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   ("sectors" in general) carry opposite local spin polarization. In bilayer MX_2, a monolayer MX_2 named   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, $\psi_v^{(n=1)}(K) = \chi_+$ and $\psi_\mp)$

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 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 $\rho \approx 1$ and large photoluminescence intensity due to their direct band gap, could be good platforms to realize intrinsic CP in a centrosymmetric system by the current synthesis technology [33,34].

In summary, by using first-principles calculations, we demystify the occurrence of intrinsic CP, accessed by direct interband transition at the K and $-K$ valley, in centrosymmetric layer stacks made of individually noncentrosymmetric layers, such as $n = even(MX_2)_n$. The intrinsic CP decreases monotonically with increasing n, in sharp contrast with the conventional expectation of odd-even oscillations based on valley symmetries. Such polarization anisotropy results from hidden spin polarization that is localized on each MX_2 layer. Our finding is expected to broaden the material selection that is currently limited to noncentrosymmetric systems for achieving CP and related phenomena and provide new possibilities for the manipulation of spin in the field of spintronics and optoelectronics.

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