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Energy gaps and optical properties of ferromagnetic semiconductors $CdCr_2S_4$ and $CdCr_2Se_4$: Improved density-functional-theory study

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ABSTRACT

We use a modified Becke–Johnson (mBJ) exchange plus local density approximation correlation functional within the density functional theory (DFT) [semi-local, orbital-independent, producing accurate semiconductor gaps, see Tran and Blaha, Phys. Rev. Lett., 102 (2009) 226401] to investigate the electronic structures of $CdCr_2S_4$ and $CdCr_2Se_4$ as two ferromagnetic semiconductors. Our results show that mBJ makes the empty Cr d-eg character bands higher by about 1.1 eV for $CdCr_2S_4$ and 0.7 eV for $CdCr_2Se_4$ for the majority-spin channel with respect to the generalized gradient approximation (GGA). For the minority-spin channel, mBJ raises the Cr d character bands by about 0.8 eV for $CdCr_2S_4$ and $CdCr_2Se_4$. The mBJ gap is enhanced by about 104% for $CdCr_2S_4$ and 170% for $CdCr_2Se_4$ compared to GGA results, and is consistent with experiment in both of the cases. Our mBJ dielectric functions and the zero frequency refractive index $n(0)$ for $CdCr_2S_4$ and $CdCr_2Se_4$ are also consistent with experimental results available. The improved DFT results can be understood in terms of mBJ-enhanced spin exchange splitting and the reduced band width of Cr d character bands.

1. Introduction

Ferromagnetic semiconductors have both semiconducting properties and spontaneous ferromagnetic orders, making them very attractive for semiconductor spintronic devices. $CdCr_2S_4$ and $CdCr_2Se_4$ are well-known ferromagnetic semiconductors with ferromagnetic transition temperatures 84.5 K and 129.5 K, respectively [1]. They assume a cubic spinel structure, with Cr^{3+} surrounded by six S or Se ions. Relaxor ferroelectricity and colossal magnetocapacitive coupling in ferromagnetic $CdCr_2S_4$ is discovered [2,3], and it is shown that colossal magnetoresistance and colossal electroresistance can be induced by electric field [4]. Field-dependent dielectric, magnetic properties and magnetocaloric effect in $CdCr_2S_4$ is investigated for possible applications [5]. $CdCr_2Se_4$ is used for electrical injection of spin-polarized electrons into an AlGaAs/GaAs-based light-emitting diode structure [6], and the epitaxial thin films of $CdCr_2Se_4$ are grown on both GaAs and GaP(001) substrates [7]. Magnetic circular dichroism of $CdCr_2Se_4$ as a semiconducting ferromagnet has been observed [8]. The critical magnetic properties of the ferromagnetic $CdCr_2Se_4$ can be described by a three-dimensional Heisenberg spin model [9]. On the theoretical side, early electronic energy band calculations showed that $CdCr_2Se_4$ is a ferromagnetic insulator, but $CdCr_2S_4$ is a ferromagnetic semimetal [10]; a first-principles study on the electronic and magnetic properties was performed for $CdCr_2Se_4$ [11]; and LDA and LDA+U approaches were used to study electronic band structure and exchange coupling constants in ACr_2X_4 spinels (A=Zn, Cd, Hg; X=O, S, Se) [12]. However, it is difficult to obtain satisfactory electronic band structures and related properties for $CdCr_2S_4$ and $CdCr_2Se_4$ because their semiconductor gaps are underestimated in usual density-functional-theory (DFT) [13] calculations.

In this letter, we use a modified Becke–Johnson (mBJ) exchange [14] plus local density approximation (LDA) correlation [15] functionals within the DFT to investigate the electronic structures of $CdCr_2S_4$ and $CdCr_2Se_4$ ferromagnetic semiconductors in cubic spinel structure. The combination of mBJ exchange and LDA correlation can produce accurate semiconductor gaps for numerous semiconductors and insulators [14,16–21]. Our mBJ results show that the energy gaps are enhanced compared to GGA results, and agree with experimental values. Our mBJ-calculated dielectric functions (both real and imaginary parts) and zero frequency refractive index $n(0)$ of $CdCr_2S_4$ and $CdCr_2Se_4$ are also consistent with experimental results available. The improved results can be understood in terms of the reduced bandwidth and enlarged spin exchange splitting of Cr d character band calculated with mBJ. More detailed results will be presented in the following.

The rest of the paper is organized as follows. We shall describe our computational detail in the next section. In the third section we shall present our main mBJ results and compare them with

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those calculated with GGA and related experimental results. Finally, we shall give our conclusion in the fourth section.

2. Computational detail

We use a full-potential linearized augmented-plane-waves method within the DFT [13], as implemented in the package WIEN2k [22]. We use mBJ plus LDA for the exchange-correlation potential [15,14] to do our main DFT calculations, and take the popular GGA by Perdew, Burke, and Ernzerhof (GGA-PBE) [23] to do comparative studies. The mBJ exchange potential [14] was developed from a semi-local exchange potential proposed by Becke and Johnson (BJ) [24]. It is required to reproduce the shape of the exact-exchange optimized-effective potential of atoms [24]. The combination of mBJ exchange and LDA correlation can produce accurate semiconductor gaps for sp semiconductors, wide-band-gap semiconductors, and transition-metal oxide semiconductors and insulators [14,16–21]. The full relativistic effects are calculated with the Dirac equations for core states, and the scalar relativistic approximation is used for valence states [25–27]. The spin–orbit coupling is neglected because it has little effect on our results. We use 10 000 k-points in the first Brillouin zone for the calculations, make harmonic expansion up to $l_{max}=10$ in each of the atomic spheres, and set $R_{mt}*k_{max}=7$. The radii of the atomic spheres of Cd, Cr, S, and Se are set to 2.47, 2.43, 2.05, and 2.15 bohr, respectively. The self-consistent calculations are considered to be converged when the integration of the absolute charge-density difference between the input and output electron density is less than $0.0001|e|$ per formula unit, where e is the electron.

3. Main results

At first, we do self-consistent calculation with the experimental lattice constant 10.240 Å and 10.735 Å for $CdCr_2S_4$ [28] and $CdCr_2Se_4$ [29], respectively, by using the popular GGA, and then use the improved exchange-correlation functional including the mBJ exchange potential because this new method improves semiconductor gaps and d-state positions for various types of materials. We present the density of states between −6 eV and 4 eV calculated with mBJ and GGA in Fig. 1. It is clear that the gap calculated with mBJ is larger than that with GGA for both majority-spin and minority-spin channels in both of the cases. For $CdCr_2S_4$, the GGA gaps 0.82 eV and 1.02 eV are replaced by the mBJ gaps 1.67 eV and 2.12 eV for the minority-spin and the majority-spin channels, respectively; and for $CdCr_2Se_4$, the GGA gaps 0.43 eV and 0.63 eV by the mBJ gaps 1.16 eV and 1.35 eV, respectively. The mBJ gap 1.67 eV of $CdCr_2S_4$ agrees well with the 0 K experimental gap 1.8 eV, and the mBJ gap 1.16 eV of $CdCr_2Se_4$ agrees very well with 0 K experimental value 1.15 eV. These DOS

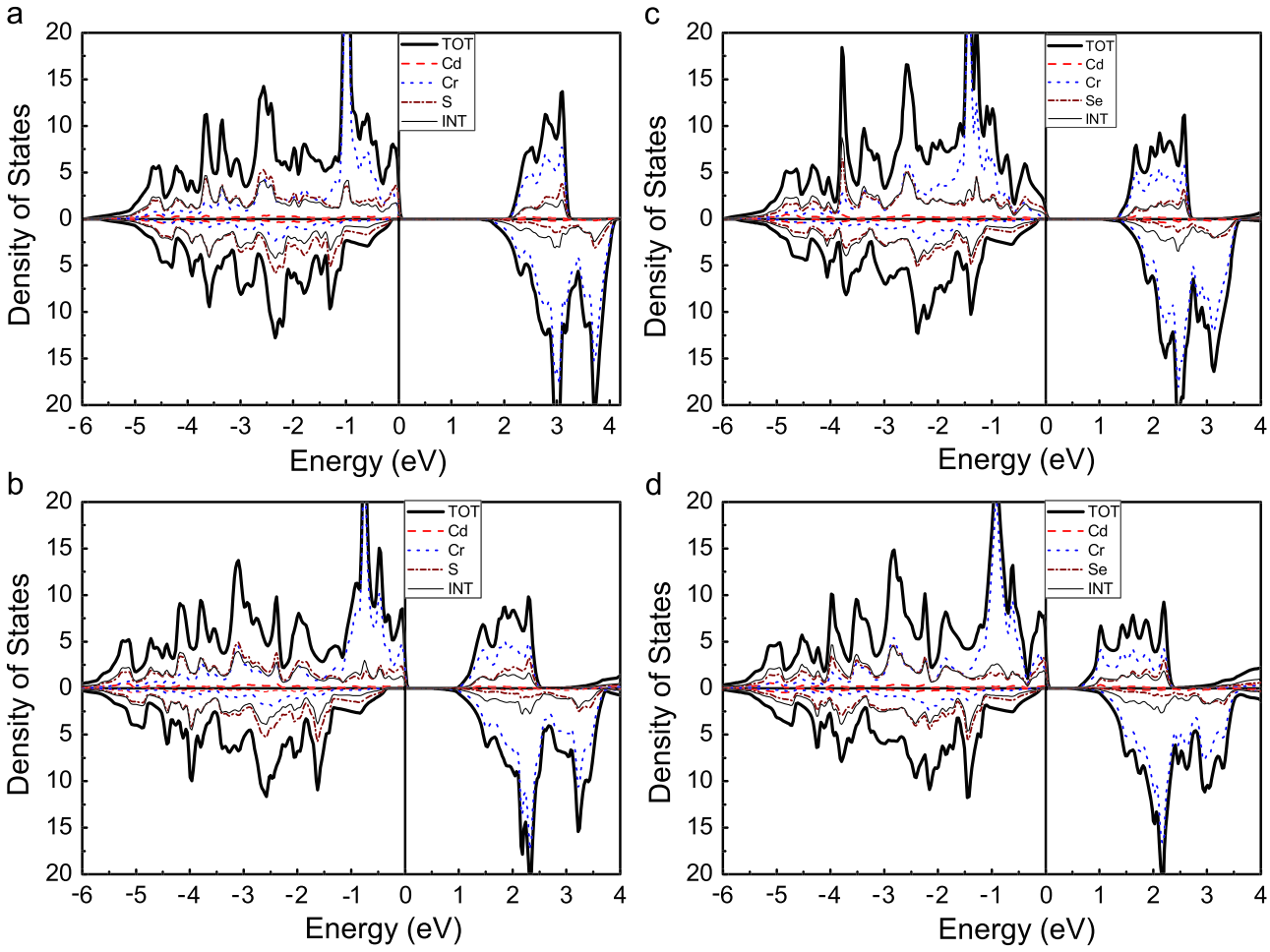

Fig. 1. Spin-resolved density of states (DOS) of the $CdCr_2S_4$ (a: mBJ; b: GGA) and $CdCr_2Se_4$ (c: mBJ; d: GGA). In each panel, the upper part shows the majority-spin DOSs and the lower part the minority-spin ones. The thick line shows the total DOS (TOT), the thin line indicates the DOS contributed by the interstitial region (INT), and the others are DOSs projected in the atomic spheres.