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Anomalous Hall effect in non-collinear antiferromagnetic antiperovskite $\text{Mn}_3\text{Ni}_{1-x}\text{Cu}_x\text{N}$

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We report the anomalous Hall effect (AHE) in antiperovskite Mn_3NiN with substantial doping of Cu on the Ni site (i.e. $\text{Mn}_3\text{Ni}_{1-x}\text{Cu}_x\text{N}$), which stabilizes a noncollinear antiferromagnetic (AFM) order compatible with the AHE. Observed on both sintered polycrystalline pieces and single crystalline films, the AHE does not scale with the net magnetization, contrary to the conventional ferromagnetic case. The existence of the AHE is explained through symmetry analysis based on the Γ_{4g} AFM order in Cu doped Mn_3NiN . DFT calculations of the intrinsic contribution to the AHE reveal the non-vanishing Berry curvature in momentum space due to the noncollinear magnetic order. Combined with other attractive properties, antiperovskite Mn_3AN system offers great potential in AFM spintronics.

Empirically, the anomalous Hall effect (AHE) in conventional ferromagnetic metals is proportional to the net magnetization [1] and was expected to vanish in antiferromagnets. However, it is now well understood that the existence of the AHE is constrained by symmetry and is not necessarily incompatible with AFM order. This principle has been exemplified by the large AHE predicted and realized in various noncollinear AFMs, such as hexagonal $\text{Mn}_3\text{Sn}/\text{Ge}$ and cubic $\text{Mn}_3\text{Ir}/\text{Pt}$, etc. where the Mn atoms form a kagome lattice along different crystalline planes [2–10]. In these materials, geometric frustration and local symmetries of the magnetic atoms together lead to a chiral noncollinear magnetic order with the essential symmetry breaking for finite AHE, which is also reflected by the small net moment in certain crystalline directions. The large AHE in the hexagonal $\text{Mn}_3\text{Sn}/\text{Ge}$ was argued to be due to Weyl points near the Fermi energy, which can be viewed as monopoles of Berry curvature in momentum space [2–10]. Technologically, the robust AHE at room temperature in these systems makes them attractive for potential applications in spintronics solely based on AFM [11]. Meanwhile, it is interesting to search for similar anomalous Hall antiferromagnets (AHE AFMs) beyond binary Mn compounds, which may have other superior properties.

Anti-perovskite manganese nitrides Mn_3AN , have received a lot of attention due to a number of unusual physical properties, such as giant negative thermal expansion [12, 13], temperature independent resistivity [14], and barocaloric effects [15, 16]. All of these phenomena are closely related to the first order phase transition from a high temperature paramagnetic cubic phase into a low temperature noncollinear AFM phase with the so-called Γ_{4g} and Γ_{5g} magnetic structures. It is interesting to notice that the Mn atoms form a 1/4-depleted fcc lattice in these manganese antiperovskites, similar to that in the AHE AFM Mn_3Ir and Mn_3Pt , whose (111) planes are kagome lattices as shown in Fig. 1(a) and (b) [17, 18].

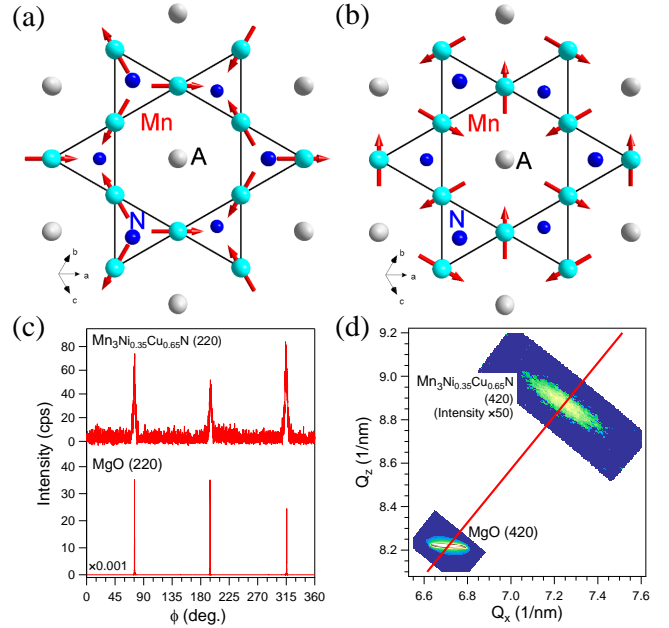


FIG. 1. (Color online) **Magnetic and crystal structures of $\text{Mn}_3\text{Ni}_{1-x}\text{Cu}_x\text{N}$.** (a)-(b) The Mn kagome lattice with noncollinear AFM structures termed Γ_{4g} and Γ_{5g} in Mn_3AN , respectively. (c) In-plane X-ray diffraction data of $\text{Mn}_3\text{Ni}_{0.35}\text{Cu}_{0.65}\text{N}$ 100 nm film grown on MgO (111) substrate, with three fold symmetry of (220) peak, (d) Reciprocal space map around (420) reflection, with the solid line as the relaxation line.

Therefore one would expect there to be AHE if the AFM order of the Mn moments is similar to these binary compounds.

In this article, we demonstrate that the AHE could indeed be realized in manganese nitrides, by studying the Mn_3NiN system [13, 14, 18, 19]. We first found that in stoichiometric Mn_3NiN , a weak signal of AHE is observed below the noncollinear AFM ordering temperature of 180K, yet disappeared as the temperature

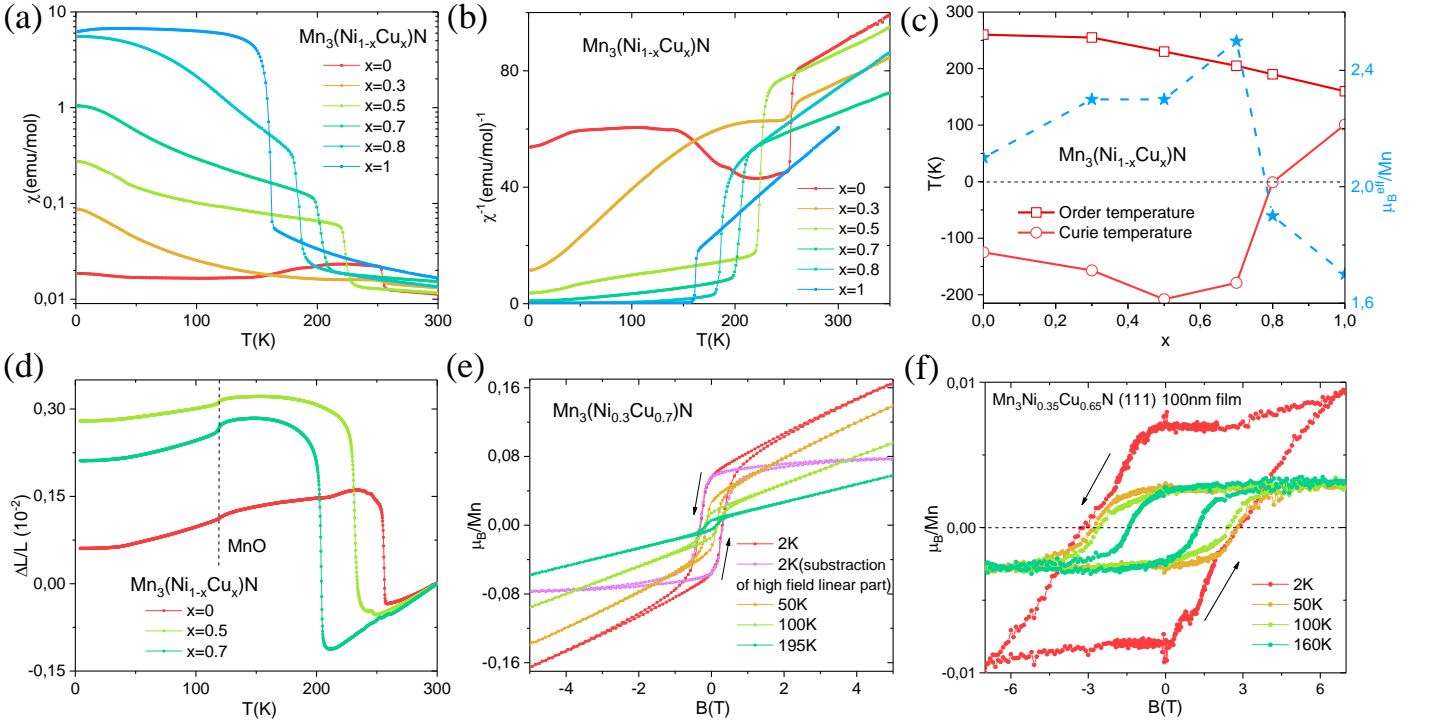


FIG. 2. (Color online) **Magnetic properties and thermal expansion of $\text{Mn}_3\text{Ni}_{1-x}\text{Cu}_x\text{N}$.** (a)-(b) DC magnetic susceptibility and inverse susceptibility measured in $H=500$ Oe in $\text{Mn}_3\text{Ni}_{1-x}\text{Cu}_x\text{N}$ with several different Cu doping levels x from 2K to 350K under field cooling. (c) Phase diagram of $\text{Mn}_3\text{Ni}_{1-x}\text{Cu}_x\text{N}$ ($0 < x < 1$), including the experimental AFM transition temperature, the Curie-Weiss temperature, and the effective moment vs. Cu doping level. The latter two are obtained from Curie-Weiss fitting of the high-temperature susceptibilities. (d) Temperature-dependent relative length change $[\Delta L/L = [L(T) - L(300\text{K})]/L(300\text{K})]$ for $\text{Mn}_3\text{Ni}_{1-x}\text{Cu}_x\text{N}$ for $x = 0, 0.5$, and 0.7 , obtained upon increasing temperature. (e) Isothermal magnetization $M(H)$ for $\text{Mn}_3\text{Ni}_{0.3}\text{Cu}_{0.7}\text{N}$ at various temperatures, with saturation moment at 2K also shown (see text). (f) Out of plane $M(H)$ for $\text{Mn}_3\text{Ni}_{0.35}\text{Cu}_{0.65}\text{N}$ 100nm film on MgO (111) substrate at various temperatures.

further decreases. Using magnetometry and thermal expansion measurements, we then show that through substantial doping of Cu substituting Ni, the noncollinear AFM order is still preserved in $\text{Mn}_3\text{Ni}_{1-x}\text{Cu}_x\text{N}$ polycrystals. Most interestingly, the AHE is enhanced and becomes more robust against temperature after Cu doping. The AHE also does not scale with the net magnetization, contrary to the ferrimagnetic Mn_3CuN system [20, 21]. We have also successfully grown single-crystalline $\text{Mn}_3\text{Ni}_{1-x}\text{Cu}_x\text{N}$ films, which exhibit large AHE as well. Finally, we analyze the symmetry origin of the AHE in the Γ_{4g} state of Mn_3NiN , complemented by first-principles density functional theory (DFT) calculations revealing the momentum space Berry curvature contributing to the AHE.

The successful homogeneous solution of $\text{Mn}_3\text{Ni}_{1-x}\text{Cu}_x\text{N}$ powders have been verified by X-ray diffraction in Fig. S1 [22], consistent with previous results [13, 14, 19]. Fig. 1 (c) shows in-plane X-ray diffraction pattern of $\text{Mn}_3\text{Ni}_{0.35}\text{Cu}_{0.65}\text{N}$ film. The out-of-plane X-ray diffraction pattern is shown in Fig. S2 [22, 23]. On the MgO (111) substrate, (111)-orientated films are epitaxially grown with three-fold in plane symmetry. Fig. 1 (d) displays the reciprocal

space map of $\text{Mn}_3\text{Ni}_{0.35}\text{Cu}_{0.65}\text{N}$ film on MgO (111) substrate. The (420) peak is observed on the relaxation line, indicating no stain condition of our high quality film.

Figure 2 (a) shows the temperature dependence of magnetic susceptibilities in field-cooling (FC) procedures under 500 Oe for $\text{Mn}_3\text{Ni}_{1-x}\text{Cu}_x\text{N}$ specimens with $x = 0, 0.3, 0.5, 0.7, 0.8$, and 1 , respectively. The pure Mn_3NiN shows the AFM transition at 260K, consistent with previous results [13, 14, 19], with the magnetic moment only on Mn site, evidenced by neutron measurement on powders before [18]. The Cu doping continuously decreases the temperature of the AFM transition and increases the low temperature $\chi(T)$, until the system becomes ferrimagnetic which is similar to pure Mn_3CuN , with transition temperature $T_N = 260$ K, 255 K, 230 K, 205K, 190 K, and 160 K, respectively. Besides, the transition temperature is taken as onset point of the sharp transition for all the samples, except for $x = 0.3$ case, determined as the middle point of the board transition. Above T_N , the samples are paramagnetic, and the inverse susceptibility $\chi^{-1}(T)$ can be fitted to the Curie-Weiss formula [Fig. 2(b)]. Fig. 2(c) summarizes the phase diagram of $\text{Mn}_3\text{Ni}_{1-x}\text{Cu}_x\text{N}$ system, by plotting the T_N versus Cu

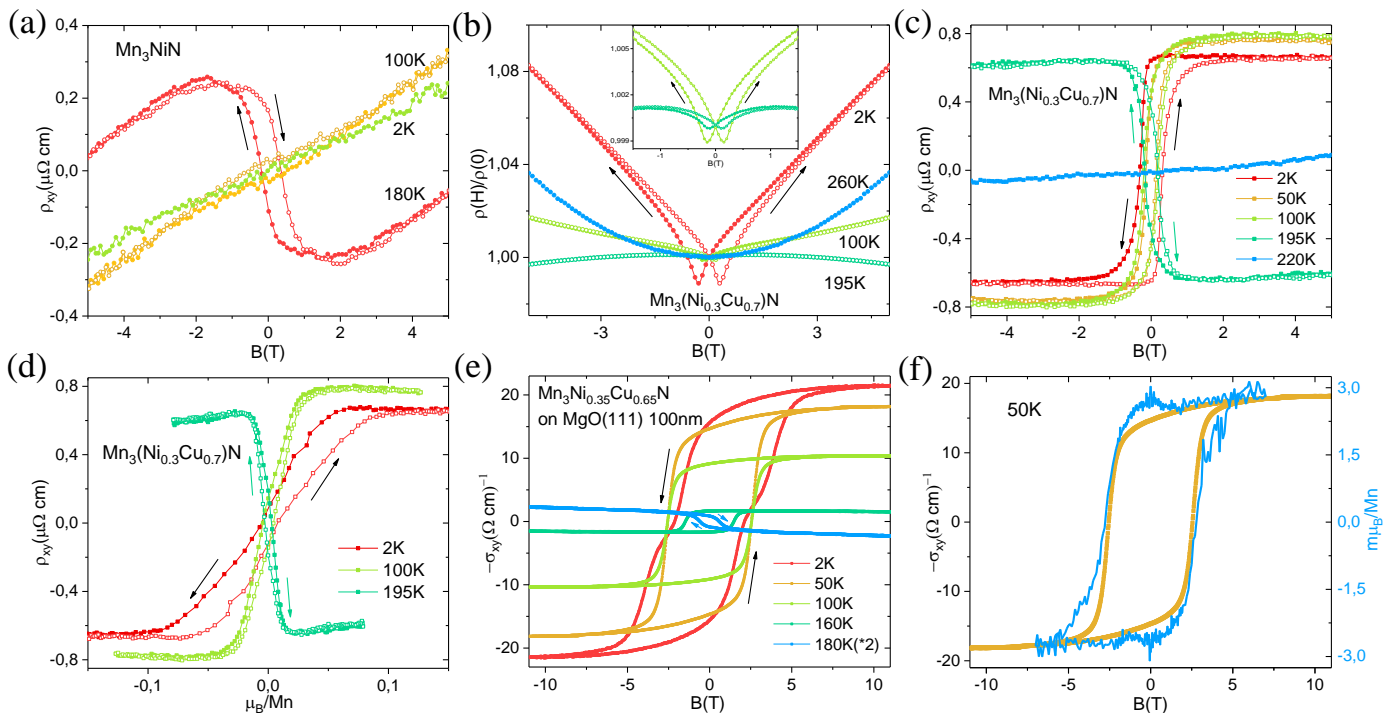


FIG. 3. (Color online) **Transport properties including the AHE in $\text{Mn}_3\text{Ni}_{1-x}\text{Cu}_x\text{N}$.** (a) Hall resistivity results from a sintered specimen of Mn_3NiN at 180K, 100K, and 2K, respectively. (b) Field dependence of the longitudinal resistivity $\rho(H)/\rho(0)$ of $\text{Mn}_3\text{Ni}_{0.3}\text{Cu}_{0.7}\text{N}$ at various temperatures, with the low field region at 195K and 100K enlarged in the inset. (c) Field dependence of the Hall resistivity ρ_{xy} of $\text{Mn}_3\text{Ni}_{0.3}\text{Cu}_{0.7}\text{N}$ at various temperatures, with the AHE clearly observed below 205K. (d) Dependence of ρ_{xy} on magnetization of $\text{Mn}_3\text{Ni}_{0.3}\text{Cu}_{0.7}\text{N}$ at 195K, 100K, and 2K, respectively. (e) The anomalous Hall conductivity (AHC) versus field measured in single crystalline $\text{Mn}_3\text{Ni}_{0.35}\text{Cu}_{0.65}\text{N}$ film on MgO (111) substrate at various temperatures (see text). (f) Comparison of the Hall conductivity and isothermal magnetization of (111) 100nm film at 50K.

doping level. Also shown in the plot are the Curie-Weiss temperature and the effective moment obtained from the Curie-Weiss fitting. Similar to the $x = 0$ case, the $x = 0.3, 0.5,$ and 0.7 samples exhibit negative Curie-Weiss temperature, suggesting AFM-type interaction, which becomes nearly zero for $x = 0.8,$ and about +100K for the ferrimagnetic Mn_3CuN [20]. When $x > 0.7,$ accompanying the change of magnetic ground state, the effective moment μ_{eff} sharply decreases.

As already verified by neutron diffraction experiments in various Mn_3AN systems [18, 24–26], the negative thermal expansion there is due to the volume expansion from the paramagnetic cubic phase to the noncollinear AFM phase, while there is no such effect from the paramagnetic-ferrimagnetic transition in Mn_3CuN . As shown in Fig. 2 (d), for $\text{Mn}_3\text{Ni}_{1-x}\text{Cu}_x\text{N}$ with $x = 0, 0.5,$ and $0.7,$ all three specimens exhibit large volume expansion through a sharp transition at T_N . Moreover, the Cu doped samples show even larger volume expansion than pure Mn_3NiN . The weak anomaly at 120K in the same plot is due to the AFM transition of MnO impurities [27], supported by the X-ray diffraction data in Fig. S1. The anomaly around 250K comes from the capacitive dilatometer based measurement system [28]. Together with the magnetic results, our thermal expansion

measurements provide clear evidence on the persistence of the noncollinear AFM order in $\text{Mn}_3\text{Ni}_{1-x}\text{Cu}_x\text{N}$ for $x < 0.7$.

As predicted and observed in Mn_3Sn and Mn_3Pt [2–4, 7, 10], a small remnant net magnetization is always accompanying the essential symmetry breaking that leads to AHE. Pure Mn_3NiN exhibits a small hysteresis in the isothermal magnetization $M(H)$ curve at 180K as shown in Fig. S3(a) [22]. However, the hysteresis is suppressed as temperature decreases, consistent with a spin glass type behavior observed at 2K. As shown in Fig. S3 (b) and (c) with $x = 0.3$ and $0.5,$ the coercive field is still large at 50K, similar to pure Mn_3NiN system at 100K [22]. Doping Cu in Mn_3NiN can gradually stabilize the small ferromagnetic (FM) component and presumably the magnetic structure that hosts AHE. This is best illustrated for the $\text{Mn}_3\text{Ni}_{0.3}\text{Cu}_{0.7}\text{N}$ specimen in Fig. 2(e). A small FM component appears below 205K, and keeps increasing as temperature decreases. After subtracting the H -linear component in the high field region, presumably due to MnO impurities, the saturation moment is about $0.006\mu_B/\text{Mn}$ at 195K, $0.05\mu_B/\text{Mn}$ at 50K, and $0.08\mu_B/\text{Mn}$ at 2K, much smaller than its effective moment, $2.5\mu_B/\text{Mn}$ from the Curie-Weiss fitting. The coercive field also increases with decreasing temperature

and reaches 0.3T at 2K.

Figure S5 shows the out of plane isothermal magnetization $M(H)$ curves of $\text{Mn}_3\text{Ni}_{0.35}\text{Cu}_{0.65}\text{N}$ (111) 100nm film after subtracting the large signal from MgO (111) substrate [22]. A rather weak remnant magnetization is clearly observed in Fig. 2(f), with the saturation moment $\sim 0.003\mu_B/\text{Mn}$ above 50K and $0.01\mu_B/\text{Mn}$ at 2K, due to symmetry-allowed spin canting in the noncollinear state. This weak moment has a similar size to that in Mn_3Sn and Mn_3Pt [4, 10], and checks with our DFT calculations below. Its direction is expected to be perpendicular to the kagome plane if the magnetic order is indeed Γ_{4g} . Presumably due to the crystalline order of the (111) films enhancing the magnetocrystalline anisotropy leading to a (111)-directed weak moment, we find the (111) orientated film shows much larger coercive field– 1.5T at 160K, 2.5T at 100K and 50K, than the polycrystalline $\text{Mn}_3\text{Ni}_{0.3}\text{Cu}_{0.7}\text{N}$ in Fig. 2(e).

Next we focus on the transport properties of $\text{Mn}_3\text{Ni}_{1-x}\text{Cu}_x\text{N}$ samples, in particular the AHE. Fig. 3 (a) shows weak signal of the AHE at 180K in pure Mn_3NiN , consistent with the small FM component shown in Fig. S3. This signal rapidly decreases with temperature, leaving only normal Hall signal at 2K, with the carrier density estimated to be $1.4 \times 10^{22}/\text{cm}^3$. Mn_3NiN (111) film exhibits similar behavior as shown in Fig. S5 [22].

Above 205K, the magnetoresistance (MR) of $\text{Mn}_3\text{Ni}_{0.3}\text{Cu}_{0.7}\text{N}$ specimen increases as H^2 as shown in Fig. 3(b), consistent with normal metal behavior. Below 205K, clear hysteresis appears with the same coercive field value as in the $M(H)$ curve. The clear positive MR at 2K and 100K is also similar to that in Mn_3Sn [8]. The slightly negative MR at 195K is likely due to strong magnetic fluctuations close to T_N .

Most interestingly, Fig. 3(c) displays large AHE in the AFM state of $\text{Mn}_3\text{Ni}_{0.3}\text{Cu}_{0.7}\text{N}$ specimen, with the same coercive field as in the $M(H)$ and MR curves. There is also sign change of the ordinary Hall resistance between 195K and 100K, suggesting a transition from hole-type carriers above 195K to electron-type carriers below 100K. To further determine the origin of such large AHE, we plot the Hall resistance ρ_{xy} versus the magnetization M in Fig. 3 (d). Similar to the arguments used for decomposing different contributions to the AHE in Mn_3Sn [4] and Mn_3Ge [5], the hysteresis with a sharp sign change in $\rho_{xy}(M)$ indicates the AFM-origin of the AHE. In contrast, ρ_{xy} of the sintered Mn_3CuN in Fig. S6 [22] is dominated by a contribution proportional to M .

Further, the high quality epitaxial $\text{Mn}_3\text{Ni}_{0.35}\text{Cu}_{0.65}\text{N}$ film on MgO (111) substrate enables us to extract the anomalous Hall conductivity (AHC) from the resistivity data, which can be more directly compared with theory. According to the longitudinal and Hall resistance data in Fig. S7 [22], the Hall conductivity σ_{xy} is estimated using $\sigma_{xy} = -\rho_{xy}/\rho_{xx}^2$, which exceeds $20 (\Omega \text{ cm})^{-1}$ at 2K

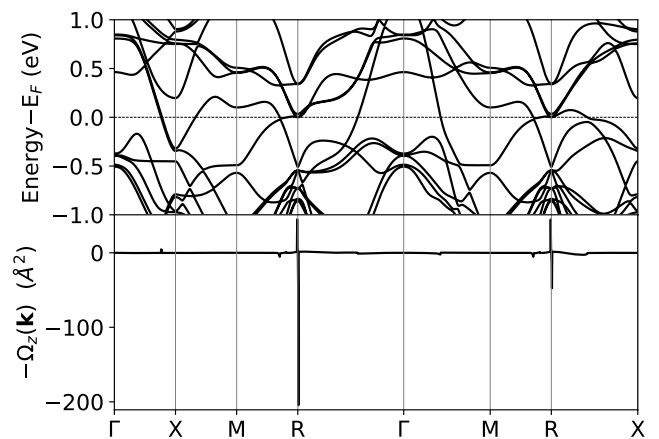


FIG. 4. **DFT calculations of Γ_{4g} Mn_3NiN .** Band structure (top) and Berry curvature summed over filled bands (bottom) along high-symmetry lines of the Brillouin zone.

in Fig. 3 (e). Similar to the powder case, the switching of AHC is very sharp, except for an additional anomaly at 2K. Both magnetization and the Hall conductivity of the (111) orientated film exhibit similar coercive field, as shown in Fig. 3(f) at 50K, indicating the large AHC is directly related with the noncollinear AFM order. The (111) orientated film also shows the sign change of the ordinary Hall signal in Fig. 3(e), which has not been observed in Mn_3Sn and Mn_3Pt [4, 10], and deserves future study.

As already mentioned in the introduction, the Γ_{4g} order of Mn_3NiN is essentially identical to the order of Mn moments in cubic Mn_3Ir and Mn_3Pt , and for the same symmetry reason as in the latter cases it should have the AHE. In contrast, the Γ_{5g} state has a cubic symmetry that forbids AHE. To get a more quantitative estimate of its size in pure Mn_3NiN , which may allow us to make connections with the Cu-doped samples, we performed DFT calculations of the intrinsic AHC of the Γ_{4g} phase of Mn_3NiN [22, 29–31]. The band structure and Berry curvature summed over filled bands plotted along high-symmetry lines in the Brillouin zone are shown in Fig. 4. We find that the local spin moment on each Mn is $2.7 \mu_B$ with a net moment of $\sim 0.007\mu_B/\text{Mn}$, qualitatively agreeing with the experimental results. However, the calculated $\sigma_{\text{AH}} = 525 (\Omega \text{ cm})^{-1}$ (along the (111) direction) is much larger than the experimental value. It is well known that the intrinsic and extrinsic contributions to the AHE are difficult to be separated in experiments unless the the systems shows quantum AHE, in which only the intrinsic contribution survives. Therefore the intrinsic contribution alone is not usually enough for comparison with experiments. Nonetheless, the large difference between the calculated results and the experimental value is likely to be due to the modification of the electronic structure near Fermi surface by the significant amount of Cu doping. The neutron measurements

indicate that right below 260K, Mn_3NiN system is in the Γ_{4g} state[18]. But the Mn moments rotate toward the Γ_{5g} state with decreasing temperature, which becomes dominant below 100K[18]. The Cu doping is therefore essential in stabilizing the Γ_{4g} order at low temperatures which allows AHE. However, its quantitative influence on the AHE in the Γ_{4g} state may depend on many system specific details and will be studied in the future.

In conclusion, we have shown that Cu-doped Mn_3NiN system is a noncollinear antiferromagnet having the AHE that beyonds binary Mn compounds. The latter encounter potential non-wetting and interfacial oxidation problems during the epitaxial thin-film growth on oxide substrates[10]. Thus, it is much easier to obtain high quality epitaxial $\text{Mn}_3\text{Ni}_{1-x}\text{Cu}_x\text{N}$ film on oxide substrates, giving much advantage for the preparation of multilayer devices in future. Combined with other attractive properties of the antiperovskite nitride systems, our finding may open a new avenue for their application in antiferromagnetic spintronics.

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Note added: During the preparation and submission of our manuscript, we became aware of several papers about the AHE in Mn_3AN system[32–34]. The experimental paper reported the observation of AHE in Mn_3NiN film, stabilized by the strain between film and substrate[34]. Meanwhile, we adopt a totally different strategy, namely Cu substituting on Ni site in $\text{Mn}_3\text{Ni}_{1-x}\text{Cu}_x\text{N}$ to stabilize the AHE.

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