Variation of spin–orbit coupling and related properties in skymionic system Mn$_{1-x}$Fe$_x$Ge

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Abstract

We report a systematic study of the magnetic and magnetotransport properties in skymionic compounds Mn$_{1-x}$Fe$_x$Ge. Helical-spin or skyrmion orders are formed in all the compositions, which allows us to study electron band-filling dependence of those periodically-winding spin textures. Magnetization characteristics reflect the variation in Dzyaloshinskii–Moriya interaction or spin–orbit coupling with chemical composition, typically as a change in the critical magnetic field. This tunable spin–orbit coupling enables control of skyrmion formation, such as its size, helicity and topology. Anomalous Hall effect in Mn$_{1-x}$Fe$_x$Ge can also be a good measure of the strength of spin–orbit coupling. Anomalous Hall conductivity $\sigma_{xy}^A = S_H M$ is moderately temperature-dependent, obeying the magnetization variation, except for those at low temperatures in FeGe accompanied by skew contribution. The constancy of anomalous Hall coefficient $S_H$ against temperature manifests that the contribution from reciprocal space Berry phase induced by spin–orbit coupling is dominant in anomalous Hall conductivity. Strength of Dzyaloshinskii–Moriya interaction and anomalous Hall coefficient show a similar tendency in their band-filling dependence. Spin–orbit coupling plays a fundamental role behind both of the chiral magnetism and spin-dependent transport phenomena in this system.

1. Introduction

Topological properties of skyrmions [1], such as topological Hall effect [2–4], ultralow-current driven skyrmion motion [5, 6], and topological stability as magnetic nano-particles [7, 8], stimulate researches on design of new topological spin textures in pursuit of further novel functionalities. Examples of those spin structures include biskyrmions [9], Néel-type skyrmions [10, 11], hedgehogs [12–14], chiral domain walls [15], and chiral soliton lattice [16]. One guiding principle for creating such a winding spin texture is utilizing antisymmetric spin orbit coupling, namely Dzyaloshinskii–Moriya (DM) interaction $[D \cdot (\mathbf{S}_1 \times \mathbf{S}_2)]$, allowed in crystals without local or global space inversion symmetry [17, 18]. The DM interaction stems from the spin–orbit coupling, therefore the control of spin–orbit coupling by selection of ingredient elements and engineering band structure is important for the design of winding spin structures.

Since the discovery of skyrmion lattice state [19] and the identification of its topological spin order [7] in B20-type silicide compounds with a chiral crystal lattice structure, those materials have been regarded as a prototypical skymronic system. In those silicide compounds, e.g. Mn$_{1-x}$Fe$_x$Si and Fe$_{1-x}$Co$_x$Si, competition between ferromagnetic exchange interaction $[J (\mathbf{S}_1 \cdot \mathbf{S}_2)]$ and DM interaction stabilizes helical or skyrmion structure with 10–200nm magnetic period $\lambda$; $\lambda$ is given by $\sim a \frac{D}{J}$, $a$ and $J$ being the lattice constant and the ferromagnetic exchange interaction. Although the strength of magnetic exchange interactions vary with chemical composition (x and y) (also see figures 1(a)–(d)), the magnetic phase diagrams in temperature (T)-magnetic field (H) plane share a generic profile: a helical structure forms at low fields; a conical structure at intermediate fields; a ferromagnetic structure at high fields above the critical field ($H_c$); a skyrmion lattice in a
narrow $T$-$H$ region just below the transition temperature ($T_N$). Here we note that the skyrmion phase can be largely expanded by geometric effects in thinned plates [21], quenching procedures under magnetic field [8], or pressure effects [22, 23].

Substitution of silicon atoms in B20-type compounds with germanium atoms largely affects their magnetic properties as shown in figures 1(a)–(d). Figure 1(a) shows composition or band-filling dependence of magnetic transition temperature ($T_N$) in both B20-type silicides and germanides. Compared to the silicides, composition range showing helimagnetic transitions is much broader in the germanides. Transition temperature is also enhanced, reaching near room temperature (280 K) in FeGe. This effect of substitution can be roughly understood by the Stoner model; larger density of states due to suppression of electron transfer between transition metal (TM) atoms by germanium atoms with the larger atomic radius, serving as spacers among TM atoms, increases the number of electrons involved in magnetic interactions [24], which results in enhancement both in transition temperature $T_N$ (figure 1(a)) and saturated magnetic moment $M_s$ (figure 1(c)).

We also observed large differences in the critical field $H_c$ between silicide and germanide compounds as presented in figure 1(b). The critical field represents the energy cost to unwind the spin spiral structure, drawing a rough index of the strength of DM interaction; $H_c \approx D^2M_s/J$ [25]. A sharp rise in $H_c$ around the composition of MnGe therefore indicates increase in DM interaction, which leads to shortening of helical pitch or miniaturization of skyrmion size. Composition dependence of magnetic-helix period and skyrmion size was determined by Lorentz transmission electron microscopy [26] and neutron diffraction [27] as shown in figure 1(d). Reflecting the large $H_c$, helical period ($\lambda$) or skyrmion lattice spacing ($2\lambda/\sqrt{3}$ in the hexagonal form and $\lambda$ in the tetragonal form) becomes short, reaching a minimum of 3 nm at MnGe with the largest $H_c$ [4]. In particular, topological change in spin texture also occurs upon the reduction of Fe content $x$. A three-dimensional topological spin texture categorized into a different topological class is realized in MnGe; a periodic array of hedgehog and antihedgehog spin singularities with integer topological charges is formed as a
consequence of mode coupling among three orthogonal spin helices (figure 1(e)), which was observed by small-angle neutron scattering (SANS) [13] and Lorentz transmission electron microscopy (TEM) (figure 1(i)) [14]. This may come from large magnetic anisotropy also as a consequence of enhanced spin–orbit interaction. At the other side, with smaller \( H_c \), there observed nonmonotonous change in \( \lambda \) with a divergent behavior at \( x \approx 0.8 \) (indicated by an arrow in figure 1(d)), accompanied by the reversal of skyrmion helicity. The helicity reversal had been observed as the reversal of bright and dark contrast of particle images of skyrmions (figure 1(f) for \( x \approx 0.5 \) and figure 1(g) for \( x \approx 0.9 \)) by Lorentz TEM, which are schematically illustrated in figures 1(f) and (g). This originates from continuous change in spin–orbit coupling with its sign change at the critical composition \( x = 0.8 \) [26].

The widely and continuously tunable spin–orbit coupling in \( \text{Mn}_{1-x}\text{Fe},\text{Ge} \) is a key for control of skyrmion spin texture in terms of size, helicity, and topology. In this study, we investigate magnetization and electrical transport properties, focusing on anomalous Hall effect, which is also rooted in spin–orbit coupling, to gain a unified picture of magnetic properties in these chiral magnets.

2. Experimental

We synthesized a series of polycrystalline \( \text{Mn}_{1-x}\text{Fe},\text{Ge} \) \((0.0 \leq x \leq 0.9)\) by a high pressure method [31]. Alloys with stoichiometric quantities of the constituents were prepared by arc melting under argon atmosphere, followed by heat treatment at 800 °C under a high pressure of 4.0 GPa for 1 hour. FeGe single crystals were grown by a chemical vapor transport method [32]. Raw ingredients of Fe and Ge powder and transfer agent of I\(_2\) were heated in an evacuated quartz tube under a thermal gradient between high (560 °C) and low (500 °C) temperatures for 2 weeks. A single crystal of FeGe show a low residual resistivity as low as 6.3 \( \mu \Omega \) cm, and other polycrystals also show good metallic conductivity below 400 \( \mu \Omega \) cm (see insets in figure 3). Especially, the mother compounds of polycrystalline MnGe and single-crystalline FeGe exhibit large residual to room temperature resistivity ratio \([\text{RRR} \equiv \rho_{200 K}/\rho_{2 K}]\) of 18.9 and 33.9, respectively. Measurements of longitudinal \( (\rho_{xx}) \) and Hall resistivity \( (\rho_{yx}) \) were performed with the electrical current parallel to the longest side \((x\text{-axis})\) and the magnetic field to the shortest one \((z\text{-axis})\). Hall conductivity \( \sigma_y \) is deduced from the measurements of longitudinal and Hall resistivities via the relation that \( \sigma_y = \rho_{yx}/(\rho_{xx}^2 + \rho_{yx}^2) \). Magnetization was measured under the same magnetic field direction as in the transport measurements.

3. Results and discussion

We show results of the systematic measurements of magnetization \( M \), magnetoresistivity \( \rho_{xx}(H)/\rho_{xx}(0) \), and Hall conductivity \( \sigma_y \) in the series of \( \text{Mn}_{1-x}\text{Fe},\text{Ge} \). Figure 2 shows their magnetic-field \((H)\) dependences at various temperatures.

Magnetization is zero at zero magnetic field due to helical spin orders, and linearly increases with applied magnetic field below the critical field \( H_c \) of ferromagnetic transition, followed by gradual increase due to the Zeeman splitting of spin–up and spin–down bands. Magnetic fields at the bent positions of \( M-H \) curves are defined as the critical field \( H_c \), whose values at the lowest temperature (e.g. 5 K) are presented in figure 1(b). Here we note that slope of \( M-H \) curve below \( H_c \) reflects the helical period; the temperature-dependent change in the slope of the \( M-H \) curve observed for \( \text{Mn}_{1-x}\text{Fe},\text{Ge} \) \((x = 0.0 \text{ and } 0.2)\) indicates that helical period varies with temperature in those compounds.

Negative magnetoresistivity (MR) effect is usually observed below \( T_N \) and \( H_c \) due to the alignment of magnetization by the external magnetic field in \( \text{Mn}_{1-x}\text{Fe},\text{Ge} \) \((0.1 \leq x \leq 1.0)\) (figures 2(h)–(l)), which is followed by positive MR above \( H_c \) observed at low temperatures in 0.6 \( \leq x \leq 1.0 \) (figures 2(j)–(l)). Detailed mechanisms for the typical magnetic-field dependence of MR were discussed in the case of an FeGe thin film [33]. The magnitude of MR ratio becomes larger in \( \text{Mn}_{1-x}\text{Fe},\text{Ge} \) with less Fe content \( x \), whose tendency seems to correspond to the \( x \) dependence of the critical field \( H_c \), i.e., the strength of DM interaction or spin–orbit coupling. Incidentally, nonmonotonous \( H \)-dependence of \( \rho_{xx}(H)/\rho_{xx}(0) \) observed in MnGe is attributed to fluctuations of emergent magnetic field, which will be discussed elsewhere [34].

Magnetic-field dependence of Hall conductivity resembles that of magnetization in all the compositions (figures 2(n)–(r)) except for MnGe (figure 2(m)), which indicates the dominant contribution to \( \sigma_y \) is the anomalous Hall effect being proportional to \( M \). Large deviation from the \( H \)-linear profile of anomalous Hall effect in MnGe (figure 2(m)) originates from topological Hall effect [4] due to the formation of the three-dimensional skyrmion lattice (figure 1(e)) [13]. Here we note that Hall voltage in FeGe could not be measured with good accuracy below 50 K due to low Hall resistivity being proportional to small value of \( \rho_{xx}^2 \) (also see inset of figure 3(f) for \( \rho_{xx} \) in FeGe).
We compare saturated magnetization $M_s$ and Hall conductivity $\sigma_{xy}$ at a high magnetic field above the respective critical field $H_c$ in various compositions in figure 3. The $T$-variations of $M_s$ and $\sigma_{xy}$ coincide with each other, except for considerable deviations at low temperatures in MnGe and FeGe (figures 3(a) and 3(f)). This means that overall Hall conductivity is attributed to the intrinsic anomalous Hall effect induced by scattering-free anomalous Hall current due to Berry phase in momentum space [35, 36], being independent of longitudinal conductivity $\sigma_{xx}$ or relaxation time $\tau$ (also see insets of figure 3). The disagreement between $M_s$ and $\sigma_{xy}$ at low $T$ in MnGe and FeGe may originate from other extrinsic contributions, such as skew scattering mechanism [37], whose contribution becomes appreciable in case of high electrical conduction as in the low-temperature region of MnGe and FeGe [38]. Here we note that anomalous Hall effect in an FeGe thin film, which shows relatively

Figure 2. Magnetic-field dependences of (a)-(f) magnetization $M_s$, (g)-(l) magnetoresistivity $\rho_{xx}(H)/\rho_{xx}(0)$, and (m)-(r) Hall conductivity $\sigma_{xy}$ in Mn$_{1-x}$Fe$_x$Ge ($x = 0.0, 0.2, 0.4, 0.6, 0.8, \text{ and } 1.0$). Data of magnetoresistivity in MnGe are shifted vertically for clarity [panel (g)].

Figure 3. Comparison between Hall conductivity (black circles) and magnetization (blue lines) at high fields. Insets are temperature dependences of resistivity at zero field.
low electrical conductivity due to large scattering of electrons at surfaces, recovers the intrinsic (\(\tau\)-independent) feature [33].

For the investigation of spin–orbit coupling effect on transport properties, we focus on the \(T\)-independent (\(\tau\)-independent) intrinsic anomalous Hall conductivity. To separate normal and anomalous Hall contributions, we fit \(\sigma_{xy}\) data with the relation \(\sigma_{xy}(H) = R_0 \sigma_{xy}^2 H + S_{ij} M_i\), where \(R_0\) and \(S_{ij}\) are \(H\)-independent normal and anomalous Hall coefficients, respectively [39]. We compare in figure 4 the anomalous Hall coefficient \(S_{ij}\) at 50 K and the strength of DM interaction, the latter of which is estimated as \(T_{\lambda}/(\lambda M_s^2)\) deduced from the following relations: \(T_{\lambda} \approx J M_s^2\) and \(\lambda \approx J/D\). Both of the quantities trace a similar band-filling dependence; this suggests that those are rooted in the same physical quantity of spin–orbit coupling, although the variations of \(\sigma_{xy}^2\) and \(D\) with \(x\) do not necessarily correlate with each other in theory. Recent first-principles calculations [40, 41] provide a comprehensive description of both parameters of \(\sigma_{xy}^2\) and \(D\) in terms of Berry phase in real and reciprocal spaces, which successfully reproduced the experimental result of the filling dependence of DM interaction. However, those theoretical calculations do not observe such correlation between \(\sigma_{xy}^2\) and \(D\) as experimentally observed here, leaving an open question.

It is worth to compare the present observation with the case of B20 silicide helimagnets. Similar investigations on the connection between spin–orbit coupling and anomalous Hall effect have been reported for Mn\(_{1-x}\)Fe\(_x\)Si [42] and Fe\(_{1-x}\)Co\(_x\)Si [28]. As in the present case of Mn\(_{1-x}\)Fe\(_x\)Ge, \(\sigma_{xy}^2\) and \(\lambda^{-1} \propto D/|J|\) in Fe\(_{1-x}\)Co\(_x\)Si trace a similar composition dependence. In contrast, \(\sigma_{xy}^2\) in Mn\(_{1-x}\)Fe\(_x\)Si shows a sign reversal with composition variation, while the helical period \(\lambda\) monotonically changes. The band-filling dependence of \(\sigma_{xy}^2\) in Mn\(_{1-x}\)Fe\(_x\)Si is reproduced by first-principles calculations on Berry curvature in reciprocal space [42]. Intrinsic anomalous Hall effect is determined by the Berry curvature produced from the anti-crossing points in band structure whose gaps are opened by the spin–orbit coupling [35]. Anomalous Hall effect depends not only on spin–orbit coupling strength but also on detailed band structure, especially the distribution of anti-crossing points in the reciprocal space. Fine tuning of Fermi level in Mn\(_{1-x}\)Fe\(_x\)Si system with small increment of Fe doping, may hit the singular points in the momentum space, where a perturbative treatment of spin–orbit coupling is invalid.

**4. Conclusion**

We observed the spin–orbit coupling effect on the skyrmion formation and anomalous Hall conductivity in B20-type Mn\(_{1-x}\)Fe\(_x\)Ge with high-\(T_{\lambda}\). Spin–orbit interaction can be continuously controlled by the electron band-filling, which results in the large change in skyrmion size, the reversal of skyrmion helicity, and even change in topology of spin texture. Strength of spin–orbit coupling can be also monitored by the measurements of intrinsic anomalous Hall conductivity originating from Berry curvature at band-crossing points due to spin–orbit coupling. Variations in DM interaction and anomalous Hall conductivity with the band-filling (i.e., \(x\)) globally coincide with each other in Mn\(_{1-x}\)Fe\(_x\)Ge, which demonstrates that the underlying dominant interaction affecting on the spin order and spin-related transport phenomena in these chiral magnets is spin–
orbit coupling. Control of spin–orbit interaction will continue to be an important issue in designing topological spin texture with various fascinating physical phenomena.

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