CHARACTERIZATION OF ELECTRONIC PROPERTIES OF POTASSIUM CHALCOGENIDES USING FIRST PRINCIPLES METHOD

HITESH SWARNKAR[*] and GUNJAN ARORA[a]

Research Scholar, Department of Physics, PAHER University, UDAIPUR – 313003 (Raj.) INDIA
[a]Department of Physics, Geetanjali Institute of Technical Studies, UDAIPUR – 313022 (Raj.) INDIA

ABSTRACT

In this paper, we report the electronic properties of potassium chalcogenides K_2X (X = S and Se) using various DFT schemes within the frame work of linear combination of atomic orbitals approach. These compounds show indirect band gap with conduction band minima at Γ point and valence band maxima at X and L point for K_2S and K_2Se, respectively. The relative nature of bonding in these chalcogenides is explained in terms of Mulliken's population analysis, which shows that the amount of charge transfer from K to chalcogen atom increases as we move from S → Se, so the ionicity increases or covalency decreases from $K_2S → K_2Se$.

Key words: Electronic band structure, Density functional theory, Wide band gap semiconductors, Potassium chalcogenides.

INTRODUCTION

The alkali metal chalcogenides crystallize in the cubic anti-fluorite (anti-CaF_2-type) structure[1]. These materials are characterized by fast ionic conduction and have technological applications in fuel cells, solid state batteries, high capacity energy storage devices for electric vehicles, gas detectors and ultraviolet space technology devices. Also, they have important role in the development of photocathode, in supporting catalytic reactions and enhancing semiconductor surfaces. These ionic compounds are also used as a power source for portable electronic devices such as mobile phones, video cameras and notebook-type personal computers[2-5].

Regarding earlier studies, the electronic, optical and elastic properties of alkali metal oxides and sulfides have been extensively studied theoretically[6-9] and experimentally[10-14],

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[*]Author for correspondence; E-mail: garora.gits@gmail.com

whereas the selenides and tellurides have received less attention except some work on cohesive energies, elastic properties and bulk modulus[15-17]. Recently, Alay-E-Abbas et al.[18] have computed the structural and electronic properties of alkali metal chalcogenides: M_2CH [M: Li, Na, K, Rb; Ch: Se, Te]. Also, they have undertaken the structural properties of alkali metal oxides and sulfides using FP-LAPW+lo method. The ground-state electronic and optical properties of alkali metal selenides M_2Se [M: Li, Na, K, Rb] have been studied using FP-LAPW method[19]. The electronic and optical properties of alkali metal sulfides have been explored by Khachai et al.[20] The effect of pressure on elastic properties of alkali metal sulfides have been studied by FP-LAPW method[21]. Eithiraj et al.[22] have employed TB-LMTO method to study alkali metal sulfides. The TB-LMTO method has been used to find the ground state and under compression electronic behavior of selenides and tellurides of Li, Na and K[23].

We report the energy bands, density of states and Mulliken's populations of potassium chalcogenides using the local density approximation (LDA) and generalized gradient approximation (GGA) within the density functional theory (DFT). In addition, a hybridized HF-DFT approach is also incorporated to study the electronic band structure.

Computational method

We have used the CRYSTAL09 code[24] of Torino group to deduce the electronic properties of K_2S and K_2Se. The code includes a variety of self-consistent treatments of exchange and correlation namely Hartree-Fock (HF), density functional theory (DFT) within the local density approximation (LDA), generalized gradient approximation (GGA) and second order corrected GGA (so called SOGGA) and also hybrid of HF and DFT.

In the LCAO technique, the Bloch orbitals of the crystal are expanded using atom-centered Gaussian orbitals of s, p or d symmetry. These crystalline orbitals are the solutions of the following Schrodinger equation

$$\hat{h}_i\,\varphi_{ki}(\vec{r}) = \varepsilon_{ki}\varphi_{ki}(\vec{r}) \qquad\qquad …(1)$$

In the HF scheme, the Hamiltonian operator is given by

$$\hat{h}_{HF} = \hat{t} + \hat{\upsilon} + \hat{J}\left[\rho(\vec{r})\right] + \hat{K}_{HF}\left[\rho(\vec{r},\vec{r}')\right] \qquad\qquad …(2)$$

where $\hat{t}$, $\hat{\upsilon}$, $\hat{J}$ and $\hat{K}_{HF}$ are the kinetic, external potential, Coulomb and nonlocal exchange operators, respectively. While in the DFT scheme, the one particle Hamiltonian operator is the Kohn-Sham operator defined as –

$$\hat{h}_{KS} = \hat{t} + \hat{v} + \hat{J}[\rho(\vec{r})] + \hat{v}_{XC}(\vec{r}) \qquad \dots(3)$$

where
$$\hat{v}_{XC}(\vec{r}) = \frac{\partial E_{XC}[\rho]}{\partial \rho(\vec{r})} \qquad \dots(4)$$

One can also say that $\hat{v}_{XC}(\vec{r})$ is the exchange-correlation potential operator that is the functional derivative of the exchange-correlation density functional energy E_{XC} with respect to density at a point $\vec{r}$.

The exchange-correlation energy is given by –

$$E_{XC}^{LDA}[\rho] = \int \rho(\vec{r}) \varepsilon_{XC}[\rho(\vec{r})] d\vec{r} \qquad for\ DFT\text{-}LDA \qquad \dots(5)$$

$$E_{XC}^{GGA}[\rho] = \int \rho(\vec{r}) \varepsilon_{XC}[\rho(\vec{r}), |\nabla \rho(\vec{r})|] d\vec{r} \qquad for\ DFT\text{-}GGA \qquad \dots(6)$$

where ε_{XC} is the exchange-correlation energy per particle in uniform electron gas.

The exchange and correlation part of hybrid functional B3LYP are given as –

$$E_{XC} = (1 - b_0)E_X^{LDA} + b_0 E_X^{HF} + b_x \Delta E_X^{B88} + b_c E_C^{LYP} + (1 - b_c)E_C^{VWN} \qquad \dots(7)$$

where $b_x \Delta E_X^{B88}$ is Becke's gradient correction to the exchange functional and the correlation functional is a combination of the functionals due to Lee-Yang-Parr (LYP) and Vosko-Wilk-Nusair (VWN). The value of the parameters b_0, b_x and b_c will be the default values. Different exchange and correlation functionals used in the present work are mentioned in Table 1.

Table 1: Different exchange and correlation potential functions used in present calculations

| Theory	Exchange	Correlation
DFT–LDA	Dirac-Slater[25]	Perdew–Zunger[26]
	VBH[27]	VWN[28]
DFT–GGA	WCGGA[29]	PWGGA[30]
	PBE[31]	PBE[31]
B3PW	Becke[32]	PWGGA[30]
B3LYP	Becke[32]	LYP[33]

In these compounds, the metal atoms are located at (0.25; 0.25; 0.25) and (0.75; 0.75; 0.75) and the chalcogen atoms are located at (0; 0; 0). In present calculations, we have used experimental lattice parameters as 7.391[34] and 7.92 Å[35] for K_2S and K_2Se, respectively. The all-electron basis sets for K, S and Se were taken from http://www.tcm.phy.cam.ac.uk/~mdt26/basis_sets. Following the default tolerances in the CRYSTAL09 code, the SCF calculations have been performed for 120 k points in the irreducible Brillouin zone using Monkhorst–Pack shrinking factor of 15.

RESULTS AND DISCUSSION

In Figs. 1 and 2, we have shown the energy bands (E–k relations) along with the density of energy states (DOS) of K_2S and K_2Se using PBE theory of DFT-GGA approach. The energy is plotted in Hartree. Except for some fine structures and band gaps, the overall shape of our energy bands is in agreement with the earlier reported data[18-20] for all compounds. In both the compounds K_2S and K_2Se the conduction band minimum (CBM) occurs at the Γ point and the valence band maximum (VBM) at the X and L point, respectively, which results in an indirect band gap (X–Γ and L–Γ). The band gaps for K_2X (X=S and Se) as calculated using various approximations of LCAO method along with the available data are summarized in Table 2. The energy gaps obtained by present calculations are overestimating the previous results for all compounds.

Table 2: Band gap of potassium chalcogenides in eV

Samples		K_2S	K_2Se
DFT-LDA	LDA-PZ	3.84	2.10
	VBH-VWN	3.52	2.12
DFT-GGA	PBE	3.80	2.33
	WCGGA-PWGGA	3.74	2.28
Hybrid HF+DFT	B3LYP	5.17	3.54
	B3PW	5.31	3.65
Previous studies		3.11[9]	2.24[18]
		2.72[18]	2.97[19]
		2.86[20]	2.19[23]
		2.46[22]	
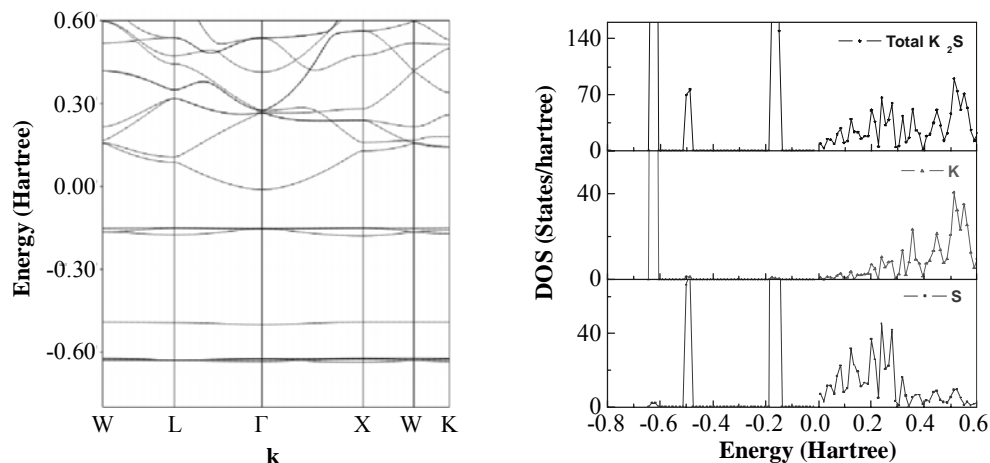
Fig. 1: Selected energy bands (*E-k* relation) and density of states of K₂S along high symmetry directions of the first BZ using DFT-GGA (PBE) calculations of LCAO method
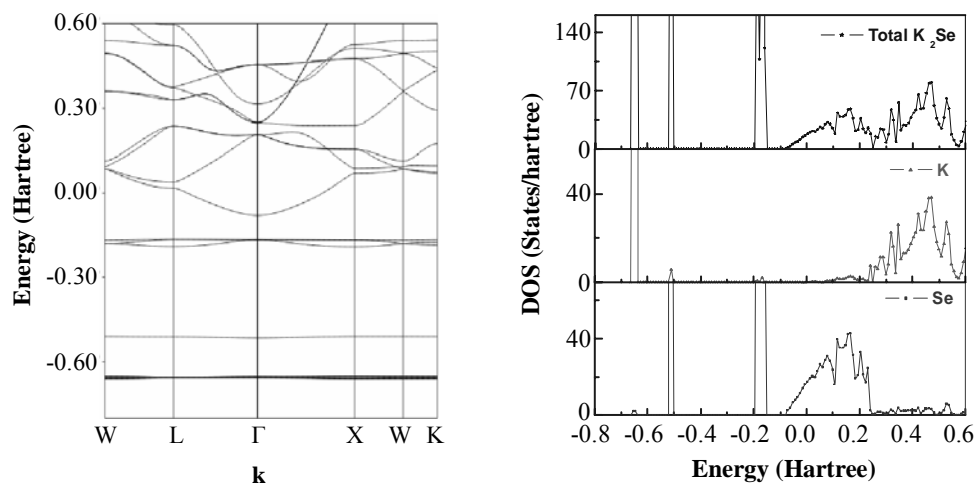
Fig. 2: Selected energy bands (*E-k* relation) and density of states of K₂Se along high symmetry directions of the first BZ using DFT-GGA (PBE) calculations of LCAO method

From the DOS figures, it can be infer that the lowest bands for K_2S (K_2Se) lying at about -0.62 Hartree (-0.65 Hartree) are dominated by p states of K and sp states of S (Se) atoms. Then in both compounds near-0.5 Hartree major contributions to the electronic states are due to S (Se) s like states. The highest valence band (just below the Fermi level) arises mainly due to p like states of S (Se) atoms. Therefore, it is clear that cation s like and p like states dominate in the lower and upper parts of the valence bands, respectively. We can

observe hybridization in conduction band, which are due to mixed states of cation and anion atoms.

The Mulliken's population analysis of K_2S and K_2Se undertaken by using DFT-LDA, DFT-GGA, B3LYP and B3PW schemes of LCAO theory is shown in Table 3. The PBE calculations show that two potassium atoms transfer 2.031 and 2.051 e[-] to S and Se atoms, respectively. Therefore, the present LCAO calculations show that the amount of charge transfer from K to chalcogen atom increases as we move from S → Se, so the iconicity increases or covalency decreases from K_2S → K_2Se. It is also observable from electron charge density plots. In Fig. 3 we have plotted charge density plots using DFT-GGA (PBE) scheme of CRYSTAL09 code. We can clearly see more surplus charge on chalcogen atoms as we move from S → Se, which indicates more ionic character from K_2S → K_2Se.

Table 3: Mulliken's Population data of K_2X

	Present theories		K_2S	K_2Se
Charge transfer from K (two atoms) to chalcogen atom (in electrons)	DFT-LDA	LDA-PZ	2.010	2.038
		VBH-VWN	2.014	2.037
	DFT-GGA	PBE	2.031	2.051
		WCGGA-PWGGA	2.032	2.056
	Hybrid HF+DFT	B3LYP	2.025	2.038
		B3PW	2.040	2.056
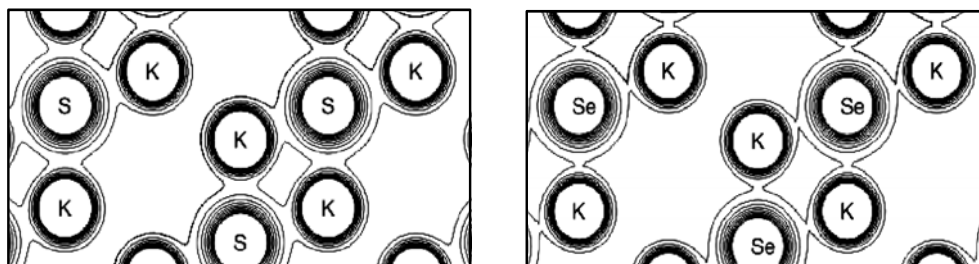
Fig. 3: Charge density plots deduced for two K atoms situated at (0.25, 0.25, 0.25) and (0.75, 0.75, 0.75) and chalcogen atom at (0, 0, 0)

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