Intrinsic Circular Polarization in Centrosymmetric Stacks of Transition-Metal Dichalcogenide Compounds

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The circular polarization (CP) that the photoluminescence inherits from the excitation source in n monolayers of transition-metal dichalcogenides $(MX_2)_n$ has been previously explained as a special feature of odd values of n

polarization" can lead to CP for $n =$ even values of $(MX_2)_n$. This is illustrated in Fig. 1, showing our first-principles calculated ρ for the emission from the direct band states at the K and $-K$ valley as a function of the number of monolayers n in $(MX_2)_n$, reaching asymptotically the bulk value for a large n. We see that the CP decreases monotonically with increasing n and the results of a fixed material lie on one curve without odd-even oscillations, in contrast to the expectation based on valley symmetries [10,15,16]. By recognizing that the spin-orbit physics can induce CP and that this effect is no longer limited to low-symmetry noncentrosymmetric structures, our finding could broaden the range of materials to be considered as spintronic CP sources.

Local spin polarization in each monolayer within bilayer MX_2.—This intrinsic CP in centrosymmetric systems originating from hidden spin polarization can be illustrated for bilayer $n = 2$ in $(MX_2)_n$, where two inversion-asymmetric individual MX_2 layers α and β ("sectors" in general) carry opposite local spin polarization. In bilayer MX_2, a monolayer MX_2 named β is introduced to form an inversion partner of layer α. The corresponding energy bands must be spin degenerate due to the combination of inversion symmetry and time-reversal symmetry. However, such global k-space compensation of spins does not occur in a point-by-point fashion in real space, i.e., on each MX_2 layer. Using density functional theory calculation implemented by VASP [19] with a projected augmented wave pseudopotential [20], we can project the twofold degenerate wave functions with plane wave expansion on the spin and orbital basis (spherical harmonics) of each atomic site. For the K valley of the top valence band (V1),

$$\psi_V^{(n=2)}(K;\uparrow) = \sum_{l;m;i} C_{l;m;i;\uparrow} |l;m;i\rangle \otimes |\uparrow\rangle;$$

$$\psi_V^{(n=2)}(K;\downarrow) = \sum$$

electrons. To interpret this effect and its impact on CP, we reconsider the valence band eigenstates of the bilayer system in Eq. (2) expanded in terms of single monolayer eigenstates, $\psi_{\mathrm{v}}^{(\mathrm{n}=1)}(\mathsf{K}) = \chi_{+}$ and $\psi\text{⊣})$

mix LH and RH components and thus affect ρ are also considered. We assume the relaxation time with spin flip much slower, and the relaxation time with spin conserving much faster, than the electron-hole recombination time, with the details listed in Supplemental Material [21].

As indicated by red and blue curled arrows [step (3)], the radiative recombination fills the holes with χ_+ and χ_-

intrinsic CP in centrosymmetric bulk MX_2 to be realized by upcoming measurements.

Dependence of ρ on the interlayer distance and material design for larger CP.—The dependence of ρ on the interlayer distance for different bilayer MX_2 compounds is shown in Fig. S2 [21]. The curves clearly exhibit that the intrinsic CP is enhanced as the interlayer separation increases, which could be achieved by tensile strain along the stacking direction or within the two-dimensional plane [31]. At the equilibrium separation, our calculated CP is 69% for MoS_2, 81% for $MoSe_2$, 90% for WSe_2, and 93% for WS_2 [32]. Furthermore, when the interlayer distance of the MX_2 bilayer exceeds 4 Å, the coupling between the α and β layer becomes negligible, implying perfect local spin polarization. As a result, the CP approaches the monolayer limit $\rho = 1$ when the interlayer distance is large enough.

Using the understanding of hidden spin polarization, we design a heterostructure with larger CP by intercalating bilayer BN as an inert medium into bilayer $MoSe_2$ (see Supplemental Material [21]). Such sandwiched structures, having both optimized polarization anisotropy ρ