 62, 16392–16401.

LSDA+U方法研究Ni掺杂CuO和Cu掺杂NiO的电子结构和反铁磁学性质

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摘要: 光催化分解水制H₂和光催化还原CO₂是解决能源危机和全球变暖的有效途径。但是, 由于粉末光催化剂存在回收效率低的问题, 因而光催化成本很高。而磁性光催化剂便于回收和重复利用, 因此人们把目光转向具有磁性的非光催化剂材料, 试图通过改性使得磁性材料具有合适的水分解或者还原CO₂的氧化还原电位。同时, 对具有光催化活性但是没有磁性的材料进行磁化改性可以得到新型的磁性光催化剂。

本文通过对本身具有磁性的NiO材料进行Cu掺杂能带调整, 使调整后的NiO具有合适的氧化还原电位; 对本身具有良好光催化氧化还原电位的CuO材料进行Ni掺杂磁化调整, 使磁化后的CuO既有良好的氧化还原电位又有磁性。最终两种材料经过掺杂变成磁性光催化材料, 既有较好的光催化性能, 又可高效回收, 因此有望在光催化领域具有潜在的应用前景。

LSDA(局域自旋密度近似)+U(有效库仑相关能)计算方法能够很好地给出磁矩和禁带宽度等电子结构性质。本文通过LSDA+U计算方法对具有磁性的宽禁带半导体材料NiO进行电子结构改性研究, 希望通过降低其禁带宽度、调整其氧化还原电位使之对太阳光有响应。因其同时具有磁性便于回收, 使得光催化分解水制H₂和光催化还原CO₂成本高的问题得到解决。对NiO的磁胞进行了Cu掺杂计算, 结果发现Cu的掺杂几乎没有引起NiO空间结构的变化, 这是因为Cu和Ni的离子半径相近。通过对电子结构的计算发现掺杂体系的禁带变窄, 并且在禁带中间出现了两条杂质能级, 该杂质能级是由掺杂原子Cu 3d态组成。杂质能级的出现能够降低光生载流子在带隙中的复合, 从而提高光催化效率。计算结果同时表明, Cu掺杂的NiO系统具有一个1 μ_B的净磁矩, 即Cu的掺杂使得NiO显示出磁性, 而Ni的磁矩在掺杂前后几乎保持不变, 由纯相的1.67 μ_B增加到掺杂体系中的1.70 μ_B。

由于CuO本身低指数(111)面和(011)面具有合适的分解水制H₂和还原CO₂的氧化还原电位, 如果对CuO进行磁化改性, 可以使光催化剂CuO同时带有磁性, 便于回收再利用。本文对CuO磁胞进行了Ni的掺杂计算。结果表明, 由于离子半径相

近, Ni掺杂几乎没有引起CuO空间结构的变化. 掺杂后的体系具有一个 $1.66 \mu_B$ 的净磁矩, 同时Ni的掺杂引起多个杂质能级出现, 靠近价带的杂质能级由Cu 3d态组成, 而在导带底位置出现的杂质能级主要由Ni 3d态组成. 整个能带向高能级方向平移.

关键词: LSDA+*U*; 氧化铜; 氧化镍; 磁矩; 电子结构; 光催化作用

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