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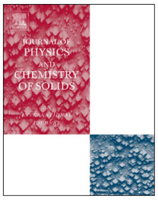

Electronic, magnetic, and optical characteristics of half-semiconductor double perovskite oxide Sr_2CrOsO_6 governed by 3d (t_{2g}^3)–5d (t_{2g}^3) antiferromagnetic coupling

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ABSTRACT

In this study, motivated by observations of the remarkable magnetic insulating nature and high Curie temperature ($T_C = 725$ K) of double perovskite oxide Sr_2CrOsO_6, the electronic, magnetic, and optical characteristics of Sr_2CrOsO_6 were determined using the full potential linear muffin-tin orbital method according to density functional theory. The spin-orbit coupling contribution was included in the local spin density approximation (LSDA) and generalized gradient approximation (GGA). In addition, the Coulomb repulsion (U) and Hund's exchange (J) energies were considered in both methods (LSDA+U and GGA+U). Full structural optimization confirmed that the ground state of Sr_2CrOsO_6 is face-centered cubic (Fm-3m symmetry). Calculations predicted that Sr_2CrOsO_6 is ferrimagnetic half-semiconductive (HSC) due to the vertical hopping of t_{2g} electrons via antiferromagnetic coupling [Cr^{3+} ($t_{2g}^3\uparrow$)–O ($2p_\pi$)–Os^{5+} ($t_{2g}^3\downarrow$)], which agreed with the experimental results. The HSC energy-gaps originate from the splitting of three partially occupied Os^{5+} (5d) bands into two fully filled bands and one empty spin-down band. The real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts of the dielectric function $\varepsilon(\omega)$ and energy-loss spectrum $L(\omega)$ were calculated, analyzed, and compared with the electronic results.

1. Introduction

Studies of transition-metal double perovskite oxides have increased greatly mainly because; double perovskite oxides possess: (i) variable crystal structures; (ii) flexible chemical compositions and (iii) various electronic, magnetic, and optical properties, as well as other physical and chemical properties. Therefore, double perovskite oxides have attracted much interest in fundamental and applied fields of material science, solid state physics, and solid state chemistry, due to their attractive properties, including high room-temperature magnetoresistance [1], half-metallic (HM), ferrimagnetic (FiM), antiferromagnetic (AFM) properties, and high Curie temperature [1–3].

Double perovskite oxides with the general chemical formula of [$A_2BB'O_6$] attributable to the ordering of B and B' cations on the octahedral site of a single perovskite [ABO_3] unit cell. In magnetic $A_2BB'O_6$ double perovskite oxide compounds, the A-site is occupied by an alkaline/rare earth metal and the B–B'-sites are occupied by magnetic and nonmagnetic (NM) transition metals, respectively. However, the HM property is characterized by the coexistence of metallic behavior due to the one spin direction and insulating or semiconducting behavior from the other spin direction. Thus, HM double perovskite oxides have three main characteristics: (i) full spin-up or spin-down polarization (SP=100%), (ii) quantization of the spin magnetic moment in Bohr magneton units μ_B ($M_S = n\mu_B$) and (iii) zero spin magnetic susceptibility ($\chi_s = 0$). Therefore, HM double perovskite oxides have many potential applications, such as memory for data storage [4,5], magnetic reordering devices [5], magnetic sensors [5], and anodes in fuel cells [6]. In the electronic band structure of HM double perovskite oxides, the density of states (DOS) as a function of energy (E) clearly indicates that the spin-up (majority spin) has an energy-gap (E_g) at the Fermi level (E_F) in the insulating or semiconducting materials. By contrast, the spin-down (minority spin) continues and crosses the E_F, due to the strong hybridization between (B –O–B') states in $A_2BB'O_6$. Extensive studies have been performed to understand the HM property of double perovskite oxide compounds due to their potential technological applications in spin-electronic devices, such as spin valves, sources for spin-polarized electrons, and in magnetic storage media [7].

In this study, we determined the electronic, magnetic, and optical characteristics of cubic double perovskite oxide Sr_2CrOsO_6 with Fm-3m symmetry using the full potential linear muffin-tin orbital (FP-LMTO) method, where previous experimental analyses

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of this material have demonstrated that it is a FiM half-semimetallic material with a high-Curie temperature of T_C=725 K [8]. We demonstrate that there is a line node near the E_F due to the AFM coupling [Cr^{3+} ($t^3_{2g}\uparrow$)–O ($2p_\pi$)–Os^{5+} ($t^3_{2g}\downarrow$)]. Thus, Sr_2CrOsO_6 is metallic with small Fermi pockets and it becomes a perfect half-semiconductor with nodal dispersion when the U and spin–orbit coupling (SOC) become stronger according to local spin density approximation (LSDA+SOC), generalized gradient approximation (GGA)+SOC, (LSDA+U)+SOC, and (GGA+U)+SOC methods.

2. Computational methods and details

The calculations in this study were based on the first-principles density functional theory (DFT). The FP-LMTO method working within the atomic plane wave expansion (PLW) [9] was used to calculate the characteristics of Sr_2CrOsO_6. FP-LMTO was implemented with the Savrasov LMTART code, version 6.50 [10,11]. The spin-dependent DOS and optical spectra were obtained from the LSDA and GGA analyses. The exchange-correlation parameterizations of Barth-Hedin [12] and Perdew-Wang (PW91) [13] were employed in the LSDA and GGA calculations, respectively. Unfortunately, the LSDA and GGA methods cannot successfully describe the strongly correlated double perovskite oxides containing transition metals [14], so, this deficiency was corrected by adding strong correlation terms to the LSDA and GGA using (LSDA+U) and (GGA+U) methods [14,15]. The LSDA+U and GGA+U techniques yield quite satisfying results for strongly correlated systems, so the correlation parameters of Coulomb repulsion (U) and Hund's rule exchange (J) were utilized for the 3d and 5d states [16,17]. Therefore, to detect the effects of the U and J parameters on Sr_2CrOsO_6, we performed the LSDA+U and GGA+U calculations in parallel with the LSDA and GGA calculations. In transition metals, the near maximum values of U were selected from the reasonable range [16]. For example, the range of U for Cr (3d) is 2.0 eV to 6.0 eV, whereas for Os (5d), the range of U is 1.0 eV to 2.0 eV [16–18]. In this study, we employed reasonable values for U and J: U(Cr)=5.0 eV, J(Cr)=0.96 eV, and U(Os)=1.0 eV, J(Os)= 0.96 eV. The settings of these parameters were examined based on the total energy convergence reached in the FP-LMTO calculations.

In addition, the SOC contribution was included in the LSDA, GGA, LSDA+U, and GGA+U calculations using the scalar relativistic scheme based on the Dirac equation [11]. The full relativistic effects were calculated with the Dirac equation for core states, whereas the scalar relativistic approximation was used for the valance states [19]. Including the SOC effect is essential for investigating the electronic and magnetic properties of Sr_2CrOsO_6 due to the presence of the relatively heavy Os atom. The SOC was included in a self-consistent manner by solving the radial Dirac equation for the core electrons and evaluated based on the second variation treatment [19,20]. Therefore, the total angular momentum coupled the orbital angular momentum to the spin (L+S) of the valence and the semicore states of Cr and Os in Sr_2CrOsO_6. The cutoff energy for PLW basis was set to 450 eV and ($6\times6\times6$) k-points grids were set in the irreducible part of the Brillouin zone. To find the stable state, the energy convergence criterion for electronic self-consistent calculation was set to 10^{-3} meV. The Wigner-Seitz radii of the muffin-tin (MT) spheres were set to 3.73 a.u. for Sr, 2.32 a.u. for Cr, 2.15 a.u. for Os and 1.49 a.u. for O.

3. Results and discussion

3.1. Ground state and crystal structure of Sr_2CrOsO_6

First, during the first-principles calculations, four magnetic phases were considered to estimate the ground state and the stable state with the minimum total energy. These magnetic phases can exist and they are specified as ferromagnetic (FM), FiM, AFM, and NM. Each phase was organized by the spin alignments (m and m') of the 3d and 5d ions in Sr_2CrOsO_6, respectively. Cr^{3+} ($3d^3$) and Os^{5+} ($5d^3$) had their own spin alignments, i.e., (Cr_1, Cr_2, Os_1, Os_2)=($+m_1$, $+m_2$, $+m'_1$, $+m'_2$) for FM and (Cr_1, Cr_2, Os_1, Os_2)=($+m_1$, $+m_2$, $-m'_1$, $-m'_2$) for FiM, as shown in Fig. 1, thereby allowing us to assume HM electronic state. The AFM phase occurred if Cr^{3+} ($3d^3$) and Os^{5+} ($5d^3$) ferromagnetically polarized along the chain but the

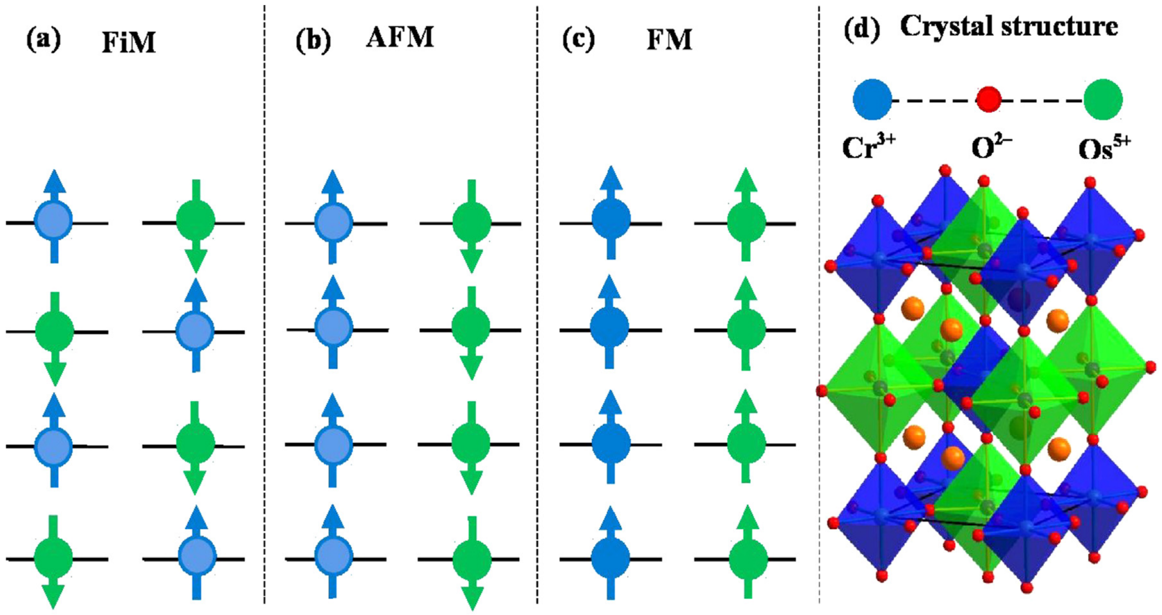

Fig. 1. Schematics show the favored magnetic phases in transition-metal cubic double perovskite oxides (a) FiM, (b) AFM, (c) FM, in Cr (3d)–O (2p)–Os (5d) 180°-super-exchange chains. Cr^{3+} ($3d^3$) and Os^{5+} ($5d^3$) ions are represented by blue and green spheres. Arrows↑and↓represent spin-up and spin-down, respectively. (d) The three dimensional arrangement of CrO_6 and OsO_6 octahedra generates a 180° bond angle in Cr (blue octahedra)–O (small red spheres)–Os (green octahedra), where the large red spheres in the gaped between the CrO_6– OsO_6 octahedra are Sr ions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)