Anisotropic Magnetoresistance Effect of Intercalated Ferromagnet FeTa₃S₆

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Intercalated transition metal dichalcogenides have been widely used to study the magnetic and magnetoelectric transport properties in a strong anisotropic and spin–orbit coupling environments. In this study, ferromagnetic FeTa₃S₆ (also known as Fe₁/₃TaS₂) single crystals were grown by using the chemical vapor transport method, and its magnetic and magnetoelectric transport properties were measured. The results show that FeTa₃S₆ has ferromagnetic ordered below 37K, with sharp switching of magnetization, butterfly-shaped double-peak magnetoresistance and anomalous Hall effect, and the magnetization and resistance have strong anisotropy. When a magnetic field is oriented parallel to the c-axis, the magnetoresistance exceeds 10% at a temperature of 10K, and negative magnetoresistance is generated when the magnetic field is larger than the switching field. When the direction of the magnetic field of 9T rotates from out-of-plane to in-plane, the anisotropic magnetoresistance exceeds 40%, and the angle-dependent Hall resistance presents a novel trend, which may be due to the existence of a topological Hall effect or other magnetic structures in the FeTa₃S₆ thin film. When the magnetic field of 9T rotates in the ab-plane of the sample, the in-plane anisotropic magnetoresistance conforms to the form of sin²φ. The experimental results of this study provide important information for the study of magnetic and magnetoelectric transport properties of intercalated transition metal dichalcogenides.

Keywords: FeTa₃S₆, magnetic property, magnetoelectric transport, anomalous Hall effect, anisotropic magnetoresistance

INTRODUCTION

In recent decades, transition metal dichalcogenides (TMDs) have attracted research interest due to their unique properties and potential applications in a broad range of areas [1–7]. TMDs are a class of layered materials whose crystal structures can be classified as, depending on the local coordination of chalcogen atoms around the central transition metal, 1H (trigonal prismatic), 1T (octahedral), 1T’ (distorted octahedral), 2H (hexagonal), 3R (rhombohedral), and Td (orthorhombic) phases, and most of them are two-dimensional (2D) van der Waal materials [8–11]. The intercalation or doping of atoms or molecules can cause significant changes in the physical properties of TMDs [12–22]. For example, Cu or Pd intercalation induces superconductivity in 1T-TiSe₂ [18, 19], and 3d transition metal intercalation leads to different kinds of long-range magnetic order in TMDs (such as TiS₂) [20]; among the compounds with Cr-intercalated NbS₂, Cr₁/₃NbS₂ is a chiral helimagnet, which confirms the strong coupling between neighboring layers [21, 22].
**EXPERIMENTAL SECTION**

High-quality FeTa$_3$S$_6$ single crystals were prepared by using the chemical vapor transport (CVT) method. High-quality pure Fe (102.1 mg, 99.9%), Ta (667.3 mg, 99.9%), and S (235.0 mg, 99.5%) were mixed (molar ratio of 1:5:3:6) and then sealed under vacuum in a quartz tube with the addition of I$_2$ (200 mg, 99.9%) as the transport agent. Then the quartz tube was placed horizontally in a two-temperature zone furnace, and the raw materials were placed in the high-temperature zone. In 10 h, the temperature in the high-temperature zone increased to 1273K, and the temperature in the low-temperature zone increased to 1173K. After 7 days, FeTa$_3$S$_6$ single crystals were grown in the low-temperature zone. The crystals were cleaned by ultrasonication in supersaturated aqueous solution of KI, deionized water, and alcohol, and finally, the single crystals are a regular polygon with a size of millimeters.

The structure of FeTa$_3$S$_6$ single crystals was characterized by using an X-ray diffractometer (XRD, Advance D8). The elemental composition of the FeTa$_3$S$_6$ crystals was confirmed by using an energy-dispersive spectrometer (EDS) of a scanning electron microscope (SEM, TESCAN MIRA 3). Magnetization measurements of the bulk FeTa$_3$S$_6$ sample and magnetoelectric transport properties of the device were performed using an integrated physical property measurement system (PPMS, Evercool-9T, Quantum Design). The six-terminal Hall electrode is prepared on a silicon wafer by photolithography and thermal evaporation. The FeTa$_3$S$_6$ thin film was mechanically exfoliated by a Scotch tape from a single bulk crystal FeTa$_3$S$_6$, and then we used polydimethylsiloxane to transfer to the electrode through a 2D material alignment transfer platform. The thickness of the thin film was measured by using an atomic force microscope (AFM) [40].

**RESULTS AND DISCUSSION**

Figure 1A shows the characterization and magnetization measurement results of FeTa$_3$S$_6$ single crystals. Figure 1A demonstrates a sharp diffraction peak in the (00l) direction in the XRD pattern (JCPDS No. 22-0360), the result shows that the sample has excellent crystallinity, the inset is an optical image of FeTa$_3$S$_6$ single crystal, and it is a regular polygonal flake with metallic luster. The structure of FeTa$_3$S$_6$ single crystals was characterized by using an X-ray diffractometer (XRD, Advance D8). The elemental composition of the FeTa$_3$S$_6$ crystals was confirmed by using an energy-dispersive spectrometer (EDS) of a scanning electron microscope (SEM, TESCAN MIRA 3). Magnetization measurements of the bulk FeTa$_3$S$_6$ sample and magnetoelectric transport properties of the device were performed using an integrated physical property measurement system (PPMS, Evercool-9T, Quantum Design). The six-terminal Hall electrode is prepared on a silicon wafer by photolithography and thermal evaporation. The FeTa$_3$S$_6$ thin film was mechanically exfoliated by a Scotch tape from a single bulk crystal FeTa$_3$S$_6$, and then we used polydimethylsiloxane to transfer to the electrode through a 2D material alignment transfer platform. The thickness of the thin film was measured by using an atomic force microscope (AFM) [40].

The anisotropic magnetoresistance effect is one of the most basic properties of magnetoelectric transport; the resistivity changes with the relative angle between the magnetization direction and the current direction [35, 36]. In ferromagnets, the anisotropic magnetoresistance effect is caused by the spin–orbit interaction, which induces the mixing of spin-up and spin-down states. This mixing depends on the magnetization direction and gives rise to a magnetization direction-dependent scattering rate [37]. Although some physical properties of Fe$_x$Ta$_2$S$_2$ have been studied to a certain extent, detailed studies on the magnetic properties and magnetoelectric transport properties of FeTa$_3$S$_6$ are still relatively lacking. There is no report about the anisotropic magnetoresistance effect of FeTa$_3$S$_6$ by measuring the angle-dependent magnetoresistance. Here, we successfully grew FeTa$_3$S$_6$ single crystals, studied their magnetic properties and magnetoelectric transport properties, and further measured their angle-dependent magnetoresistance and Hall resistance. These results show that FeTa$_3$S$_6$ has rich potential applications in the field of magnetic properties and spintronics, which is worthy of further theoretical and experimental research.
appearing of a weak magnetic hysteresis loop may be due to the fact that the ab-plane of the sample is not completely parallel to the magnetic field [36].

Figure 2 exhibits the magnetoelectric transport measurement results of the FeTa₃S₆ device. Figure 2A is the AFM measurement result of the thickness of a FeTa₃S₆ thin film on the electronic device, showing that the thickness is about 180 nm, and the inset is the optical image of the device. Figure 2B shows the temperature dependence of resistance under zero field and magnetic field of 5T. Resistance decreases with decreasing temperature, showing metallic behavior, and the resistance of the ferromagnetic state drops rapidly near the Curie temperature due to the loss of spin disorder scattering [36]; the inset is a schematic diagram of the device measurement configuration. Magnetoresistance $R_{xx}$ is a crucial measurement for inferring information about the interaction between itinerant charge carriers and magnetic degrees of freedom in magnetic materials [35], defined as

$$ MR = \frac{\Delta R_{xx}}{R_{xx}(H=0)} = \frac{R_{xx}(H) - R_{xx}(H=0)}{R_{xx}(H=0)}. $$

(1)

where $R_{xx}(H)$ is the resistance value when the magnetic field is $H$. Figure 2C displays the magnetoresistance of the FeTa₃S₆ device measured at the selected temperature by applying a magnetic field along the c-axis. Figure 2D shows the magnetoresistance at 10 K, and the magnetoresistance can reach more than 10%. When the temperature is below the Curie temperature, and the magnetic field $H$ increases from 0T to 3T, the magnetoresistance first increases steadily and reaches the maximum value at the switching field, then decreases within a very narrow magnetic field interval, and then almost linearly decreases until the magnetic field is 3T. If the measuring magnetic field is increased, the magnetoresistance will continue to decrease. The sudden change of magnetoresistance at the switching field can be attributed to the domain reorientation parallel to the direction of the field [25], and the domain nucleation and domain wall propagation are the cause for the formation of the butterfly-shaped double-peak magnetoresistance [44]. When the magnetic field is 3T, the magnetoresistance is negative, and the negative magnetoresistance reaches a peak near the Curie temperature, which is mainly due to suppression of spin disorder resistivity with the magnetic field [45]. Figure 2E presents the Hall resistance of the FeTa₃S₆ device measured at the selected temperature when the magnetic field is along the c-axis (for clarify, the data are equally spaced in the vertical direction). Obvious hysteresis loops caused by the anomalous Hall effect can be observed below the Curie temperature, which originates from the spontaneous ferromagnetic order caused by the intercalation of Fe atoms [28]. When the magnetic field is larger than the switching field or the temperature is higher than the Curie temperature, only the nearly linear Hall resistance contributed.

FIGURE 1 | (A) XRD pattern of a FeTa₃S₆ single crystal, and the inset is an optical image of the FeTa₃S₆ single crystal; the scale is 1 mm. (B) EDS pattern of the FeTa₃S₆ single crystal, and the inset shows the actual atomic ratio. (C) Temperature-dependent magnetization measured of zero-field cooling (black) and field cooling (red) with H∥c, and the inset shows the dM/dT curve of zero-field cooling with H∥c. (D) Temperature dependence of the magnetization measured of zero-field cooling (black) and field cooling (red) with H∥ab. (E) Field-dependent magnetization (M-H) at different temperatures with H∥c. (F) Field-dependent magnetization (M-H) at different temperatures with H∥ab.

FIGURE 2 | (A) AFM measurement result of the thickness of a FeTa₃S₆ thin film on the electronic device, showing that the thickness is about 180 nm, and the inset is the optical image of the device. (B) Temperature dependence of resistance under zero field and magnetic field of 5T. Resistance decreases with decreasing temperature, showing metallic behavior, and the resistance of the ferromagnetic state drops rapidly near the Curie temperature due to the loss of spin disorder scattering [36]; the inset is a schematic diagram of the device measurement configuration. Magnetoresistance $R_{xx}$ is a crucial measurement for inferring information about the interaction between itinerant charge carriers and magnetic degrees of freedom in magnetic materials [35], defined as

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Figure 2: (A) Profile line information extracted from AFM image on the edge of the FeTa$_3$S$_6$ thin film, and the inset shows the optical image of the FeTa$_3$S$_6$ device. (B) Temperature-dependent resistance with zero field and 5T magnetic field, and the inset shows a schematic diagram of the device measurement configuration. (C) Magnetoresistance measured at selected temperature with applied magnetic field $H|$c. (D) Magnetoresistance measured at $T = 10$K with applied magnetic field $H|$c. (E) Hall resistance measured at selected temperature with applied magnetic field $H|$c. (F) Determine the switching field of the FeTa$_3$S$_6$ sample by $R_{xy}$-H (black), MR (red), and $M$-H (green).

Figure 3: Measured angle-dependent magnetoresistance with the magnetic field rotates in the ac-plane (A,B) and bc-plane (C,D) at 10, 20, 40, 60K. The insets in (B,D) show the schematic of the corresponding measurement configuration. The measured angle-dependent Hall resistance with the magnetic field rotates in the ac-plane (E) and bc-plane (F).
by the normal Hall effect is observed. These results indicate that the spin–orbit coupling of FeTa$_3$S$_6$ is very strong [35]. As shown in Figure 2F, the observed switching field is very close in the magnetization measurements of FeTa$_3$S$_6$ and the magnetoelectric transport property measurements of the device. When the magnetic field changes, the spin direction of FeTa$_3$S$_6$ switches rapidly at the switching field, indicating that the crystal may be a nearly single-domain ferromagnet [25].

Figures 3A–D present the measurement results of the angle-dependent magnetoresistance of FeTa$_3$S$_6$ when the magnetic field H is gradually rotated in the ac and bc planes, that is, from the c-axis to the ab-plane. The current I is inputted along the a-axis, the angle between the external magnetic field and the normal of the sample plane is defined as $\theta$, and the interval of measured angle is 2°. The angle-dependent magnetoresistance at different temperatures is measured at $T = 9T$, where $\Delta R_{xx} = R_{xx}(\theta) - R_{xx}(\theta = 0)$. The magnetoresistance shows a changing trend with a period of 180°. When the magnetic field is rotated in the ac and bc planes, the magnitude of $R_{xx}$ is almost the same at the same angle, and the difference may be caused by a slight misalignment of the angle. It can be seen in this figure that $R_{xx}$ reaches its maximum at $\theta = 90°$ and 270°, and $R_{xx}$ reaches its minimum at $\theta = 0°$, 180°, and 360°, which means that the magnetoresistance is maximum when the magnetic field is parallel to ab-plane, and the magnetoresistance is minimum when the magnetic field is perpendicular to ab-plane, which is consistent with the property of conventional metal ferromagnets [46]. Experimental data suggest an inversion symmetry for this sample; AMR has a two-fold symmetry and is dominated by M and c-axis when field rotates in ac and bc planes [47]. At low temperatures (approximately below the Curie temperature), the curve has a sharp peak at $\theta = 90°$ and 270°, and it is caused by the sudden flip of the magnetization when the magnetic field is parallel to the sample [48], which causes the curve not to conform to the form of $\sin^2\theta$. It shows that the magnetization of the sample is not strictly saturated under the magnetic field of 9T, except for magnetic field oriented parallel to the hard axis and the easy axis [49]. In addition, the largest magnetoresistance exceeding 40% was observed at $T = 40$ K (near the Curie temperature). As the temperature increases, the curve peak disappears and turns into a smooth curve. Figures 3E,F show the measured angle-dependent Hall resistance of FeTa$_3$S$_6$ by the same measurement method. The angle-dependent Hall resistance at different temperatures is measured at $T = 9T$, where $\Delta R_{xy} = R_{xy}(\theta) - R_{xy}(\theta = 0)$. The Hall resistance shows a non-periodic curve that is symmetric along the axis of $\theta = 180°$. The maximum and minimum values of Hall resistance are both around $\theta = 90°$ and 270°. The discontinuities at low temperatures are caused by the sudden flip of the magnetization across the parallel positions ($\theta = 90°$ and 270°) [48]. We found that the peak at the maximum value at the parallel position is very close to the peak of the magnetoresistance measurement; the reason may be due to the deviation of the angle between the two terminals of the Hall bar of the device. Due to the huge perpendicular magnetic anisotropy of FeTa$_3$S$_6$, the influence of longitudinal magnetoresistance in the measurement of Hall resistance has not been completely eliminated by data processing. The novel change trend of the angle-dependent Hall resistance may be due to the presence of other Hall effects (such as topological Hall effect) in addition to the normal Hall effect and the anomalous Hall effect [28, 48]. It is also possible that there are field–induced magnetic structures in the FeTa$_3$S$_6$ thin film [50], which requires further study.

Figure 4A shows the in-plane anisotropic magnetoresistance of the FeTa$_3$S$_6$ device measured at different temperatures with the fixed 9T magnetic field rotates in the ab-plane, where current I is applied along the a-axis, $\varphi$ is defined as the angle between the direction of the b-axis and the applied magnetic field in the ab-plane, and the interval of measured angle is 2°, where $\Delta R_{xx} = R_{xx}(\varphi) - R_{xx}(\varphi = 0)$. The observed AMR is dominated by magnetization when field is in the ab-plane. Thus, the AMR follows the standard cosine-square law [51]. Due to the defined angle between H and a-axis, the magnetoresistance conforms to the form of $\sin^2\varphi$. The maximum resistance is at $\varphi = 90°$ and 270°,
and the minimum resistance is at $\phi = 0^\circ$, $180^\circ$, and $360^\circ$, which means that the magnetoresistance is highest when the magnetic field is parallel to the current, and the magnetoresistance is the lowest when the magnetic field is perpendicular to the current. As shown in the figure, FeTa$_3$S$_6$ in-plane anisotropy magnetoresistance is very small, indicating that the in-plane anisotropy of this uniaxial ferromagnet is very weak. The anisotropic magnetoresistance effect comes from the interplay of the magnetic order and spin–orbit interactions [52]. The fitting formula of anisotropic magnetoresistance can be described as follows:

$$R_{xx} = R_\parallel + (R_1 - R_\parallel)\sin^2 \phi,$$

(2)

Where $R_\parallel$ and $R_1$ represent the magnetoresistance of the in-plane magnetic field parallel and perpendicular to the current, respectively. Figure 4B shows the fitting results of the in-plane magnetoresistance angle curve (for clarify, the data are equally spaced in the vertical direction), the hollow point curve is the experimental data, and the solid point curve is the fitting result. It can be found that the measured curve is relatively consistent with the fitting curve, and part of the slight deviation may be because the sample placement is not completely parallel to the magnetic field; therefore, the data are to be mixed with out-of-plane magnetoresistance components [53].

CONCLUSION

We successfully prepared ferromagnet FeTa$_3$S$_6$ single crystals. XRD, SEM and Curie temperature measurements prove their elemental composition. The magnetic and the magnetoelectric transport properties of the devices were measured. The results show that FeTa$_3$S$_6$ exhibited sharp switching of magnetization, butterfly-shaped double-peak magnetoresistance, anomalous Hall effect, and anisotropic magnetoresistance effects at low temperatures. The magnetoresistance exceeds 10% at $T = 10$ K, and the maximum anisotropic magnetoresistance exceeds 40% when the magnetic field of 9T rotates from out-of-plane to in-plane. The novel change in trend of the angle-dependent Hall resistance may be attributed to the existence of the topological Hall effect or the existence of other magnetic structures. The specific reasons need to be further studied. In addition, in-plane anisotropic magnetoresistance in the form of $\sin^2 \phi$ was measured. In the future, we will explore the magnetoelectric transport properties of limit thickness FeTa$_3$S$_6$ films by exfoliating thinner samples, and further study the magnetoresistance and Hall effect of FeTa$_3$S$_6$ to provide potential application opportunities for FeTa$_3$S$_6$ in promising fields such as magnetoelectricity and spintronics.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

Q-LX and Y-QM conceived the idea. Y-QM and J-JG performed the experiments and conducted the characterization. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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