Interfacial crystal Hall effect reversible by ferroelectric polarization

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Recently, a crystal Hall effect (CHE) has been predicted to occur in collinear bulk antiferromagnets with a non-centrosymmetric non-magnetic sublattice. The CHE may be interesting for application in spintronics due to its reversal with switching the non-magnetic sublattice, provided that suitable means for realizing this property are found. Here, we predict that the CHE is not only limited to bulk antiferromagnets but may also occur in heterostructures composed of compensated antiferromagnetic metals and non-magnetic insulators due to reduced symmetry at the interface. We further show that such an interfacial CHE (ICHE) can be made reversible in engineered heterostructures where an antiferromagnetic layer is sandwiched between two identical ferroelectric layers. We explicitly demonstrate these phenomena using density functional theory calculations for three material systems: a MnBi₂Te₅/GaI₂ van der Waals heterostructure, an In₂Te₅/MnBi₂Te₅/In₂Te₅ topological van der Waals heterostructure, and a GeTe/Ru₂MnGe/GeTe layered heterostructure composed of three-dimensional materials. We show that all three systems reveal a sizable ICHE, while the latter two exhibit a quantum ICHE and CHE, respectively, reversible with ferroelectric polarization. Our predictions open a new perspective for the emergence of the CHE and its use in spintronics.

Since its discovery in 1881 [1], the anomalous Hall effect (AHE) [2,3] has been attracting continued interest. In recent years, this interest has raised due to the demonstration of the AHE in unconventional materials and its relevance to the topological properties and spintronics [4]. There are two mechanisms of the AHE: intrinsic and extrinsic. Both originate from broken time-reversal symmetry and spin-orbit coupling (SOC), but the former is driven purely by the electronic band structure which gives rise to the spin-dependent transverse (anomalous) velocity [5] and the associated Berry curvature [6], whereas the latter is due to spin-dependent impurity scattering, such as the skew scattering [7] or the side jump scattering [8]. There is an increasing evidence that in many real systems, especially those with not too strong disorder, the intrinsic contribution to the AHE provides the dominant contribution [3].

The intrinsic AHE is driven by the Berry curvature Ω, an inherent property of a material arising from its spin-dependent band structure [9,10]. The anomalous Hall conductivity (AHC) is determined by the integral of Ω over the whole Brillouin zone, and thus it is non-zero for systems with no symmetry operation 湔, with respect to which the Berry curvature is antisymmetric, i.e. 湔Ω(k) = −Ω(k′) for Ṇk = k′. This property implies that the AHC vanishes for non-magnetic systems, preserving time-reversal symmetry  Tits due to the Berry curvature being odd with respect to this symmetry operation, i.e. TitsΩ(k) = −Ω(−k).

Usually, the AHE is found in ferromagnetic metals, where a transverse voltage generated by a longitudinal charge current is proportional to the net magnetization. The AHE is expected to vanish in fully-compensated antiferromagnetic (AFM) metals. This is due to the existence of a symmetry operation 湔 which connects different AFM sublattices, and leads to the antisymmetric Berry curvature, i.e. ṆΩ(k) = −Ω(k′). This condition holds, however, not for all types of antiferromagnets. For example, in non-collinear antiferromagnets, such as Mn₃X alloys (X = Ga, Ge, Ir) [11-15] and ANMₓ antiperovskites (A = Ga, Zn, Ag, Ni) [16-18], the non-collinear alignment of Mn magnetic moments breaks the symmetry between different AFM sublattices. The broken AFM sublattice symmetry eliminates the antisymmetry of the Berry curvature and leads to a sizable AHC in these compounds. Recently, it has been found that the AHE can also emerge in collinear antiferromagnets, such as RuO₂ [19,20], NiFe [21], CoNb₅S₁₆ [22], and monolayer SrRuO₃ [23], where the AFM sublattice symmetry is broken due to the presence of non-magnetic atoms at non-centrosymmetric positions of the crystal, which makes the AHC non-vanishing. This phenomenon was coined the crystal Hall effect (CHE) [19].

An interesting consequence of the CHE is that the switching of the positions of non-magnetic atoms is equivalent to the application of the symmetry operation that changes sign of the Berry curvature, and hence reverses the AHC. The reversal of the AHC does not require magnetic moment switching typical for the conventional AHE. Such a functional property could be useful for applications in low-power spintronics, eliminating the need for large energy-dissipating electric currents to switch the AFM order parameter [24].

Unfortunately, there are no means to exploit this property in bulk materials, due to no external stimulus which could possibly switch the non-magnetic sublattice in a metal alone. This property however can be obtained in a heterostructured material where the magnetic group symmetry is affected across
the interface due to the proximity effect. This brings a new perspective to realize a reversible CHE.

In this letter, we demonstrate that the CHE may occur not only in bulk materials but also in heterostructures composed of compensated AFM metals and non-magnetic insulators due to reduced symmetry at the interface. Different from the bulk CHE, such an interfacial CHE (ICHE) does not require the non-symmetric atomic positions in the bulk antiferromagnet. The interfacial proximity effect alone breaks the antisymmetry of the Berry curvature and produces an interfacial crystal Hall conductance (ICHC). We further show that using ferroelectric materials for non-magnetic insulators in the heterostructure allows the realization of the reversible ICHE, where the ICHC changes sign with ferroelectric polarization switching. We explicitly demonstrate these phenomena using first-principles density functional theory (DFT) calculations [25] for three material systems: a MnBi$_2$Te$_4$/GeI$_2$ van der Waals heterostructure, where we show the emergence of a sizable ICHC; an In$_2$Te$_3$/MnBi$_2$Te$_4$/In$_2$Te$_3$ topological van der Waals heterostructure, where we predict a quantized ICHC reversible by ferroelectric polarization; and a GeTe/Ru$_2$MnGe/GeTe layered heterostructure composed of three-dimensional (3D) materials, where we predict a reversible ICHC.

All compensated antiferromagnets are expected to exhibit an ICHC in appropriate heterostructures. As a representative example, we focus on A-type antiferromagnets with an out-of-plane AFM order parameter, where the two sublattices are connected by $\tilde{P}\tilde{T}$ symmetry (Fig. 1(a)). This type of the AFM order has been found in many compounds, such as 3D metals Ru$_2$MnGe [26,27], MnPd$_2$ [28,29], and CaCo$_2$As$_2$ [30], and two-dimensional (2D) van der Waals semiconductors MnBi$_2$Te$_4$ [31] and CrI$_3$ [32]. In these materials, the Berry curvature is zero everywhere in the Brillouin zone enforced by $\tilde{P}\tilde{T}\Omega(k) = -\Omega(k)$, and hence the CHE is prohibited. However, in a heterostructure composed of such an antiferromagnet and a non-magnet (Fig. 1(b)), the $\tilde{P}\tilde{T}$ symmetry is broken at the interface, resulting in a non-zero $\Omega(k)$ and a non-vanishing ICHC (Fig. 1(c)).

By inserting a slab of such an antiferromagnet between two identical ferroelectric layers with out-of-plane polarizations (Fig. 1(d)), we design a heterostructure for a reversible ICHC. The polarization of the top and bottom layers ($P_1$ and $P_2$) can be controlled by the top and bottom gates separately in a device schematically shown in Figure 1(e). These polarizations control the magnetic group symmetry of the heterostructure that determines the ICHC. When $P_1$ and $P_2$ are parallel, the $\tilde{P}\tilde{T}$ symmetry is broken and hence $\Omega(k)$ is non-zero resulting in the ICHC. Switching $P_1$ and $P_2$ simultaneously is equivalent to applying the $\tilde{P}\tilde{T}$ symmetry operation to the heterostructure, which changes sign of $\Omega(k)$ and reverses the ICHC. When $P_1$ and $P_2$ are antiparallel, the $\tilde{P}\tilde{T}$ symmetry is preserved, leading to zero Hall voltage. Therefore, the three non-volatile ICHC states coupled to ferroelectric polarization are realized in the spintronic device based on this heterostructure.

To demonstrate these properties, we first consider a 2D van der Waals heterostructure composed of four-monolayer AFM MnBi$_2$Te$_4$ deposited on non-magnetic monolayer GeI$_2$ (Fig. 2(a)). Bulk MnBi$_2$Te$_4$ is an A-type AFM topological insulator with out-of-plane magnetic moments. It preserves the $\tilde{P}\tilde{T}$ symmetry and has the Néel temperature ($T_N$) of 25 K [31]. Bulk GeI$_2$ is a centrosymmetric wide gap semiconductor (band gap is ~2.5 eV) [33,34] with the cleavage energy lower than that in graphite [35].

Both freestanding MnBi$_2$Te$_4$ and GeI$_2$ have the symmetry operations preventing linear or nonlinear AHE [36,37]. However, these symmetries are broken in the MnBi$_2$Te$_4$/GeI$_2$ heterostructure. Figure 2(b) shows the calculated band structure of MnBi$_2$Te$_4$/GeI$_2$, where the bands near the Fermi energy ($E_F$) originate from MnBi$_2$Te$_4$. The Kramers degeneracy enforced by $\tilde{P}\tilde{T}$ symmetry is lifted in this heterostructure, as seen from the
small but non-negligible band splitting in Figure 2(b). We note that the change in the crystal structure of MnBi2Te4 is vanishingly small and Mn magnetic moments are the same as these in a freestanding MnBi2Te4 layer, indicating that the reduced symmetry is purely due to the interfacial proximity effect. This small band splitting is sufficient to produce a sizable Berry curvature given by  

\[ \Omega_{nk} = -2\text{Im} \sum_{m \neq n} \frac{n}{E_{nk} - E_{mk}} \left( \frac{\partial^2 \tilde{H}}{\partial k_x \partial k_y} \right) \Omega_{nk}, \]  

and \( E_{nk} \) is the energy of the \( n \)-th band at momentum \( k \). Figure 2(c) shows the calculated \( k \)-dependent Berry curvature \( \Omega(k) \) at energy \( E_1 \) located 64 meV below the top of the valance band (Fig. 2(b)). The sizable \( \Omega(k) \) seen near the Brillouin zone center is not antisymmetric. This provides a non-vanishing ICHC \( \sigma_{xy} \) given by [3]

\[ \sigma_{xy} = -\frac{e^2}{h} \int_{BZ} \frac{d^2k}{2\pi} \Omega(k). \]  

Figure 2(d) shows that \( \sigma_{xy} \) is zero at \( E_F \), indicating a trivial insulating state of this heterostructure. In experiment, however, the \( E_F \) of a few-layer MnBi2Te4 is usually located slightly below the valence band maximum [38]. As seen from Figure 2(d), \( \sigma_{xy} \) is non-zero for \( E_F \) shifted to the valence band. This is in contrast to a freestanding MnBi2Te4, where \( \sigma_{xy} \) is zero for all energies due to \( \tilde{\rho} \tilde{T} \) symmetry (Figs. 2(d) and S1(e)). Thus, the presence of GeI2 breaks the \( \tilde{\rho} \tilde{T} \) symmetry and produces an ICHC.

Experimentally non-zero \( \sigma_{xy} \) has been observed in four- and six-layer MnBi2Te4 on substrates [38,39], which may serve as the evidence of the ICHC. The ICHC can be enhanced up to \(-0.5 \) eV/\( h \) at \( E_F \) (Fig 2(d)) by adjusting the \( E_F \) of MnBi2Te4 with a gate voltage similar to that done in Ref. [38].

An ICHC heterostructure can be engineered to make the ICHC quantized. A quantum AHE has been predicted at zero magnetic field in MnBi2Te4 with AFM layer ordering [40-44], but the experimental realizations are missing. Here, we show the emergence of a quantum ICHC in a designed heterostructure, where MnBi2Te4 is sandwiched between two identical ferroelectric layers. For the ferroelectric component, we choose In2Te3 due to its lattice matching to MnBi2Te4 [25]. In2Te3 belongs to the group of 2D materials In2X3 (\( X = S, Se, Te \)), where ferroelectricity with out-of-plane polarization has been predicted [45] and in the case of In2Se3, experimentally confirmed [46,47].

Specific calculations are performed for a GeI2/In2Te3/MnBi2Te4/In2Te3/GeI2 heterostructure (Figs. 3(a) and S1(d)), where a GeI2 capping layer is used to eliminate a band overlap in a In2Te3/MnBi2Te4/In2Te3 trilayer separated by vacuum [25]. This is reminiscent to experiments where capping layers are used to prevent open surfaces in van der Waals heterostructures. For parallel polarization of the top and bottom In2Te3 layers (\( P_t \) and \( P_b \)), we find that polarization charges generate a built-in electric field resulting in a large band splitting and band bending, reducing the band gap (Figs. 3(b) and S1(h)). In the heterostructure with four-layer MnBi2Te4, a small band gap of \(-9 \) meV is obtained. A huge Berry curvature is calculated within this gap at the \( \Gamma \) point (Fig. 3(c)). Simultaneous switching of \( P_t \) and \( P_b \) changes sign of the Berry curvature, due to this switching being equivalent to applying the \( \tilde{\rho} \tilde{T} \) symmetry operation to the heterostructure. The calculated Chern numbers are \( \pm 1 \) depending on the polarization direction of the In2Te3 layers, indicating the topological state of this heterostructure. A quantized ICHC reversible with ferroelectric polarization is found within the topological band gap, as shown in Figures 3(d) and S1(i).

Finally, we explore a GeTe/Ru2MnGe/GeTe system (Fig. 4(a)), where Ru2MnGe is a 3D Heusler alloy with \( T_C = 316 \) K and out-of-plane A-type AFM order within the (111) planes [25-27]. GeTe is a ferroelectric semiconductor with the Curie temperature (\( T_C \)) of about 700 K and spontaneous polarization arising from the polar displacement of Ge atoms with respect to Te atoms [48]. This heterostructure is composed of six-layer Ru2MnGe and six-layer GeTe slabs and has symmetric Ru-Te interfacial terminations at the top and bottom interfaces.

The strong bonding across the interfaces in this heterostructure produces atomic displacements in the AFM layer, which enhances the symmetry breaking when the out-of-plane polarization of the top and bottom GeTe layers (\( P_t \) and
$P_2$ are parallel. This leads to small changes of the interfacial Mn moments (Fig. S5(c)) and net magnetization of about 0.026 $\mu_B$ per Mn layer. Figure 4(b) shows the band structure of GeTe/Ru$_2$/MnGe/GeTe for parallel $P_1$ and $P_2$. There are several bands crossing the Fermi energy, which are majorly contributed by the Ru-5d electrons. Notable is the band splitting enforced by the broken $\hat{P}^T$ symmetry, which supports a non-vanishing Berry curvature (Fig. S5(f)) and sizable ICHC reversible by ferroelectric polarization (Fig. 4(c)). For $P_1 = P_2 > 0$, $\sigma_{xy} = -1.4 \ e^2/h$, which is comparable to AHC of 2D ferromagnetic metal Fe$_2$GeTe$_2$ [49, 50]. The ICHC can be enhanced down to $\sigma_{xy} = -5.5 \ e^2/h$ by proper electron doping. When $P_1$ and $P_2$ are reversed the ICHC changes sign. For $P_1$ and $P_2$ having opposite directions, the $\hat{P}^T$ symmetry enforces Kramers degeneracy (Fig. S3(e)) and vanishing ICHC (Fig. 4(c)). We note that different interfacial configurations do not affect our conclusions about the reversible ICHE, as long as the symmetry of the designed heterostructure is guaranteed [25].

The predicted ICHE is expected to occur in other types of heterostructures. As discussed in Supplemental Material [25], in the heterostructure, the ferroelectric layers can have in-plane polarization and the AFM layer can have various types of magnetic ordering. As long as the designed heterostructure does not have the symmetry operation to prevent the ICHE, and the ferroelectric switching in this heterostructure is equivalent to a symmetry operation which changes sign of the Berry curvature, the ferroelectric-reversible ICHE is supported.

In conclusion, we have predicted the emergence of the ICHE in heterostructures composed of compensated antiferromagnets and non-magnets. The effect occurs due to the broken symmetry between the two AFM sublattices resulting from the proximity effect. We have also proposed the ICHE reversible with ferroelectric polarization in designed AFM heterostructures with symmetric top and bottom ferroelectric layers. The predicted phenomena have been demonstrated for the specific material systems. For MnBi$_2$Te$_4$/GeI$_2$, we confirmed a sizable ICHE. For In$_2$Te$_3$/MnBi$_2$Te$_4$/In$_2$Te$_3$, and GeTe/Ru$_2$/MnGe/GeTe, we predicted a quantized ICHE for the former and a sizable ICHE for the latter, both reversible by ferroelectric polarization. The emergence of the ICHE in compensated antiferromagnets broadens the material choice for CHE-based spintronic devices. We hope that our theoretical predictions will motivate experimentalists to explore the predicted ICHE in suitable heterostructures.

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**FIG. 3:** (a) A schematic of the GeI$_2$/In$_2$Te$_3$/MnBi$_2$Te$_4$/In$_2$Te$_3$/GeI$_2$ van der Waals topological heterostructure for reversible quantized ICHE. (b) The band structure of this heterostructure with four-monolayer MnBi$_2$Te$_4$ for polarizations of top and bottom In$_2$Te$_3$ monolayers are parallel. (c) The Berry curvature of this heterostructure along the high symmetric directions at energy $E_F$ denoted in (b). (d) The ICHC as a function of energy for different polarization states.

**FIG. 4:** (a) GeTe/Ru$_2$/MnGe/GeTe heterostructure with parallel out-of-plane polarizations of the top and bottom GeTe layers ($P_1$ and $P_2$), for $P_1 = P_2 > 0$ (left) and $P_1 = P_2 < 0$ (right). (b) The band structure of this heterostructure. (c) The ICHC as a function of energy for different polarization states.
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