OBSERVATION OF SPIN POLARIZATION IN TRANSITION METAL DICHALCOGENIDE

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Monolayer transition-metal dichalcogenides (TMDC) have been attracting great attention as the candidate material for next-generation electronic devices utilizing spin and/or valley degrees of freedom [1-5]. As shown in Fig. 1(a), for example, the monolayer-MoS_2 is formed by the 2-dimensional network of Mo sitting in the center of S triangular prisms, thus possessing the 3-fold symmetry without an inversion center. Because of this peculiar trigonal structure, in contrast to the simple honeycomb graphene, the spontaneous spin and valley coupled band structure (*i.e.* spin/valley polarization) is realized at the Brillouin zone corners. Indeed, the control and detection of the valley polarization are demonstrated by using the photoluminescence circular dichroism in monolayer-MoS_2 [1-4]. Monolayer-MoS_2 hitherto has been mostly obtained by mechanically exfoliating the 2H-polytype bulk crystal, which itself lacks the spin/valley polarization due to its centrosymmetric structure recovered by the hexagonal stacking. The exfoliated monolayer-MoS_2 thus obtained has the limited size of area ($< 1\ \mu m^2$), thus preventing the direct investigations on its spin and electronic structure. Here we focus on another stable phase of polytype, 3R-MoS_2 (space group *R3m*) [6-8], which is composed of the so-called *abc* stacking where the 3-fold symmetry of monolayer-MoS_2 remains in bulk, as shown in Fig. 1(b). In 3R-MoS_2, the spin/valley coupling similar to monolayer-MoS_2 should reside in bulk, appearing as the opposite spin-polarizations at $\overline{K}$- and $\overline{K'}$-points [Fig. 1(c)].

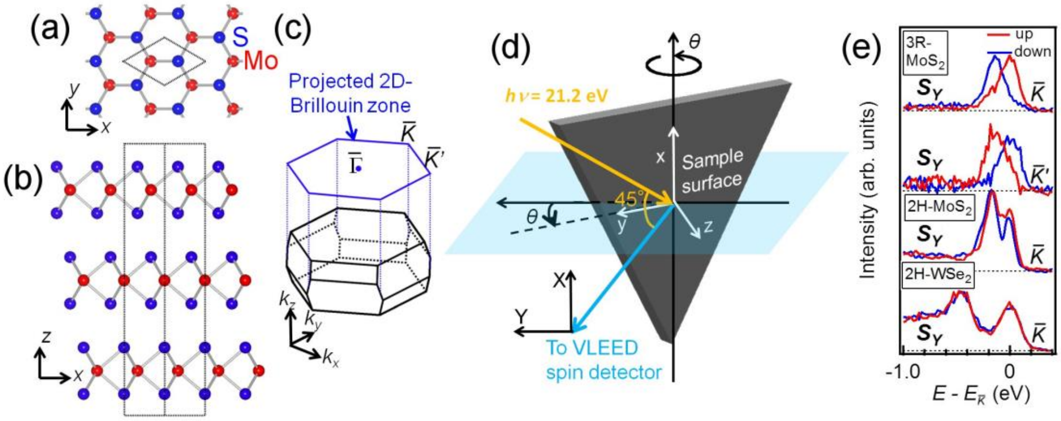

FIGURE 1. (a) Top view of MoS_2 monolayer. (b) Side view of 3R-MoS_2. (c) The first Brillouin zone of 3R-MoS_2. The blue hexagonal plane with $\overline{\Gamma}$, $\overline{K}$, and $\overline{K'}$ represents the corresponding two-dimensional projected Brillouin zone. (d) Schematic of the SARPES experimental geometry at BL19A in photon factory, KEK[9]. (e) SARPES energy distribution curves at the $\overline{K}$ ($\overline{K'}$) point, with detection of the spin component along *Y*-direction [as shown in (d)], for 3R-MoS_2, 2H-MoS_2, and 2H-WSe_2.

Spin-resolved angle-resolved photoemission spectroscopy (SARPES) with HeIα light source ($h\nu = 21.2$ eV) was performed by using the VLEED (Very Low Energy Electron Diffraction) spin detector at BL19A in photon factory, KEK [9]. The angular resolution was set to ±1° and the total energy resolution was set to 100 meV. Samples (~ 1 mm × 1 mm) were cleaved in situ near room-temperature and measured at 110 K. Measurement geometry is shown in Fig. 1(d). The VLEED detector can measure the spin polarization along *X* and *Y* directions. Note that the sample orientation (*x*, *y*, *z*) is rotated around *X*-axis to measure the $\overline{K}$-point.

Figure 1(e) shows the SARPES spectra detecting *Y*-oriented spin ($I_Y^{\uparrow,\downarrow}$) of 3R-$MoS_2$, 2H-$MoS_2$ and 2H-WSe_2, measured at $\bar{K}$- and $\bar{K}'$-points. $I_Y^{\uparrow,\downarrow}$ includes the information on spin polarization along *z* and *y*, due to the sample orientation. $I_Y^{\uparrow,\downarrow}$ data for 3R-MoS_2 at $\bar{K}$-point clearly indicate the huge spin polarization, *i.e.* spin up (down) dominant for the upper (lower) band, which gets inverted at $\bar{K}'$-point. By comparing with the *ab*-initio calculation, the opposite spin-polarizations at $\bar{K}$- and $\bar{K}'$- points observed in 3R-MoS_2 offer the evidence of the spontaneous out-of-plane spin polarization which consequently accompanies the $\bar{K}$- and $\bar{K}'$-valley polarization, as similarly expected in monolayer-MoS_2 [1-5]. 2H-MoS_2 and 2H-WSe_2, on the other hand, show the nearly equivalent intensities of $I_Y^{\uparrow}$ and $I_Y^{\downarrow}$, indicating that the spin polarization is absent or very weak. It should be reflecting the centrosymmetric crystal structure of 2H-polytype, which at the same time suggests the spin-splitting observed in 3R-MoS_2 is indeed from bulk, not arising from the inversion breaking at the surface.

To summarize, we investigated the spin- and electronic structure at the Brillouin zone corner for noncentrosymmetric 3R-MoS_2 and centrosymmetric 2H-MoS_2 and 2H-WSe_2 by using spin-resolved ARPES. The observed spin polarization in 3R-MoS_2 is identical to that expected in monolayer-MoS_2 and other TMDC families. The noncentrosymmetric 3R phase should be useful for future device fabrications, that will drive the valley/spin-tronics based on 2 dimensional crystals

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