Room-Temperature Skyrmion Thermopower in Fe₃Sn₂

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We present the room-temperature thermoelectric signature of skyrmion bubbles. This is observed in Fe₃Sn₂, a Kagome Dirac crystal with massive Dirac fermions that features a high-temperature skyrmion phase. The room-temperature skyrmion bubbles show magnetic-field dependence of the wavevector whereas the thermopower is dominated by the electronic diffusion mechanism, allowing for the skyrmionic bubble detection. The results pave the way for future skyrmion-based devices based on the manipulation of the thermal gradient.

1. Introduction

Strong electronic correlations and topology are widely recognized as fundamental sources of novel states of matter [1–5] and technologically important material properties. [6,7] Nanoscale magnetic skyrmions in spin textures of chiral magnets are quintessential embodiment of this concept. [8,9]

Magnetic skyrmions are commonly observed by microscopy techniques in the real space and neutron scattering in the reciprocal space. [10,11] Experiments available far below room temperature reveal no discernible [12] or relatively small changes [13] in magnetic-field dependent thermoelectric properties in the course of transition to the skyrmion crystal.

In magnetic metals thermopower includes electronic diffusion, phonon, or magnon-drag thermopower. [14] Thermoelectric signature of the skyrmions, in particular, is of interest in spintronics and spincaloritronics for information processing. [15,16] Ferromagnetic Fe₃Sn₂ with a geometrically frustrated kagome bilayer of Fe attracts considerable interest due to its magnetic structure, anomalous Hall effect, Dirac electronic states, and room-temperature skyrmions. [17–21] Previous studies also show that skyrmions in Fe₃Sn₂ can be manipulated by spatially geometric confinement. [22] Moreover, single-chain skyrmion bubbles in 600 nm nanostripes were reported to be stable far above the room temperature, up to 630 K, thus making significant progress toward nanoscale skyrmion -based spintronics. [23]

On the other hand, it is also of interest to manipulate skyrmionic textures by thermal gradients in magnetic nanodevices. [24–26] In this paper we show first evidence of the room-temperature skyrmion detection by thermopower in Fe₃Sn₂ in a simple thermal gradient and discuss relevant mechanism.

2. Results and Discussions

2.1. Results

The powder X-ray diffraction (XRD) pattern of Fe₃Sn₂ shows that all observed peaks can be well fitted with the R-3mh space group (Figure 1a) confirming high purity of the single crystals. The determined lattice parameters a = b = 5.345(2) Å and c = 19.780(2) Å are in good agreement with the reported values. [27] In the single-crystal XRD (Figure 1b), only (00l) peaks are detected, indicating that the crystal surface is parallel to the hexagonal plane and orthogonal to the c-axis. Figure 1c shows the unit cell of Fe₃Sn₂ under the high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM), showing no evidence for atomic defects.

In Figure 2 holographically reconstructed magnetization map shows hexagonally packed skyrmionic bubbles at the room temperature. [19] Interestingly, the helicity (in-plane spin rotation sense) is either clockwise or anticlockwise, yielding +1 and −1, respectively, as topological charges.

We performed real-space imaging of magnetic spin structures in the ab plane and their evolution under external magnetic field along the c-axis in transmission electron microscope at room temperature and we also show the magnetic-field-dependent thermopower (S) in the well-established skyrmionic bubble phase. [19] (Figure 3). The Lorentz contrasts of skyrmionic bubbles (Figure 3a–d) are similar to the previous Lorentz microscopy study. [19] We mapped out the projected in-plane magnetization by off-axis electron holo graphy under the residual magnetic field (11.7 mT) at room temperature. In order to stabilize the skyrmionic bubbles at 11.7 mT, a large external magnetic field ≈1000 mT was abruptly turned off. Under the residual magnetic field (≈ 11.7 mT with the objective lens fully off) in our microscope, Lorentz microscopy image (Figure 3a) shows coexistence...
materials with substantial carrier density Lorentz force will affect thermal and electrical transport alike, whereas dominant carriers are often either electrons or holes.\cite{29,30} When the magnetic field is applied along the c-axis, resistivity is either unchanged or somewhat decreased above about 120 K, but magnetoresistance is positive below 120 K. There is a up to 20% decrease in $\kappa(9 \ T)$ when compared to the $\kappa(0 \ T)$ below 100 K, suggesting that electronic contribution to thermal conductivity is not negligible.

Low-temperature heat capacity offers further insight (Figure 4c). From the fits (Figure 4c inset) using the Debye model $C_v = (12\pi^4/5)(\theta_D^3 \ T)^3 + \gamma T$ the Debye temperature $\theta_D$ and Sommerfeld coefficient ($\gamma$) are obtained. The values are $\theta_D = 237.0 \pm 0.6$ K and $\gamma = 2.003(S) \times 10^{-2} \ J \ molar^{-1} \ K^{-2}$. The phonon velocity is $\approx 2010 \ m \ s^{-1}$\cite{31} Both electron and phonon part of heat capacity are calculated up to the room temperature and are also shown in Figure 4c.

Next, we evaluate phonon drag versus electronic diffusion mechanism on thermopower. The characteristic peak in thermal conductivity observed on cooling (Figure 4a) is phonon-related and it commonly arises due to competition between the point-defect/boundary scattering and the Umklapp phonon scattering mechanism.\cite{32} Possible phonon drag effects are supported by the sign change of $S(T)$ at 124 K (Figure 4b). If we take change in the band structure and effective mass of Fe$_3$Sn$_2$ into consideration, the low-temperature sign change cannot be explained by electron diffusion within the framework of Mott formula: $S = -(\pi^2 k_f^2 E_F/3e)[(1/\sigma)(d\sigma/dE)]_{E=E_F}$\cite{33-35} As a qualitative estimation, if Drude’s formula $\sigma = n e^2 \tau/m^*$ is adopted for the conductivity $\sigma$, where $n$ is carrier concentration, $m^*$ is effective mass, and $\tau$ is relaxation time inversely proportional to the density of states, then the energy dependencies from the charge carrier density and $\tau$ are approximately balanced out, i.e., $\sigma$ has the same energy dependence as $1/m^*$. For Fe$_3$Sn$_2$, the Fermi energy the effective mass decreases.\cite{21} This means $\sigma$ will increase with energy and yield the negative sign of $S$. Consequently contributions from other scattering processes such as phonon-drag or magnon-drag must be taken into consideration. Fermi surface of Fe$_3$Sn$_2$ features two dominant electron pockets.\cite{20,21} Negative thermopower should be expected if the electronic diffusion part $S_d$ in $S = S_d + S_p$ prevails over phonon-drag contribution $S_p$. This is indeed observed above 124 K (Figure 4d) and is in agreement with a decrease in the absolute values of the temperature-dependent thermopower in 9 T when compared to the S(0 T) (Figure 4b). As we show below, electronic diffusion mechanism can explain the linear change of $S$ with temperature above 124 K but not the positive thermopower at lower temperatures.

In order to study the sign change, we plot only measured $S(T)$ below 124 K (Figure 4d, red solid circles). For a single parabolic band system, the $S_d$ can be defined by the equation $\pi^2 k_f^2 E_F/3e$.\cite{36} By linear fitting the data above 124 K (Figure 4b) and extrapolating it down to 2 K, we obtain the diffusive part of thermopower at low temperature. The fitted value of $E_F$ is 0.25(1) eV. This is an order of magnitude less than what is expected in metals but is also in agreement with carrier concentration in Fe$_3$Sn$_2$, $n \approx 10^{22} \ cm^{-1}$.\cite{20} Phonon scattering part of thermopower $S_p$ (Figure 4d, blue open circles) obtained by subtracting $S_d$ from the measured $S$ clearly indicates positive contribution, resulting in thermopower sign change and net positive $S$ values. It should be noted that magnon-drag $S_{m} \propto BT^2$\cite{37} could also

Figure 1. a) Powder X-ray diffraction (XRD) and b) single crystal 2θ scans of Fe$_3$Sn$_2$ at room temperature. The vertical tick marks in (a) represent Bragg reactions of the R-3mh space group. c) High-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) image of Fe$_3$Sn$_2$ taken along the c-axis. Fe columns are somewhat less visible as the heavier Sn columns have two times more atoms that of Fe columns in addition to large atomic number difference. A unit cell model is embedded in the image.
Figure 2. a) Reconstructed phase-shift image and b) color-contour composite image obtained from the phase-shift image shown in (a). The electron hologram was taken with external magnetic field 11.7 mT. The skyrmionic bubbles are induced by rapidly changing magnetic field from 1000 to 11.7 mT. Based on the in-plane spin rotation sense, the topological charge of skyrmionic bubble is determined as $\pm 1$.

Figure 3. a–d) Lorentz images showing the magnetic field dependence of the hexagonal plane spin textures in Fe$_3$Sn$_2$. The defocus value was about $\pm 500 \mu$m. The arrows show the crystallographic directions determined from the electron diffraction (not shown here). The external magnetic field was applied along the imaging direction using the objective lens coil. c) There are two independent sets of triple-$q$ systems in 584.1 mT. d) With further increasing magnetic field to 727.5 mT, one set ($q'$) disappears and the other set ($q$) becomes dominant in the sample. e) Thermopower versus magnetic field at several temperatures near where the skyrmionic phase exists. The same data at 10 and 50 K are also plotted for comparison. The shadow area indicates the skyrmionic phase. Note that the temperature of the best-defined thermopower anomalies in skyrmion phase corresponds well to temperature where maximum density of skyrmion bubbles was observed. $^{[19]}$ f) Relative change of heat capacity in magnetic field at the identical temperature; legend in (e) also denotes temperatures in (f).
Figure 4. a) Temperature dependence of electrical resistivity and thermal conductivity. b) Temperature dependence of thermopower. The blue cubic shows zero field data and the red circle shows data in 9 T field along ab plane. The green star shows data in 9 T field along c-axis. Note linear S(T) dependence at high temperatures indicated by red dashed-dotted line. c) Temperature dependence of heat capacity. d) Temperature dependence of positive part of thermopower. The red circles are the measured thermopower below the 124 K. The blue open circles represent the S_p extracted. The green lines show the power law fitting of S_p. The inset shows the phonon MFP below 124 K.

Influence thermopower in Fe_3Sn_2. In Figure 4d, green line shows the fitting of low temperature S_p ∝ B^n from the power law S_p = AT + BT^n. The fitted n is 2.67±0.06 with A = 0.182 ± 0.002 μV K^-2 and B = -(1.9 ± 0.6) × 10^-4 μV K^-4. The coefficient A reflects the low-temperature diffusion thermopower that comes from the change in carrier concentration below 100 K. Hence, coefficient A describes the difference between the diffusion part Seebeck coefficient below and above 124 K. Whereas magnon-drag contribution cannot be completely excluded, it is evident that the fitted exponent is closer to T^3 dependence, expected in the phonon-drag mechanism of thermopower. The phonon mean free path (MFP) which is closely related to the phonon transport can be calculated by Fourier’s law (κ_p = 1/3 Cv_l) with the Debye model, where κ_p is phonon thermal conductivity obtained from by subtracting electronic thermal conductivity κ_e from measured κ(T). The κ_e is estimated from the Wiedemann–Franz law κ_e/T = L_0/T, where L_0 = 2.45 × 10^-8 W Ω K^-2 and ρ is the measured resistivity. The C, v, and l_e are the phonon specific heat (Figure 4c), phonon velocity, and MFP of the phonon, respectively. The results are shown in the inset of Figure 4d. Whereas phonon-drag mechanism is commonly associated with much longer mean-free path, we note that phonon drag in metals may not vary significantly with mean free path if energies of electron and phonon distributions are well matched, i.e., if the probability of electron interaction with quasi-ballistic phonons is proportional to the size of the region where phonons propagate without mutual collisions. [38,39] The presence of phonon contribution to thermopower explains the magnetic-field induced changes at low temperature. The absolute value of S_d decreases in 9 T due to the Lorentz force whereas the S_p remains unchanged. Since S_d and S_p have the opposite sign and at low temperature S_d dominates, the net thermopower will increase. This explains the increase of thermopower crossover temperature from 124 to 129 K for magnetic field in the hexagonal plane or 130 K when the magnetic field is applied along the easy magnetization c-axis.

3. Discussion

The above discussion confirms that, whereas phonon or magnon drag contributes to low-temperature thermopower, electronic diffusion mechanism is dominant at the room temperature. In Figure 3e the magnetic field is applied along the c-axis and perpendicular to the thermal current flow, so that the thermal transport is measured in the plane of the skyrmionic bubbles. When a thermal gradient VT is applied, a diffusion electric current density J_d is generated. The diffusion part of thermopower S_d is the ratio between the electric field required to stop J_d and the VT. [40] When a conduction electron transverses a skyrmion, it is affected by the local magnetization and hence continuously changes direction acquiring Berry phase. [41,42] Consequently, carriers experience effective Lorentz force which increases the Hall effect. Similar effects should take place when carriers are driven by external thermal gradient. [15] Indeed, as shown in Figure 3e, thermopower shows well-defined anomaly in the
skyrmionic bubble phase. This is in contrast to thermopower outside the skyrmion region, such as for example in the spin glass state at 50 K. When electronic system enters skyrmion region, there is an increase in the absolute values of $S(B)$. For systems with spin degree of freedom, the entropy is composed by the entropy from spin and crystal lattice. Ordering spin texture in skyrmionic phase will decrease the spin entropy and transfer the entropy from spin and crystal lattice. Ordering spin texture in skyrmionic phase will decrease the spin entropy and transfer the entropy from spin and crystal lattice. Ordering spin texture in skyrmionic phase will decrease the spin entropy and transfer the entropy from spin and crystal lattice. Ordering spin texture

4. Summary and Conclusion

In summary, we present first signature of room-temperature skyrmion spin textures by thermopower in a simple thermal gradient. Thermal transport in the high-temperature region is governed by electronic diffusion mechanism, enabling detection of topologically protected skyrmionic spin textures. Our results open new possibilities for skyrmion manipulation in future information storage and spin caloritronics devices using thermal gradients. \[\text{45, 46}\]

5. Experimental Section

Crystal Synthesis: Single crystals of Fe$_{12}$Sn$_2$ were grown using flux method.\[\text{47}\] Whereas some crystals were initially grown by mixing Fe and Sn in 5:95 stoichiometry, heating to 1150 °C, holding at this temperature for 24 h, fast-cooling to 910 °C and then slow cooling to 800 °C,\[\text{48}\] cooling to 770 °C was used to increase the size of crystal to about 3 mm length.\[\text{20}\]

Characterization: Crystal structure was determined by analyzing powder XRD pattern taken with Cu K$_\alpha$ ($\lambda = 0.15418$ nm) radiation of Rigaku Minix powder diffractometer. Transmission electron microscopy (TEM) samples are prepared by focused ion beam using 5 keV Ga+ ions for a final milling (FEI Helios 600). The range of the collection angle used for HAADF STEM was 68–280 mrad. The HAADF STEM image was filtered using a Fourier mask in the Digital Migray software (Gatan, Inc.). Aberration-corrected JEOL atomic resolution microscope (ARM) 200CF and JEOL 2100F Lorentz were used for Lorentz imaging and off-axis electron holography, respectively, at the 200 keV operation voltage. The external magnetic field was applied by controlling excitation of the objective lens.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

magnetic materials, skyrmions, thermoelectrics

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