Field-induced metamagnetism transition with anisotropic magnetoresistance in helical magnetic order on MnRuP single crystals

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Measurements of physical properties, including transport and magnetic properties and thermal conductivity, have been performed on single crystal MnRuP with helical magnetism structure. A field-induced first-order metamagnetism transition with a magnetization jump is discovered when the magnetic field is applied perpendicular to the *c* axis. The arising transition is a result of the competition between magnetic energy and elastic energy with a complex noncollinear character in the vicinity of the metastable state in MnRuP, which is due to the transition from the incommensurate helical phase to the commensurate Yafet-Kittel ferrimagnetic phase or from the helical phase to the conical phase. It is worthwhile to note that both negative and positive magnetoresistance (MR) are observed when the field is parallel or perpendicular to the electric current, respectively, which is rarely found in the other system simultaneously. Such positive MR is unexpected on the basis that the application of magnetic field should favor a low-resistive state due to alignment of spins. The ability to manipulate magnetic properties with current directions may pave the way to a new method of realizing magnetic memories based on the spin internal degrees of freedom.

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I. INTRODUCTION

The metallic systems with helical magnetism exhibit a range of unusual behavior such as superconductivity in CrAs and MnP under an external pressure [1–3], quantum phase transition [4], and giant magnetoresistance [5,6]. Helical magnetic order essentially arises as a result of the Dzyaloshinsky-Moriya (DM) interaction which involves two or more competing magnetic exchange interactions, for example, nearest neighbor and next-nearest neighbor interactions or two-sublattice exchange interaction [7,8]. Therefore the intriguing physical properties of these systems are very sensitive to the external field, pressure, and doping, which often disturb the subtle balance in the correlation leading to novel effects.

It is therefore of interest to investigate the materials with helical magnetic structures. We spotlighted ternary phosphide MnRuP with helical magnetism structure, whose properties have not been investigated sufficiently so far [9–11]. MnRuP belongs to the Fe2P-type crystal hexagonally structure [space group $P62m$, $a = 6.25(7)$ Å, $c = 3.52(3)$ Å]. An earlier study of polycrystalline samples shows three magnetic transitions: an incommensurate antiferromagnetic helical transition at $T_N = 250$ K, and two first-order magnetic transitions phase taking place at $T_1 = 180$ K and at $T_2 = 100$ K with a reorientation of the magnetic moments [9]. Neutron diffraction of MnRuP indicates that three distinct localized magnetic moments in the Mn atoms of the layers, ranging in site 1 from $1.44\mu_B$ to $1.02\mu_B$ and in sites 2 and 3 from $3.12\mu_B$ to $2.20\mu_B$. For $T_1 < T < T_N$, the magnetic structure found is an incommensurate spiral structure with propagation vector $q_1 = (0,\ q_y\, 0)$, and the localized Mn moments contained in the *a-c* plane. With temperature down to T_1, a new set of satellites appear which require a second propagation vector $q_2 = (q_x,\ 0,\ 0)$.

In this paper, we have synthesized single crystals of MnRuP and carefully measured the transport and magnetic properties of anisotropy, specific heat, and thermal conductivity. Our key finding of this study is the observation of a field-induced first-order-like magnetic transition within the incommensurate helical antiferromagnetic transition when the magnetic field is applied perpendicular to the *c* axis at a critical field. This is the result of competition between magnetic energy and elastic energy in the vicinity of the metastable state in MnRuP. Another noteworthy finding is that both negative and positive magnetoresistance (MR) are observed when the field is parallel or perpendicular to the electric current at the critical field, respectively, due to the spin flop phase transitions at the critical field. Such positive MR is unexpected on the basis that the application of magnetic field should favor a low-resistive state due to the alignment of spins and both negative and positive MR are rarely found in one crystal simultaneously for other systems. The ability to ma-

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nipulate magnetic properties with current directions allows new strategies to design magnetic/electronic devices. Realization of control and detection of helicity may open up new possibilities for magnetic memory applications based on helimagnets.

II. EXPERIMENTAL METHODS

The MnRuP crystals were grown using the Sn-flux method. The starting materials were Mn (Cerac, powder, 99.95%), Ru (Alfa Aesar, powder, 99.95%), P (Alfa Aesar, powder, 99.999%), and Sn (Cerac, shot, 99.999%). All of the manipulations were done in an argon-filled glove box with moisture and oxygen levels less than 1 ppm. The materials with an atomic ratio of Mn : Ru : P : Sn = 1 : 1 : 1 : 36 were added to an alumina crucible, which was placed in a quartz ampoule, and subsequently sealed under a reduced pressure of 10^{-4} Torr. The quartz ampoule was heated up to 650 °C for 20 h, held there for a period of 8 h, then heated up to 1100 °C for 15 h, held for 6 h, and slowly cooled down to 600 °C for 50 h. At this temperature, liquid Sn flux was filtered by centrifugation. The resulting products were metallic needle-shaped black crystals with dimensions up to $0.25 \times 0.25 \times 3\,\mathrm{mm}^3$. The crystals were grown along the c axis and they were stable in air and water.

The room temperature XRD lines could be indexed to MnRuP-type hexagonal structure with the lattice constants $a = 6.26(5)$ Å and $c = 3.53(3)$ Å. Energy-dispersive x-ray (EDX) analysis on these crystals was carried out using a Hitachi S-2700 scanning electron microscope. The results show that the chemical compositions are 33(2)% Mn, 34(2)% Ru, and 33(2)% P. No Sn elements were detected in the crystals analyzed. The magnetic susceptibility was measured in the temperature range 2–300 K using a superconducting quantum interference device VSM magnetometer of Quantum Design Company. The resistivity, specific heat, and thermal conductivity was measured between 2 and 300 K in a PPMS system of Quantum Design Company.

III. RESULTS AND DISCUSSION

A. Structure and characterization

Figure 1(a) shows the structure of MnRuP, which indicates MnRuP crystallized in a hexagonal structure. Figure 1(b) shows a photo of single crystals of a MuRuP section along the c axis. A standard hexagonal section is shown in this picture. Figure 1(c) shows the magnetic structure of MnRuP when $T_1 < T < T_N$, an incommensurate spiral structure with propagation vector $q_1 = (0,\ q_y\, 0)$, and the localized Mn moments contained in the a-c plane.

B. Transport and magnetic properties in MnRuP

Figure 2 shows a complete set of experimental results for MnRuP including resistivity, magnetic properties, and thermal conductivity. Figure 2(a) shows the temperature dependent resistivity for MnRuP at zero magnetic field with the current along the c axis. MnRuP exhibits metallic behavior which means it is an itinerant system. An obvious loop is observed at 100 K corresponding to the first-order magnetic transition at

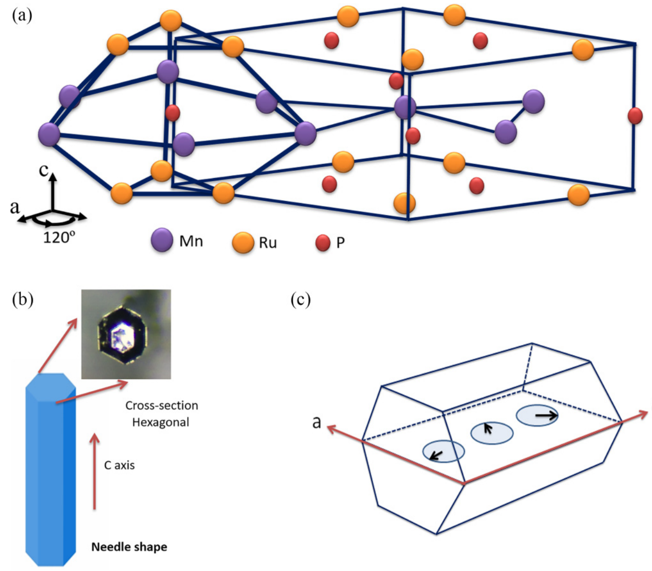

FIG. 1. (a) Structure of MuRuP. (b) Photo of single crystals of MuRuP section along the c axis. (c) Magnetic structure of MnRuP when $T_1 < T < T_N$, an incommensurate spiral structure with propagation vector $q1 = (0,\ q_y\, 0)$, and the localized Mn moments contained in the a-c plane.

T_2. Three magnetic transition peaks show from the derivation of resistivity: an antiferromagnetic transition at $T_N = 250$ K, two first-order magnetic transitions at $T_1 = 180$ K and at $T_2 = 100$ K, respectively. Although the AC magnetic susceptibility of MnRuP has been reported in the literature, the DC magnetic susceptibility of MnRuP shown in Fig. 2(b) is from heating and cooling experiments in this work. Three magnetic transitions show clearly from DC magnetic susceptibility corresponding to the transitions from resistivity. The specific-heat data C/T will be used to get the electronic contribution $\gamma = 13\,\mathrm{mJ\,K^{-2}\,mol^{-1}}$ and the confirmed three magnetic transitions in Ref. [11]. The high temperature magnetic susceptibility of MnRuP is shown in Fig. 2(c) with the Curie-Weiss law, and the fitted effect magnetic moment $\mu_{\mathrm{eff}} = 5.36\,\mu_B$ is shown in the inset of Fig. 2(c), this is fit for the valence of Mn^{+3} magnetic moment Mn^{+3} $(RuP)^{-3}$ [11], from the formula of $\mu_{\mathrm{eff}} = [n(n+2)]^{1/2} = 4.8\,\mu_B$, n is the unpaired electrons when the Mn^{+3} has four unpaired electrons. These magnetic transitions are also confirmed from the derivation of thermal conductivity. The measured thermal conductivity κ of MnRuP are shown in Fig. 2(d). The thermal conductivity increases abruptly below about 100 K which corresponds to $T_2 = 100$ K with a reorientation of the magnetic moments accompanying the first transition which would suggest strong coupling between the charge carriers and the lattice vibrations.

C. Field-induced first-order magnetic transition

Magnetic measurements were carried out for MnRuP. The influence of the temperature and the magnetic field on the incommensurate magnetic structure is of independent interest. Figures 3(a) and 3(b) shows the magnetic susceptibility $\chi = MH$ as a function of temperature at various magnetic fields applied both parallel and perpendicular to the c axis. Three distinguishable magnetic transitions shown at

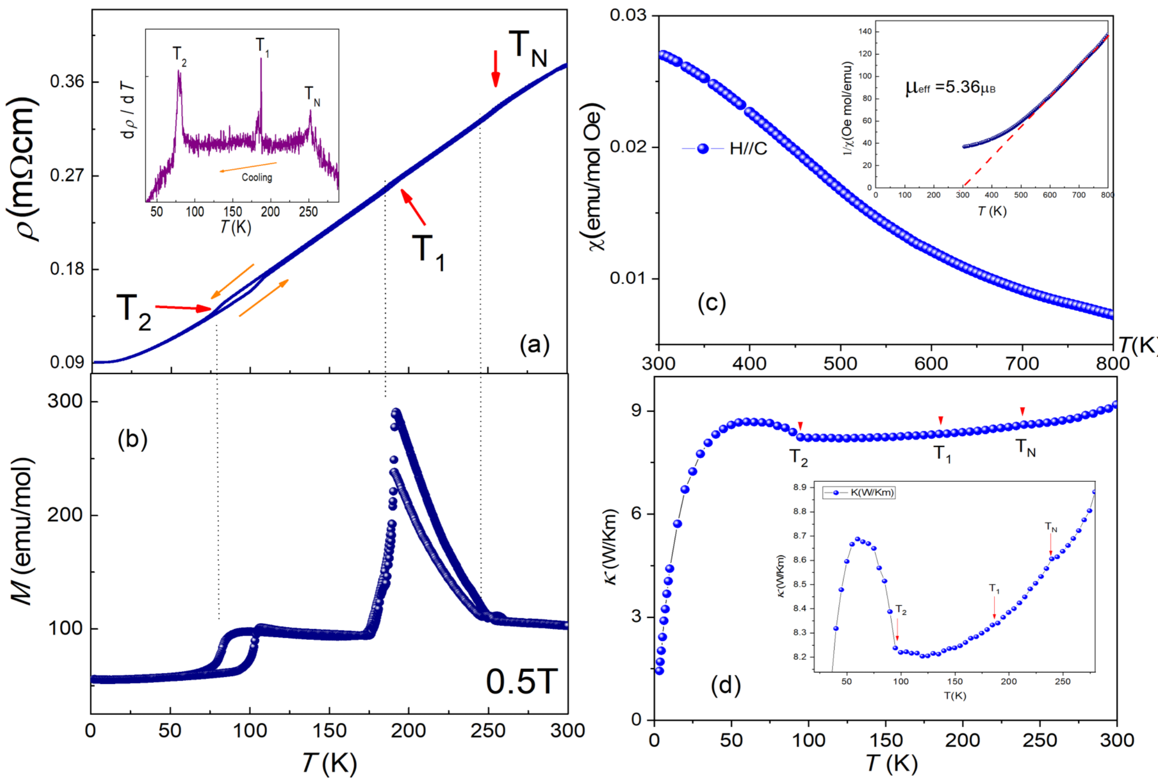

FIG. 2. (a) Temperature dependence of resistivity. Inset of (a): temperature dependence of derivation of resistivity. (b) Temperature dependence of the magnetic susceptibility, (c) temperature dependence of the high temperature magnetic susceptibility from 300 to 800 K. Inset of (c) shows the temperature dependence of $1/\chi$ and the fitted effect magnetic moment. (d) Temperature dependence of thermal conductivity, for MnRuP.

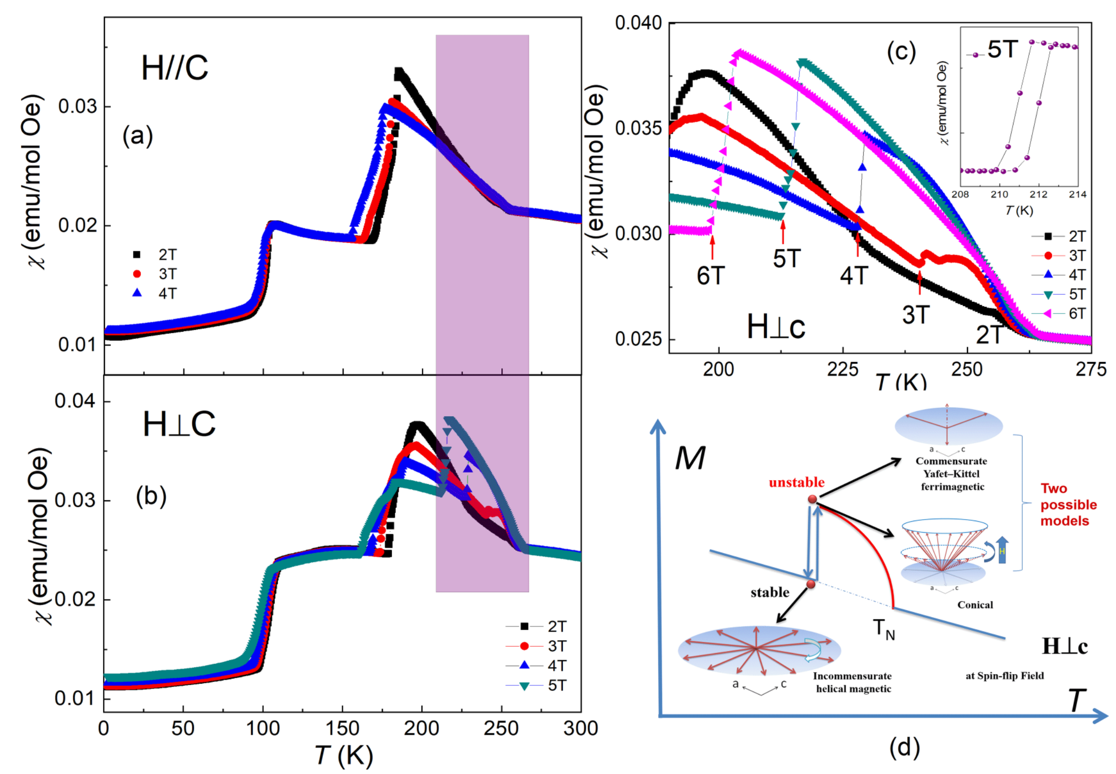

FIG. 3. (a), (b) Anisotropic magnetic susceptibility χ versus field for $H//c$ and $H \perp c$. (c) Detail of this transition at more various fields. Inset of (c) shows temperature hysteresis of magnetization at 5 T. (d) Two possible models of field-induced first-order magnetic transition.

$T_N = 250$ K, $T_1 = 180$ K, and $T_2 = 100$ K are obvious. For the two first-order magnetic transitions with a reorientation of the magnetic moments taking place at $T_1 = 180$ K and at $T_2 = 100$ K, these transition temperatures decrease when the field increases which is typical in antiferromagnetic (AFM) transitions.

For $T_1 < T < T_N$, at low field, the system keeps the incommensurate helical phase. When increasing the field above 2 T, an obvious bump and a sharp first-order-like transition take place when $H \perp c$ axis at the M-T plot. Figure 3(c) shows the detail of this transition at various fields. The bump of magnetization then abruptly decreases at the first-order transition temperature. This field-induced transition continuously moves to low temperature quickly when increasing the field. A clear loop of temperature hysteresis of magnetization shown in the inset of Fig. 3(c) indicates that this is a first-order field-induced magnetic transition.

To understand this field-induced first-order magnetic transition, we provide a model of two possibilities from low to high critical field shown in Fig. 3(d): the incommensurate helical phase to the commensurate Yafet-Kittel ferrimagnetic phase or from the helical phase to the conical phase. The Yafet-Kittel model [8,12,13] which considers competition between two-sublattices ferrimagnet with an antiferromagnetic exchange interaction in each sublattice so as to system undergo with increase in temperature a first order transition from antiferromagnetic state in low temperature side to ferrimagnetic state in high temperature side. Normally, at zero magnetic field, when this first-order transition takes place as the temperature changes in a magnetic system, the magnetic exchange interactions J in different sublattices are sensitive to the length of the lattice and changes its sign at the critical length with changing temperature; it is the result of competition between magnetic energy and elastic energy in the vicinity of the metastable state. An incommensurate helical magnetic structure is not robust and is unstable in the high field due to the competition between many interactions, and it has a complex noncollinear character. So the incommensurate helical magnetic order of MnRuP essentially arises from the first-order AFM-Ferrimagnetic (FIM) magnetic transition in the high field which disturbs the subtle balance leading to the comparable magnitude between magnetic energy and elastic energy. Martynov calculated the influence of the temperature and the magnetic field on the incommensurate helical magnetic structure in CuB2O4 [8]. There are rare cases of this transition within the Yafet-Kittel model applying in the helical order in the high field, and maybe the exchange interactions J connecting different sublattices change sign at the critical length when changing the temperature above the critical field as in the Yafet-Kittel model. There are rare cases of this transition within the Yafet-Kittel model applying in the helical order.

D. Field-induced anisotropy magnetoresistance (MR)

We report an extensive study of anisotropy magnetoresistance in MnRuP with a combination magnetic field and current along different crystal axes. Figure 4 shows one of the conditions of M-H and MR-H with the field perpendicular to the c axis and the current along the c axis. This enhancement of the MR should be readily observable by sweeping the magnetic field across the spin flop transition at a same characteristic field H at various temperatures. If decreasing the temperature, the characteristic field H_c will increase corresponding to the M-T plot at various fields. The change of M-H like a spin flop transition due to the field-induced first-order magnetic transition observed from M-T only happened with $H \perp c$ axis. Such positive MR is unexpected on the basis that the application of magnetic field should favor a low-resistive state due to alignment of spins.

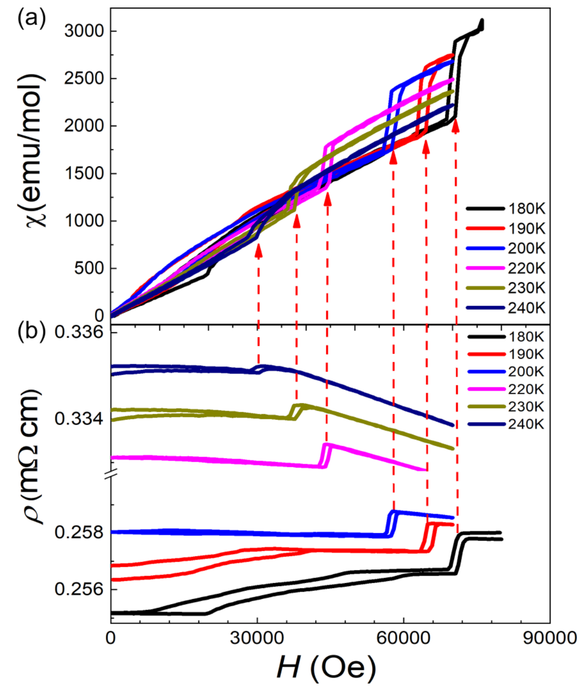

FIG. 4. (a) Magnetic field dependence of M. (b) Magnetic field dependence of resistivity versus temperature with the field perpendicular to c axis and the current along c axis.

In order to study the effect of field-induced anisotropy magnetoresistance, we carefully measure a complete set of MR with magnetic field and current are along different crystal axes including five distinct situations at 180 K as shown in Fig. 5.

It is worthwhile to note that with $H \perp c$ axis both sharp negative and positive MR are observed with the field parallel or perpendicular to the electric current, respectively, as shown in Figs. 5(a)–5(c). When $H // c$, there is no MR effect when the field gets to $H_c = 7.2$ T corresponding to the no spin flop induced by field along the c axis shown in Figs. 5(d) and 5(e). From these results, one can speculate that positive MR only happens with the spin moment parallel to the current accompanying spin flop. Negative MR only happens with the spin moment perpendicular to the current accompanying spin flop. So the field-induced inherent magnetic constituent with anisotropic geometry leads to the anisotropic electrical transport governed by spin-associated scattering.

IV. CONCLUSIONS

We synthesized single crystals of MnRuP and carefully measured their anisotropic transport and magnetic properties.

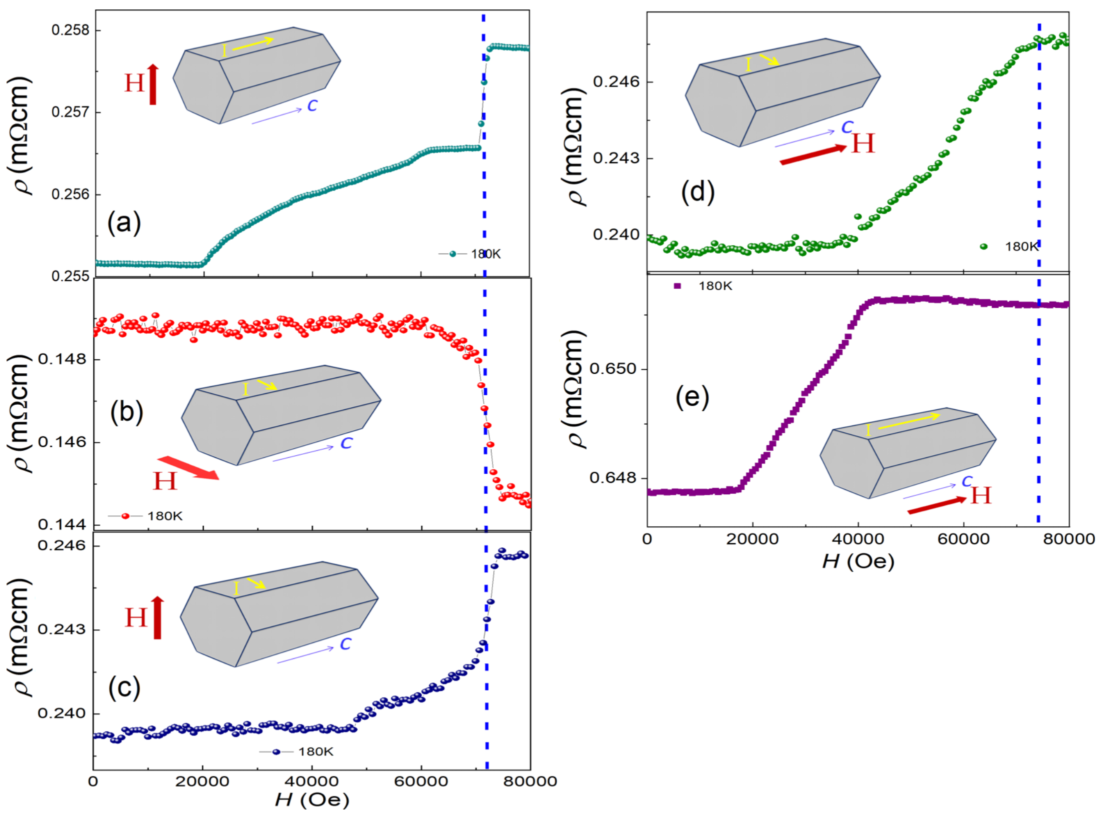

FIG. 5. Anisotropy magnetic resistivity in MnRuP with combination magnetic field and current along different crystal axes at 180 K.

Our key finding of this study is the observation of an obvious field-induced first-order antiferromagnetic-ferrimagnetic transition. This transition arises from the competition between magnetic energy and elastic energy in the vicinity of the spiral magnetic order metastable state in MnRuP. Interestingly, this transition is a rare occurrence within the Yafet-Kittel model when applied to the helical order. Another noteworthy finding is that we observed both negative and positive magnetoresistance (MR) accompanying spin flop transitions in MnRuP. Most metallic systems with spin flop transitions systems show negative MR (low resistive state) due to the alignment of spins, but in the MnRuP crystal, the field-induced inherent magnetic constituent with anisotropic geometry leads to the anisotropic electrical transport governed by spin-associated scattering. Overall, our present work provides valuable insights into the field-induced magnetic transition and the electrical transport properties of MnRuP, which could open up exciting possibilities for the development of novel magnetic/electronic devices.

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