Extrinsic $n$-type semiconductor transition in ZrSe$_2$ with the metallic character through hafnium substitution

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Abstract:

Two-dimensional (2D) layered materials exhibit versatile electronic properties in their different phases. The intrinsic electronic properties of these materials can be modulated through doping or intercalation. In this study, we investigated the electronic properties of Hf-doped ZrSe$_2$ single crystals using angle-resolved photoemission spectroscopy (ARPES) combined with first-principles density functional theory (DFT) calculations. It is observed that the valence band maxima of ZrSe$_2$, located below the Fermi level, undergo a significant change with the introduction of Hf substitution. Hf can introduce extra charges into the conduction band, rather than making a mixed structure of HfSe$_2$ and ZrSe$_2$ band structure, which can cross the Fermi level. Compared to the semiconducting band structure of ZrSe$_2$, we observed that the conduction band crosses the Fermi level at the high symmetry M point in Hf-doped ZrSe$_2$. This suggests an increase of electron-type carriers around the Fermi level, resulting in an extrinsic charge carrier density in the conduction band, which can form a metallic behaviour. It can be noticed that the Hf cations can create disorder in the form of excess atoms of Zr, which yields more carriers in the conduction band in the shape of “smeared bands”. The tails of the “smeared band” occupied the $d$-orbitals extended into the Fermi level and left the $d$-band below. Similarly, the electrical resistance measurements further confirm the metallic-like character of Hf-doped ZrSe$_2$ compared to the semiconductor ZrSe$_2$, indicating increased carriers. This metallic-like behavior is suggested to be predisposed by the extrinsic electrons induced by the substitutional disorder. This study further demonstrates the possibility of band gap engineering through heavy metal doping in 2D materials.

Keywords: Disorder effect, Doping, Extrinsic electrons, Metallic transition, Smeared band shifting
Introduction

The transition metal dichalcogenides (TMDs) exhibit unique and distinct electronic characteristics in different hybrid structures. Changing the band gap property allows tuning the electronic and optical properties [1]. TMDs possess two phases with diverse electronic structures: the semiconductor 2H phase and the metallic 1T phase [2–4]. These phases coexist in two-dimensional (2D) TMDs [5], and their conversion can be achieved through atomic intercalation, atom substitution, or atomic plane gliding [2, 6–9]. Phase transitions in TMDs depend on growth conditions such as temperature and pressure [10]. The transition metal is sandwiched between two atomic chalcogens in a TMD layer, offering additional degrees of freedom in structural transformations [11]. The electron-phonon coupling is attributed to the structural instabilities in metallic layered transition metal dichalcogenides. The phonon-electron instability may somehow be connected to the electron or hole-type carriers, which changes the phase in layered crystals. However, the band structures of the crystals reveal the presence of saddle points near the Fermi surface, indicating the occurrence of a phase transition [12].

Electronic phase transition plays a crucial role in various physical properties [13–15]. TMDs possess versatile electronic structures that find applications in p-n junctions and other applications [16], high-mobility field-effect transistors [17–19], switching and memory devices [20], and optoelectronics [21]. 2D layered TMD materials can also be found in hybrid forms [22, 23] with distinct electronic structures. The electronic properties of TMDs can be modulated through substitution or intercalation [24–26], leading to altered electronic properties and new applications [27–31]. Atomic substitution or intercalation effectively modifies the intrinsic electronic properties by altering the band gap characteristics [32–34]. For instance, heavy atomic doping of W into MoTe₂, MoSe₂, and MoS₂ lattices induces a transition from semiconducting to metallic phases [27, 35–37]. Strain can be used to tune the band gap properties of IVB TMDs (e.g., TiX₂, ZrX₂, and HfX₂, where X = S, Se, and Te) [38]. Intercalation of Cu in ZrSe₂, a semiconductor, provides extra electrons to the d-orbitals of zirconium atoms, leading to a metallic transition [39]. Similarly, in ZrSe₂, the conduction band maximum (CMB) crosses the Fermi level at the M point due to the in situ surface doping of sodium, acting as an electron dopant [40]. Intercalation of Cu in 2H-TaSe₂ [41], Se doping 1T-ZrTe₂ [42], and Cu intercalation 2H-NbSe₂ [43] can alter the electronic structure by introducing charge carriers. Recently, Yongji et al. investigated the
semiconductor-to-metallic transition in SnS\textsubscript{2} through Co-intercalation, which modifies the electronic structure [9]. The strong interaction between electrons and holes has prompted the proposal of a mechanism to explain the phase transition.

In this study, we examine the electronic properties of Zr\textsubscript{1-x}Hf\textsubscript{x}Se\textsubscript{2} (x = 0.12, determined via ICP) single crystal alloys compared to ZrSe\textsubscript{2}. The samples were synthesized using the chemical vapor transport (CVT) method. The electronic structures were analyzed using synchrotron-based Angle-Resolved Photoemission Spectroscopy (ARPES) and first-principles density functional theory (DFT) calculations. Our findings reveal a substantial change in the band structures of pristine ZrSe\textsubscript{2} upon substituting Hf atoms. In Zr\textsubscript{0.88}Hf\textsubscript{0.12}Se\textsubscript{2}, the electronic properties exhibit additional electron carriers near the bottom of the CB at the M point, crossing the Fermi level and behaving as a metallic character. However, the overall structure is intact and preserved.

**Experiments**

**Single crystal growth:**

The single crystals of ZrSe\textsubscript{2} and Zr\textsubscript{1-x}Hf\textsubscript{x}Se\textsubscript{2} were synthesized by using the chemical vapor transport (CVT) method. A highly purity of 99.98\% zirconium (Zr) and hafnium (Hf) powders from (Alfa-Aesar, UK) and 99.98\% Se from (Sigma-Aldrich, USA) was used for the single crystal growth. The stoichiometric amount with a transport agent of iodine in the ratio of 5 mg/ml was ground for some time to mixed very well and kept in a quartz tube. Later, the tubes containing the accumulated amount of the reactants and purified iodine were attached to the vacuum line with argon gas to evacuate and seal silica tubes with pressure at \(\sim 10^{-4}\) torr. The evacuated quartz tubes were then placed into a two-zone furnace with reaction temperature of 950 °C and a growth temperature of 850 °C. The temperature of the furnace was gradually increased to the transport temperature in 5 hours. With the increase in temperature, the vapor pressure was increased, and the reaction of selenium with the Zr and Hf was continued slowly. The ampule was kept at this temperature for 5 days, after that it was slowly cooled down to 500 °C in 5 hours, followed by a transition to room temperature. After finishing the experimental process, we successfully attained the high-quality single crystals of pristine ZrSe\textsubscript{2} and Zr\textsubscript{1-x}Hf\textsubscript{x}Se\textsubscript{2} (shown in **Fig. 1**). After proper cleaning the samples was further characterized.
Results and discussion

We synthesized ZrSe$_2$ and Hf-doped ZrSe$_2$ using the CVT method. **Fig. 1(a)** provides a schematic illustration of the CVT process, images of the single crystal inside the quartz tube and the structural configuration of ZrSe$_2$ and Hf-doped ZrSe$_2$. Additional details regarding the growth conditions of the single crystal can be found in the experiment part. **Fig. 1(b)** presents the X-ray diffraction (XRD) patterns of ZrSe$_2$ and Hf-doped ZrSe$_2$. All XRD patterns closely match the standard diffraction pattern of ZrSe$_2$ (JCPDS 65-3376). However, the diffraction peaks of Hf-doped ZrSe$_2$ exhibit slight shifts to higher diffraction angles and a new peak (-103) corresponding to HfSe. These slight peak shifts in the diffraction patterns towards higher angles are attributed to the smaller ionic radii of Hf (Hf$^{4+}$) compared to Zr (Zr$^{4+}$) during the substitution process [44]. XRD analysis further reveals that the c-lattice parameter of ZrSe$_2$ is c = 6.16 Å, which decreases to c = 6.19 Å for Hf-doped ZrSe$_2$. The lattice expansion occurs due to the larger atomic number (Z) of hafnium atoms. A similar trend has been previously observed in Hf$_x$Zr$_{1-x}$NiSn$_{0.99}$Sb$_{0.01}$ [45].

The energy-dispersive X-ray spectroscopy (EDS) was performed to estimate the appropriate amount of each element in the single crystal of Hf-doped ZrSe$_2$ (see **Fig. S1**, in supporting information); while further confirmed by Inductively coupled plasma mass spectrometry (ICP). From the EDS and ICP, we have confirmed the elemental composition as Zr$_{0.88}$Hf$_{0.12}$Se$_2$. Additionally, X-ray photoelectron spectroscopy (XPS) also revealed the detailed elemental composition along with the chemical states of Hf, Zr and Se, respectively.
The XPS spectra were analyzed to investigate the chemical states of Zr$_{0.88}$Hf$_{0.12}$Se$_2$ compared to ZrSe$_2$, as depicted in Figs. 2 (a-c). Fig. 2(a) displays the Zr-3$d_{5/2}$ and Zr-3$d_{3/2}$ peaks. On the other hand, Figure 2(b) illustrates the splitting of the Se-3$d$ band in Zr$_{0.88}$Hf$_{0.12}$Se$_2$, which is slightly shifted to lower binding energy compared to the ZrSe$_2$ spectra. The shift of the Zr peaks towards higher binding energies after Hf substitution can be attributed to charge transfer, while the Se peaks remain relatively unchanged. This shift has been previously observed in similar studies [46, 47].

The primary cause of this shift is the reduction in bond length or lattice contraction, which increases the binding energy of the Zr 3$d$ core level spectra. Similar observations have been made in Me$_x$TiSe$_2$ (Me = Cr, Mn, Cu) [48] and V$_x$Ti$_{1-x}$Se$_2$ [47]. Fig. 2(c) clearly shows the presence of Hf$^{4+}$ (as indicated by the binding energy position of Hf-4$f$) rather than Hf$^0$, demonstrating the formal Hf$^{4+}$ oxidation state [49]. As the Hf$^{4+}$ substitutes on the Zr$^{4+}$ site, the charge carriers differ from those in the pure sample, resulting in a shift to lower binding energies. Therefore, the extrinsic charge contribution modifies the valence states, leading to a change in the binding energy position.
Figure 2. Microstructural and elemental analysis of Zr$_{0.88}$Hf$_{0.12}$Se$_2$ in comparison with ZrSe$_2$. XPS spectra of (a) Zirconium (Zr 3d), (b) Selenium, (Se 3d) and (c) Hafnium (Hf 4f). (d) Z-contrast high-resolution HAADF STEM images of Zr$_{0.88}$Hf$_{0.12}$Se$_2$ and its corresponding (e) SAED patterns, (f) ZrSe$_2$ and inset: SAED patterns. (g) HAADF-STEM image of Zr$_{0.88}$Hf$_{0.12}$Se$_2$ and the corresponding (h) intensity profile along the line marked in (g). (i) Typical TEM image of Zr$_{0.88}$Hf$_{0.12}$Se$_2$ and corresponding elemental mapping (Zr, Hf and Se, respectively).

Scanning transmission electron microscopy (STEM) was employed to investigate the microstructure of Zr$_{0.88}$Hf$_{0.12}$Se$_2$ compared to ZrSe$_2$. Fig. 2(d) presents a high-resolution Z-contrast HAADF STEM image of Zr$_{0.88}$Hf$_{0.12}$Se$_2$, revealing the hexagonal arrangement of Zr/Hf atoms with six Se atoms surrounding them. Fig. 2(e) shows selected-area electron diffraction (SAED) patterns, which exhibit regular diffraction superlattice spots along the rotational direction in the hexagonal axis. Comparatively, the microstructure of ZrSe$_2$, as depicted in Fig. 2(f), displays a similar arrangement. The inset in Fig. 2(f) shows SAED patterns of ZrSe$_2$ with similar diffraction patterns. The microstructure of both compounds is similar to each other rather than structural change. In
order to reduce noise, a Wiener filter is applied to the high-resolution HAADF-STEM image of Zr$_{0.88}$Hf$_{0.12}$Se$_2$, as shown in Fig. 2(g). Fig. 2(h) displays the corresponding intensity profile along a line cut in Fig. 2(g), indicating three distinct atomic column profiles. The profile with the highest intensity corresponds to Hf atoms ($Z = 72$), while the less intense profile corresponds to Se atoms ($Z = 32$). Regarding peak intensity, the intensity profile of Zr atoms ($Z = 40$) lies between Hf and Se. This confirms that Hf is substituted on the Zr site in the crystal structure.

Furthermore, Fig. 2(i) displays a typical TEM image of Zr$_{0.88}$Hf$_{0.12}$Se$_2$ along with the corresponding elemental mapping, revealing a uniform distribution of Zr, Hf, and Se atoms. The interlayer spacing of both samples is confirmed by high-resolution transmission electron microscopy (HRTEM) images (refer to Fig. S2 in the supporting information). The interlayer spacing of Zr$_{0.88}$Hf$_{0.12}$Se$_2$ is observed to be smaller than that of ZrSe$_2$, which is consistent with the X-ray diffraction (XRD) analysis.

The Raman spectra were used to compare the in-plane and out-of-plane structural properties of Zr$_{0.88}$Hf$_{0.12}$Se$_2$ with the pristine sample. The lattice vibration is observed to be well retained compared with ZrSe$_2$ (Fig. S3, in supporting information), showing that the sample’s structure is unchanged. The Raman peaks of Zr$_{0.88}$Hf$_{0.12}$Se$_2$ show a minor energy shift (1.9 cm$^{-1}$) for in-plane vibration mode $E_g$ to lower energy, which exhibits the reduction of photon energy. Similarly, the out-of-plane vibration $A_{1g}$ mode shows a slight high energy shift (2.8 cm$^{-1}$) to higher energy, demonstrating the local shortening of Zr-Se covalent bonds due to Hf substitutions. A similar trend was also observed in Hf$_x$Ti$_{1-x}$Se$_2$ and Zr$_x$Ti$_{1-x}$Se$_2$ [50, 51]. These findings are further supported by X-ray absorption fine structure (XAFS) measurements.

X-ray absorption near-edge structure (XANES) spectroscopy experiments were conducted to investigate the possible corrugations of Zr$_{0.88}$Hf$_{0.12}$Se$_2$ compared with ZrSe$_2$ as presented in Fig. 3. Fig. 3(a) illustrates the Zr K-edge XANES spectra of Zr$_{0.88}$Hf$_{0.12}$Se$_2$ in comparison with Zr K-edge of ZrSe$_2$ single crystals. The slight chemical shift in energy for Zr$_{0.88}$Hf$_{0.12}$Se$_2$ strongly depends upon the charge transfer in the ionic bond and the number of nearest neighbor atoms [52, 53]. Therefore, it has been investigated that the valence and conduction states of the elements are slightly affected in the case of Hf-doping. Fig. 3(b) displays the corresponding Fourier transform (FT) spectra, which can show the spectral shape of the atomic structure for both ZrSe$_2$ and Zr$_{0.88}$Hf$_{0.12}$Se$_2$. The FT curves indicate two peaks at ~2.31 and 3.45 Å, corresponding to Zr-Se and
Zr-Zr correlations of ZrSe$_2$ and Zr$_{0.88}$Hf$_{0.12}$Se$_2$, respectively. The intensities of these two peaks are marginally decreased, which suggests that the Zr-neighboring structure of Zr$_{0.88}$Hf$_{0.12}$Se$_2$ has changed as associated with ZrSe$_2$. The minor shift shows the decrease of metal-metal bond length from 3.79 to ~3.43 Å (see Table S1).

**Figure 3.** XAFS analysis of as-grown ZrSe$_2$ and Zr$_{0.88}$Hf$_{0.12}$Se$_2$ single crystals (a) Zr K-edge XANES spectra of Zr$_{0.88}$Hf$_{0.12}$Se$_2$ compared with ZrSe$_2$ single crystals and the corresponding (b) Fourier transforms (FT($k^3\chi(k)$)) curves. (c) Hf L3-edge Zr$_{0.88}$Hf$_{0.12}$Se$_2$ compared with pure HfSe$_2$ and its equivalent (d) Fourier transforms (FT($k^3\chi(k)$)) spectra. (e) Structural models showing the bond length of pure ZrSe$_2$ and Zr$_{0.88}$Hf$_{0.12}$Se$_2$.

Similarly, Fig. 3(c) shows the comparison of Hf L3-edge XANES spectra of Zr$_{0.88}$Hf$_{0.12}$Se$_2$ with the Hf L3-edge of HfSe$_2$, which are similar to each other except slight shift to higher energy was observed for Zr$_{0.88}$Hf$_{0.12}$Se$_2$ sample. Fig. 3(c) revealed that Hf is bonded well with Se. The slight increase in the intensity of the Hf L3-edge of HfSe$_2$ compared with Zr$_{0.88}$Hf$_{0.12}$Se$_2$ shows the different alternation of dissimilar atoms in Zr$_{0.88}$Hf$_{0.12}$Se$_2$. Similarly, Fig. 3(d) shows the FT curve of Zr$_{0.88}$Hf$_{0.12}$Se$_2$ in association with HfSe$_2$, with a smaller Hf metal-metal bond length shift from 3.79 to ~3.43 Å (see Table S1). The minor difference in the structure is the cause of bond length
shortening for the doped case. The XAFS results are well in accordance with XRD and Raman data, which can support the extrinsic charge contribution. The XAFS spectra were subjected to further analysis to obtain quantitative structural results. This was achieved by performing least-squares fittings of the Zr and Hf K-edge data, and the summarized findings can be found in Table S1 of the supporting information. Fig. 3(e) shows the structural model based on the structural parameters obtained from XAFS data, which illustrates the different bond lengths of the Zr-Se, Zr-Zr, Zr-Hf, Hf-Se, Zr-Se-Zr, Zr-Se-Hf and Hf-Se-Hf etc. with different coordination (see Table S1). Compared with pure ZrSe₂, the Zr-Se and Zr-Zr bond length in the Zr₀.₈₈Hf₀.₁₂Se₂ was relatively shortened, thus impairing the Hf to make a covalent bond on the Zr site.

To investigate the electronic band structures of Zr₀.₈₈Hf₀.₁₂Se₂ compared with the parent compound using angle-resolved photoemission spectroscopy (ARPES) for a detailed study. Further details of the ARPES measurement can found in the supporting information. Notably, we know that the nature of ZrSe₂ is semiconducting, which is well understood, while it needed to be clarified whether the Hf-doped ZrSe₂ ternary alloy is still a semiconducting phase. Therefore, the electronic structure of Zr₀.₈₈Hf₀.₁₂Se₂ single crystals compared to pure ZrSe₂ was investigated using ARPES combined with DFT calculations as shown in Fig. 4. The details of the DFT calculation can be found in the supporting information.

Fig. 4(a) shows the corresponding structure's Brillouin zone (BZ), indicating the high symmetry k-points. Fig. 4(b) indicates the constant energy contour plots ZrSe₂ and Zr₀.₈₈Hf₀.₁₂Se₂ along the high symmetry ΓM in the first BZ. The upper panel in Fig. 4(b) shows the Fermi surface (FS) of the pristine ZrSe₂ sample, and the lower panel indicate the FS of Zr₀.₈₈Hf₀.₁₂Se₂. It is observed that the spectral weight appeared at the FS along the M direction of the BZ compared to ZrSe₂, having no spectral weight on FS. It is suggested that substituting the Hf atom on the Zr site shows excess charges, which can cross the bottom of the CBM at the Fermi level (FL). These tiny electron pockets are visible at the FS at high symmetry M point, which probably comes from the bottom of the d band. In principle, the extrinsic electron concentrations due to Hf doping can create large spectra weight of electron pockets in k space, which is clearly visible at the FS. In Fig. 4(c, d), we compared the band dispersion of both ZrSe₂ (adopted from our previous work [39]) and Zr₀.₈₈Hf₀.₁₂Se₂ along ΓM direction in a large range of k-space. By comparing the band structure of ZrSe₂ with Zr₀.₈₈Hf₀.₁₂Se₂, it can be observed that the top of the valence band maximum (VBM) of
pristine and Zr$_{0.88}$Hf$_{0.12}$Se$_2$ are located at about -0.87 eV and -1.05 eV below the Fermi level, respectively, suggesting a non-linear variation of the band gap with Hf concentration due to charging. With Hf substitution, the VBM moves approximately 0.18 eV to deeper binding energy without any evident changes in the band dispersion. Starnberg et al. observed the same effect in the photoemission study of Hf$_x$Ti$_{1-x}$Se$_2$ alloy [54]. Meanwhile, the Fermi level leaves down the bottom of the CB around the zone boundary marked by the red circle and Fig. 4(d) and can be clearly seen from their second derivative. These results indicate the extrinsic electron concentration in Zr$_{0.88}$Hf$_{0.12}$Se$_2$. The sample shows extrinsic $n$-type behavior of the metallic character, which can be further observed from resistivity measurement.

Figure 4. (a) The hexagonal Brillouin zone of high symmetry K-points, (b) Fermi surface plot of ZrSe$_2$ (upper panel) and Zr$_{0.88}$Hf$_{0.12}$Se$_2$ (lower panel) at $E_b = 0$ eV for high symmetry $\Gamma M$ direction, are indicated by the yellow dashed lines. Band dispersion of (c) ZrSe$_2$ and (d) Zr$_{0.88}$Hf$_{0.12}$Se$_2$ and its second derivative along $\Gamma M$ direction, respectively. (e) Spectral weight of the CB around M point for Zr$_{0.88}$Hf$_{0.12}$Se$_2$ as shown in (d). The data was measured at a photon energy of 33 eV and temperature of 160 K. (e) The charge density calculation and (g) the calculated unfold band
structure of Zr$_{1-x}$Hf$_x$Se$_2$ (x = 12.5%) combined with ZrSe$_2$ along the high symmetry $k$-points. (h) Resistance vs temperature (R-T) measurement of Zr$_{0.88}$Hf$_{0.12}$Se$_2$ compared with ZrSe$_2$.

Fig. 4(e) reveals a similar dispersion around the M point, as extracted from Fig. 4(d), encircled by a red-marked square. The appeared parabolic dispersion shows the $d$-band of the Zr-$d$ orbital. The CBM of Zr$_{0.88}$Hf$_{0.12}$Se$_2$ is located at 90 meV below the Fermi level, whereas the VBM is located at -1.05 eV, which indicates an indirect band gap of 0.96 eV. The results also reveal a decrease in the band gap of ZrSe$_2$ through Hf substitution rather than within those two compounds, compared to the previous work about pristine, which shows a band gap of about 1.10 eV [55]. Typically, the overall band structure remains unchanged, but merely the Hf induced more charges; due to increased extrinsic $n$-type charges in the $d$ band, whose carrier density can increase the conductance [56]. In Fig. 4(f), we calculated the charge density of Hf-doped ZrSe$_2$. The charge density distribution suggests that around the doped atom, the distribution shows dense charge regions compared to the other atoms, which indicates that maximum charge transfer accumulation around Hf exists. Thus, Hf substitution has a strong correlation with carrier doping, leading to a change in the effective mass around the conduction. Hence, it shows the extrinsic electrons type carrier, which behaves as a metal. Fig. 4(g) displays the unfold band structure of Zr$_{0.88}$Hf$_{0.12}$Se$_2$ (x = 12.5%), which shows that the CB slightly shifted down toward the Fermi level and the VBM moves to lower energy as compared to ZrSe$_2$ and HfS$_2$ (see Figure S4). It can be noticed that Hf can deliver extra freedom for manipulating the electronic properties of ZrSe$_2$ due to charge carrier transfer to the Zr $d$ orbital with a similar oxidation state.

Resistance vs temperature (RT) measurement was performed on Zr$_{0.88}$Hf$_{0.12}$Se$_2$ and ZrSe$_2$, as shown in Fig. 4(h). The RT measurements clearly demonstrate the typical semiconducting behavior for ZrSe$_2$ with decreasing temperature resistance, while for Zr$_{0.88}$Hf$_{0.12}$Se$_2$, the resistance increases with decreasing temperature, exhibiting metallic character. Specifically, the room temperature resistance of Zr$_{0.88}$Hf$_{0.12}$Se$_2$ is lower than one-and-a-half orders of magnitude than that of ZrSe$_2$, suggesting that the conductivity of Zr$_{0.88}$Hf$_{0.12}$Se$_2$ is increased. Taguchi observed a similar in the transport study of Ti$_{1-x}$Hf$_x$Se$_2$ using a series of Hf substitutions after a specific limit of x value; the resistivity is decreased [57]. Salvo and Waszczak detected that the phase transition in TiSe$_2$ via substituting Ta or V donates electrons can cause a rigid band shift, which tunes their carrier densities [58]. It is suggested that the cation disorder and increase in charge density are the
primary causes of this effect. Shkvarin et al. proposed the partial charge transfer effect from dopant to host [47] in TiSe$_2$ via Ta and V doping, which can decrease or increase the electrical conductivity of TiSe$_2$. The band below the CB is effectively induced in our sample, implying that the $d$ electron of the Hf$^{4+}$ is delocalized into the Zr $d$ band, increasing the electron carrier and decreasing the hole concentration, which can affect transport properties. Zhang et al. [59] observed a similar trend in ZrNiSn alloy by replacing Hf on the Zr site, which can increase electron density and CB across the Fermi level.

![Figure 5](image_url)

**Figure 5.** Constant energy contours of (a) pristine ZrSe$_2$ and (b) Zr$_{0.88}$Hf$_{0.12}$Se$_2$ at various binding energies, respectively. (c) Photoemission intensity was measured along $\Gamma$ direction for Zr$_{0.88}$Hf$_{0.12}$Se$_2$ at 24 eV, 27 eV, 30 eV, 33 eV and 36 eV, respectively.

**Fig. 5(a & b)** shows various constant energy contours of ZrSe$_2$ and Zr$_{0.88}$Hf$_{0.12}$Se$_2$ measured within the first Brillouin zone at different binding energies. **Fig. 5(a)** shows no evident spectral weight at
the Fermi surface for the parent compound at 0 eV. In contrast, Fig. 5(b) reveals the evident spectral weight of electron pockets at the FL around the M point in Zr$_{0.88}$Hf$_{0.12}$Se$_2$, indicating the typical electron type carriers at the FS at 0 eV. The electron pockets' spectral weight disappears at lower binding energies from the FS, indicating that these electron pockets originate from the bottom of conduction bands. In contrast, the spectral weight of the hole pocket increases for both samples, as observed in Fig. 5(a) and Fig. 5(b), respectively. About 0.18 eV energy, difference was set between the constant energy contours for both samples, which indicates that the lattice structure of Zr$_{0.88}$Hf$_{0.12}$Se$_2$ is consistent with the parent compound, while the pocket size is a bit shifted for Zr$_{0.88}$Hf$_{0.12}$Se$_2$. This suggests that band structures move by 0.18 eV to a deeper binding energy in Zr$_{0.88}$Hf$_{0.12}$Se$_2$ due to charge doping. Fig. 5(c) illustrates the band dispersion plots of Zr$_{0.88}$Hf$_{0.12}$Se$_2$ at different photon energies measured along the Γ direction from 24 eV to 36 eV, respectively. While, at different photon energies, the dispersions around the VBM do not show any indistinct change, which indicates that the bands around VBM have no noticeable $k_z$ dependence, thereby preserving the overall system with other transitions. However, only at the ΓM direction can the CB at the M point cross the FL in the Zr$_{0.88}$Hf$_{0.12}$Se$_2$ compound due to the excess charge density.

As considering the excess carriers in the conduction band can be created by the disorder effects via replacing Zr with Hf, which can’t be observed in similar oxidation states atoms in any other way. It can be detected that the presented disorder can be created by the excess Zr in the van der Waals gaps and other forms of lattice defects due to the substitution of the Hf. This is called a substitutional disorder. This kind of effect cannot be seen in the $k$-space if not too severe, but the energy bands can have some excess spectral weight that can be counted in the spectral functions representing, in some sense, “smeared bands”. It is suggested that these extrinsic $n$-type electrons can be observed in some particular atoms, which are sensitive to these kinds of disorders, as seen in [54, 57]. Thus, band edges may become slightly prolix due to extrinsic electrons and can be extended slightly down in energy and sometimes the tail of those bands can cross the FL. This effect can reduce the effective band gap, as seen in our measurements in the form of extrinsic carriers. One might also expect that the $d$ band center can appear below the FL in the band structure representing the low-energy tail of these “smeared bands”, which can reach below the FL. In contrast, it could not be seen in the dispersion of the un-doped system. Therefore, it is evident that the charge density in Zr $d$-orbitals increases by extrinsic $n$-type electrons induced by the Hf atom...
through substitutional disorder, which can be seen from the tail of the “smeared bands” as appeared below the FL. Furthermore, the shortening of metal-metal and metal-chalcogen bond length observed from XAFS and Raman results shows evidence of extrinsic electrons in $\text{Zr}_{0.88}\text{Hf}_{0.12}\text{Se}_2$. Similar results were also observed in $\text{V}_{x}\text{Ti}_{1-x}\text{Se}_2$ and $\text{Ta}_{x}\text{Ti}_{1-x}\text{Se}_2$ [47, 58]. On the other hand, one might also imagine that the increased carriers may come from defects due to heavily doped atoms or self-doping. However, the data in Fig. 2(d, h) shows no evident defect in the sample having no super lattice points. The data suggest that the cation disorder is the major cause of this rigid band shift tail, which can cross the FL. R. D. Kirby et al. also predicted the effect of Zr doping in TiSe$_2$ [59]. They suggested that introducing Zr atoms could induce the impurity band or possibly result from minor deviations for exact stoichiometry with doping, showing the metallic-like effect. Therefore, the excess electrons from additional Ti presumably enter both into $\Gamma$ point hole pockets and the L/M point electron pockets of Ti, which can reduce the number of holes and increase the number of electrons [59]. Those excess numbers of electrons populate the Ti $d$-band, so the conductivity at low temperatures can be changed. Thus by doping, the excess electrons are present in the $\text{Zr}_{x}\text{Ti}_{1-x}\text{Se}_2$ doped crystals; perhaps the deviations from exact stoichiometry exist. Similarly, the recent DFT calculations showed that the excess Zr shifts the bands to lower binding energies [60].

Notably, it can be clearly seen in the band dispersion and FS contour plots that the electrons appear at the FL with Hf substitution due to excess electrons. Our study shows only the shift in the band structure and increased conductivity due to the excess electrons in the Zr $d$-band due to Hf doping. The Hf substitution on the Zr site can cause the disorder in the lattice by introducing excess Zr in the layers, which induces extrinsic electrons. The excess electrons enter the hole and electron pockets, reducing the hole number and enhancing the electron number. The excess electrons can increase the spectral weight of the conduction bands whose tail shows a rigid shift that can cross the FL. Furthermore, the VB moves to lower binding energy due to the reduction of the hole numbers. The extrinsic electrons can increase the carrier density, enhancing their conductivity and showing a metallic-like character.
**Conclusion**

The electronic structure of Zr$_{0.88}$Hf$_{0.12}$Se$_2$ in compression with pristine ZrSe$_2$ single crystals synthesized by the CVT method is investigated through ARPES measurement combined with first-principles DFT calculations. We have found the weak metallic-like transition in ZrSe$_2$ with Hf substitution. ARPES measurements and DFT calculations revealed the typical semiconducting behavior of ZrSe$_2$, while Zr$_{0.88}$Hf$_{0.12}$Se$_2$ shows metallic character due to excess electrons. Interestingly, it has been observed that substituting a significant amount of Hf on the Zr site leads to creating extra Zr atoms, which can enter into the hole and electron pockets that can shift the conduction and valence band to the lower binding energy. Furthermore, the reduced bond length shows the lattice change with Hf doping. Moreover, from the ARPES results, we have observed that the overall system remains preserved, except that the conduction band's tail crossed the Fermi level due to extrinsic electrons. Similarly, the transport measurements further confirm the metallic character of Zr$_{0.88}$Hf$_{0.12}$Se$_2$ due to excess charge carriers. These results highlight the importance of cation substitution-induced transition in 2D layered materials, which can enable these materials for future quantum electronics and valleytronic applications.

**Acknowledgements**

This research was supported by the by Princess Nourah bint Abdulrahman University Researchers Supporting Project number (PNURSP2024R1), Princess Nourah bint Abdulrahman University, Riyadh, Saudi Arabia, National Natural Science Foundation of China (Grants No. 62150410438), the Beihang Hefei Innovation Research Institute (project no. BHKX-19-02) and Deanship of Scientific Research at King Khalid University, Saudi Arabia, under grant number RGP. 2/445/44. We thank the Beijing Synchrotron Radiation Facility (1W1B, BSRF) for the XAFS experiments. We acknowledged beamline 13U of the National Synchrotron Radiation Laboratory (NSRL) for the ARPES experiments.
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