

Electronic Structures and Optical Properties of Spinel ZnCr_2O_4

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The electronic structures and optical properties of zinc chromite, ZnCr_2O_4 , were calculated using the density-functional theory within the local-spin-density approximation (LSDA), the LSDA plus Hubbard-like parameter U , LSDA+ U , and the spin-polarized generalized-gradient approximation. ZnCr_2O_4 was found to be a direct-band-gap semiconductor with an optical band gap of 2.9 eV, with the uppermost valence bands (lowermost conduction bands) having mainly Cr- t_{2g} (Cr- e_g) characteristics. The calculated band gap using LSDA+ U showed better agreement with the available experimental data than previous calculations. The optical-conductivity and the reflectivity spectra were also calculated. The calculated reflectivity spectrum exhibited two peaks, one at ~ 3.5 eV and the other at ~ 5.8 eV, which were assigned to the electronic interband transitions from the O-2p to the Cr-3d states and from the O-2p derived bands to the Cr e_g bands, respectively.

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I. INTRODUCTION

Oxides with a “spinel” structure are some of the most studied compounds in solid-state sciences owing to their interesting physico-chemical properties and are useful in many technological applications such as magnetic materials [1], super hard materials [2], and high-temperature ceramics [3]. In particular, zinc chromite (ZnCr_2O_4) ceramic spinels are commonly used as catalytic materials [4–6], as humidity sensors [7–9] and magnetic materials [10,12].

Crystal-field splitting in transition-metal oxides is mainly the result of hybridization between the oxygen 2p levels and the metal d states. However, because this splitting originates from hybridization with ligands, larger values can be obtained in materials with stronger hybridization, particularly 3d, 4d, and 5d oxides. Zinc chromite forms a normal cubic spinel crystal structure in which Cr^{+3} ions occupy the B-sites of ZnCr_2O_4 . In ZnCr_2O_4 , a crystal field of almost cubic symmetry splits the five 3d orbitals of Cr^{+3} ions into a t_{2g} triplet and an e_g doublet, similar to the case of FeCr_2O_4 and FeIn_2O_4 [12]. The presence of d electrons near the Fermi level localized on magnetic Cr^{+3} ions in this compound suggests that electronic correlation effects are important in this material.

The so-called LSDA+ U approximation [13] has been used in previous calculations for chromium-based com-

pounds to include the correlation effects of 3d electrons. Fennie and Rabe [14] studied the influence of magnetic ordering on the phonon frequencies in ZnCr_2O_4 within the LSDA+ U approximation, while Toropova *et al.* [15] studied the electronic structure and magnetic anisotropy of CrO_2 and found that the LSDA is better than the LSDA+ U . A generalized-gradient approximation (GGA), which has been shown to give better agreement with experiment than the L(S)DA for some systems [16,17], was also considered, whereas the opposite conclusion was also reported [18]. Sushkov *et al.* studied the spin correlations with phonons in ZnCr_2O_4 [19]. Chan *et al.* [20] reported phonon splitting in antiferromagnetic ZnCr_2O_4 and found the correlation effect to be important in this compound. The magnetically-induced phonon anisotropy in ZnCr_2O_4 was also studied by Fennie and Rabe within the LSDA+ U approximation [14].

Recently Cheng *et al.* [21] studied the optical and the photocatalytic properties of spinel ZnCr_2O_4 nanoparticles and found that ZnCr_2O_4 was a direct-band-gap semiconductor with an optical band gap of 3.46 eV. Furthermore, the sample exhibited apparent photocatalytic activity under UV-light irradiation. Parhia *et al.* [22] reported that ZnCr_2O_4 with a normal spinel structure had a band gap 3.4 eV. Previously, we reported the results of calculations for ZnRh_2O_4 [23], which had a smaller energy band gap (experimental value of 2.1 eV) than ZnCr_2O_4 , and we found ZnRh_2O_4 to be a good photo-electrode material. These studies on ZnCr_2O_4 have stimulated further research into this compound. Accord-

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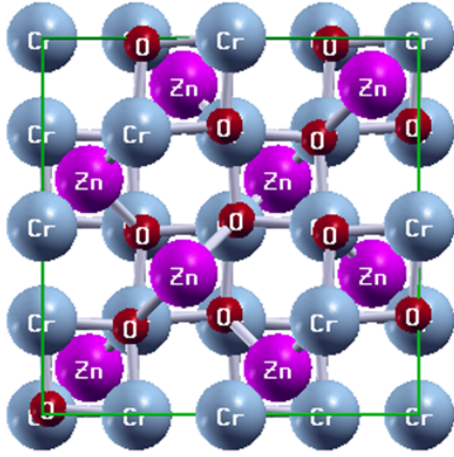


Fig. 1. (Color online) Crystal structure of spinel ZnCr_2O_4

ingly, this paper reports the results of density-functional calculations of the electronic structures and the optical properties, with a focus on the potential applications of ZnCr_2O_4 . Such knowledge of the electronic structure will help researchers understand the relative positions of the bands, which can be useful for analyzing the optical transitions in ZnCr_2O_4 .

II. COMPUTATIONAL DETAILS

ZnCr_2O_4 forms a normal cubic spinel crystal structure in the space group $Fd-3m$ (Space Group No. 227), with Zn, Cr, and O ions occupying $8a$ ($\frac{1}{8}, \frac{1}{8}, \frac{1}{8}$), $16d$ ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$), and $32e$ (u, u, u) Wyckoff positions, respectively. The cubic spinel structure is characterized by two parameters: the lattice constant and the anion parameter u , which governs the positions of oxygen ions within Zn-Cr lattice. The experimental cubic structure, $a = 8.327 \text{ \AA}$ and $u = 0.2216$ [24] was used for the calculations. The spinel crystal structure plotted in Fig. 1 can be considered to be the lattice of distorted Cr_4O_4 cubes that share a Cr site. Each cube is linked to four regular ZnO_4 tetrahedra via an O ion. The centers of the Cr_4O_4 cubes and the ZnO_4 tetrahedra form two diamond lattices shifted by the vector $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$. The Cr ions are arranged along chains running in the $\langle 110 \rangle$ directions and form a so-called pyrochlore lattice that consists of a corner-sharing regular tetrahedron.

Our LSDA [25], GGA [26] and LSDA+ U [27] calculations were performed using the full-potential linearized-augmented-plane-wave method implemented in *WIEN2K* code [28]. Both the valence and the core states were treated self-consistently, and spin-orbit coupling was included using a scalar relativistic approximation. A set of 163 special \mathbf{k} -points in the irreducible wedge was used for Brillouin-zone sampling during the iteration for self consistency, and well-converged basis sets of approximately 1500 LAPW functions plus local orbitals

were employed. The muffin-tin sphere radii were 2.0 a.u. for Zn and Cr and 1.7 a.u. for O. The optical calculation was performed with 286 \mathbf{k} -points in the irreducible wedge. The results were obtained with $U = 3.0 \text{ eV}$ and $J = 0.9 \text{ eV}$ for Cr^{+3} d electrons in the LSDA+ U . The same U value was used in previous LSDA+ U calculations for ZnCr_2O_4 [14] and CrO_2 [16,29] and has reproduced the features in the photoemission data in the other Cr^{+3} spinels [30]. Similar calculations were also performed for different U values.

III. RESULTS AND DISCUSSIONS

Figures 2 and 3 show the calculated band structure for the minority spin and the density of states (DOS) of ZnCr_2O_4 by using the LSDA+ U approximation, respectively. The band structure consists of several manifolds. The order of increasing energy is as follows: (1) from $\sim -8.5 \text{ eV}$ to $\sim -2 \text{ eV}$, O $2p$ -derived bands, (2) from $\sim -2 \text{ eV}$ to the valence band edge (set to be 0 eV), Cr t_{2g} -derived bands, and (3) from the conduction band edge to $\sim 2.5 \text{ eV}$, Cr e_g -derived bands and from $\sim 2 \text{ eV}$ to $\sim 5 \text{ eV}$, Zn s -derived bands. Both the Cr t_{2g} and e_g manifolds are narrow. This localization is a characteristic of spinel-structure transition-metal oxides, AB_2O_4 , with a divalent metallic A ion and a trivalent B , which have bent $A\text{-O-B}$ bonds. Therefore, according to the LDA calculations, the band gap appears to be located between the two crystal field split Cr $3d$ manifolds, and the oxygen $2p$ states are deeper. Each of the LSDA, the GGA and the LSDA+ U methods provides an insulating ground state. The bands near the band gap have predominantly a Cr d -character.

The LSDA, the GGA and the LSDA+ U calculations show that ZnCr_2O_4 is a direct-band-gap semiconductor, which is in agreement with the experiment. However, the LDA band gap is substantially smaller than the measured value. Although the calculated band gaps are in the same order, the gap increases from the LSDA (1.2 eV) to the GGA (1.65 eV) and the LSDA+ U (2.9 eV). The LSDA+ U gap is the largest of the approximations, which agrees with our expectations because Hubbard $\text{emph}U$ term pushes the unoccupied (occupied) d -bands up (down) in energy. The energy band gap and the bandwidth of d -bands increased with increasing U value in the LSDA+ U calculations. This increase in the bandwidth of the d -bands is counterintuitive because the LDA+ U method normally decreases the bandwidth. The occupied d -bands in the bare LDA calculation were located in an energy range in which orbital characters, other than d -orbital, were hardly present. The application of the LDA+ U method pushes the occupied d -bands down to the energy range where orbital characters other than those of the d -orbital are abundant, resulting in strong hybridization between the d -orbitals and sp -orbitals. This hybridization significantly increases the

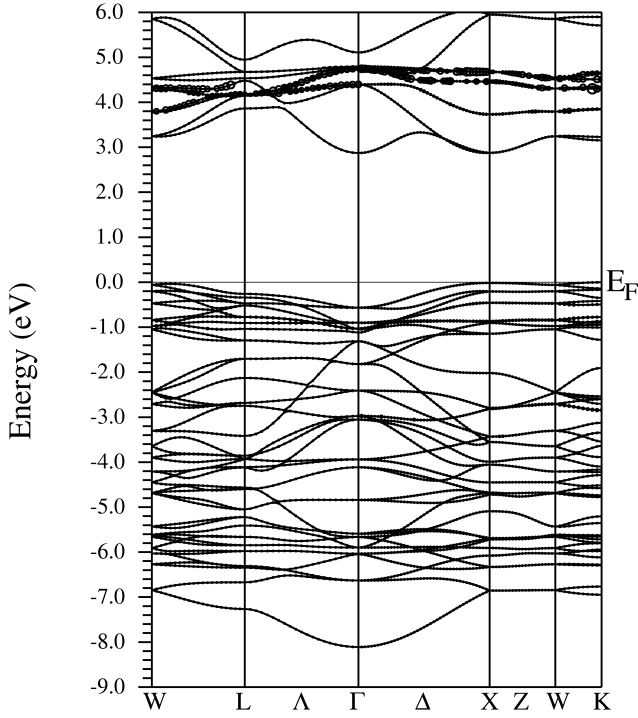


Fig. 2. Calculated minority-spin (LSDA+ U) band structure of ZnCr_2O_4 (with Cr- d partial characteristics).

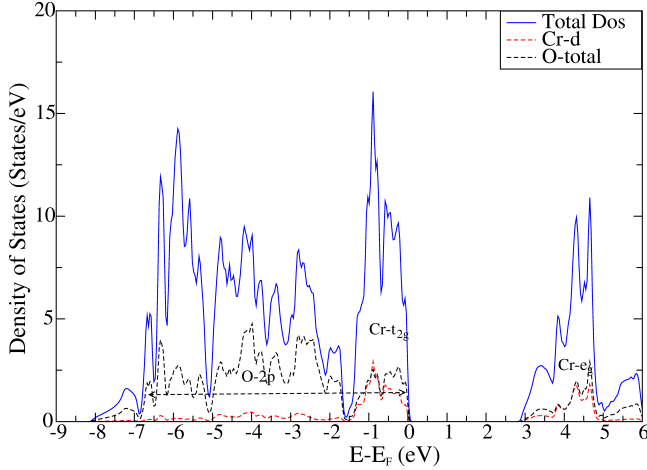


Fig. 3. (Color online) Calculated (LSDA+ U) total DOS of ZnCr_2O_4 along with the partial DOS of the Cr- d states and the total DOS of the O species. The dominant character of the site DOS at various energies has been labeled.

bandwidth of the occupied d -bands. This increase due to hybridization overcompensates for the decrease in the bandwidth owing to the LDA+ U method. Therefore, the bandwidth of the occupied d -bands increases upon application of the LDA+ U method.

The calculated band gap is in better agreement with the experiment and is better than previous calculations [14] for this compound. ZnCr_2O_4 is a direct-band-

gap semiconductor, while another similar compound ZnRh_2O_4 is an indirect-band-gap semiconductor with an optical band gap of 1.2 eV. The LDA to the density-functional theory has a well-known deficiency of substantially underestimating the band gaps in most semiconductors and insulators. This deficiency is due mainly to a discontinuity in the exchange-correlation functional and is expected to persist even for the exact density functional. However, Mattheiss [31] suggested that the band gaps should be better described within the LDA to the density-functional theory because the crystal-field gaps arise from metal hybridization, which can be well described, and the characteristics of the valence- and the conduction-band states are essentially the same. Even if this argument is correct, there still would be errors in the band gaps, but these would be due to the particular approximate exchange-correlation functional employed. For example, the LDA tends to overestimate hybridization, leading to overestimated exchange interactions, while the GGA has other errors. If the argument of Mattheiss holds, the main error in the gap would be due to the approximate exchange-correlation functional itself and not to the discontinuity of the exchange-correlation functional. This approach is appealing from a practical point of view because, if correct, an investigation of the density-functional band structures can be used as a direct search method for novel oxide photo-electrode materials. However, even in that case, the values obtained in the calculation are not consistent with the 3.4-eV experimental gap [13] of ZnCr_2O_4 .

The shape of the LDA DOS (not shown) indicates a possible solution to this discrepancy. In particular, the bands at the top of the t_{2g} and the e_g manifolds are much less dispersive than the bands at the bottom of the respective manifolds. This shape is characteristic of spinels [32,33], and has been discussed in tight-binding terms [32]. However, the optical spectra involve matrix elements, which may be very important because the basic d - d characters of the transitions are dipole forbidden. Accordingly, hybridization with ligands and \mathbf{k} -dispersion might be important. Therefore, the wave functions, which were used to estimate the dipole-transition matrix elements, were calculated based on the band structure to simulate the optical-conductivity spectra by using the optical package of the WIEN2K code [28].

Figure 4 displays the calculated optical-conductivity and reflectivity spectra of ZnCr_2O_4 . The LSDA and the GGA calculations provide similar shapes, except that the onsets are at somewhat different energies. On the other hand, the LSDA+ U calculation provides a shape with a higher magnitude and rich structures in the spectra compared to that of both the LSDA and the GGA. The rich structure and the higher magnitude in the LSDA+ U spectra were attributed to the splitting of Cr 3d states. The peaks near 5.5 and 6 eV are due to transitions from the O 2p derived bands to the metal e_g band. Based on the electronic structure calculations, the small feature in the LSDA+ U spectra centered at ~ 4.5 eV might

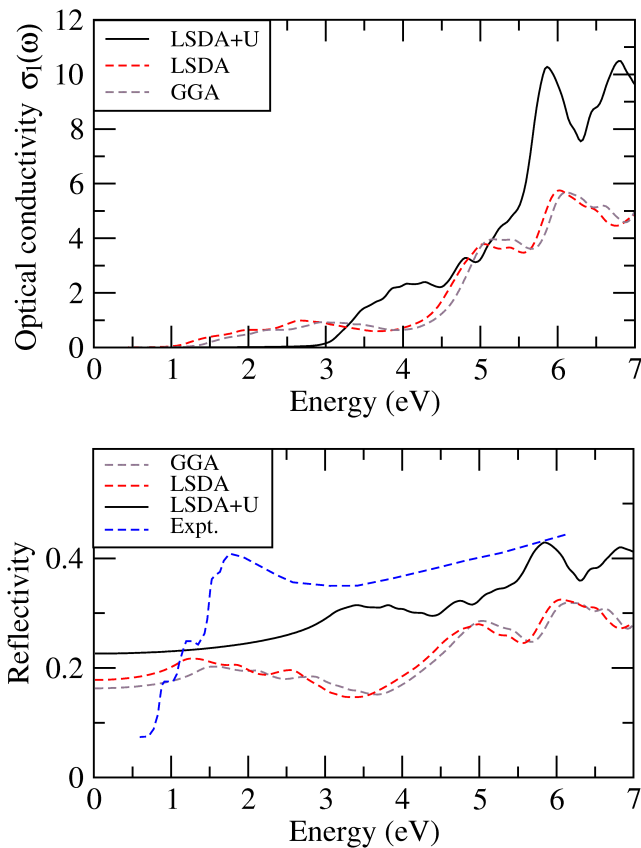


Fig. 4. (Color online) Calculated (LSDA+ U) optical-conductivity (top) and reflectivity (bottom) spectra, along with experimental data for ZnCr_2O_4

be due to a Cr^{+3} d -to- d (t_{2g} to e_g) on-site excitation. This symmetry-forbidden transition is possible due to the crystal-field splitting of the Cr $3d$ orbitals and the hybridization of the Cr $3d$ and the O $2p$ states. Similarly, the electronic excitations near 3.5 eV were assigned to charge transfer excitations from the O $2p$ to the Cr- $3d$ states. The behavior and the peaks in the reflectivity spectrum also belong to similar transitions, as found in the optical-conductivity spectrum. A comparison with the experimental spectrum was inconclusive because the 3.5-eV peak was not present in the experimental spectrum [21] and the 5.8-eV peak was not observed due to the spectral limits of the experiment.

IV. CONCLUSIONS

Density-functional calculations, specifically the LSDA+ U calculation, revealed spinel ZnCr_2O_4 to have a band gap of 2.9 eV, which is in a better agreement with experiments than previous calculations were. The correspondence between the experimental measurements and the calculated band structure supports the view that the density-functional calculations can be used to

calculate the band gaps in this type of material, which is in agreement with Mattheiss [31]. The correlation effects were found to be important in ZnCr_2O_4 . Further application of the LSDA+ U method to the electronic structure, the optical properties and the spin-orbit coupling in spinels and magnetic oxides can provide a more complete picture of the electron correlation. A comparison with the experimental spectrum was inconclusive because the 3.5-eV peak was not present in the experimental spectrum and the 5.8-eV peak was not observed due to the spectral limit of the experiment. The optical properties are very useful for identifying a suitable material for various applications, such as ZnCr_2O_4 whose band gap would strongly depend on chemical modifications that either enhance the crystal-field splitting or reduce the width of the t_{2g} and/or the e_g manifolds to produce a larger band gap.

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