

High-pressure synthesis of orthorhombic SrIrO₃ perovskite and its positive magnetoresistance

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The orthorhombic SrIrO₃ perovskite was synthesized under 5 GPa and 1000 °C. It is paramagnetic below about 170 K and transfers to an unknown magnetism under higher temperature. A band type metal to insulator transition caused by a pseudogap was observed at about 44 K. Interestingly a positive magnetoresistance, i.e., resistance increased with applying magnetic field, was observed in the orthorhombic SrIrO₃ perovskite below about 170 K. © 2008 American Institute of Physics.
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I. INTRODUCTION

Recently, the 4*d*- and 5*d*-electron transition oxides, e.g., the ruthenates and iridates, have received growing attention for their exotic physical properties. It is well known that Sr₂RuO₄, with the K₂NiF₄-type structure, is a superconductor of unconventional *p*-wave pairing mechanism.¹ Comparing with the 3*d* electrons, the *d*-electron orbitals of the 4*d* and 5*d* electrons are highly extended. So the 4*d*- and 5*d*-electron transition oxides are usually regarded as metals. However, many of the iridates are nonmetallic, due to the distorted structure, being contrary to the corresponding ruthenates. Most iridates show exotic magnetism. For example, the ambient pressure phase of BaIrO₃ is the first known ferromagnet that contains a 5*d* transition metal cation in the ternary oxides.² This weak ferromagnetism originates from spin polarization of Ir cations rather than from spin canting.³

The alkaline-earth iridate AIrO₃ (where A is the alkaline-earth element Ca, Sr, and Ba) is an important system of oxide iridates. However, the crystal structure and physical property of AIrO₃ strongly depend on size of A-site cations. CaIrO₃ adopts the postperovskite structure with the space group *Cmcm*.⁴ It is an antiferromagnetic insulator.⁵ The ambient phase of BaIrO₃ is very closely related to that of the 9R BaRuO₃, so it is denoted to 9R.⁶ It is a weak ferromagnetic semiconductor.³ Although the tolerant factor of 0.992, as calculated from the ion radii in Shannon table,⁷ is approximately equal to 1, SrIrO₃ adopts the distorted 6H BaTiO₃ structure with the space group *C2/c* at ambient condition. So it is denoted to “6H” for its similarity with the 6H form.⁸ The Sr–Ir–O system, which includes SrIrO₃, Sr₂IrO₄ and Sr₄IrO₆, has the potential application in catalysis and electrochemistry.⁹ Under high temperature and high pressure, the structure of SrIrO₃ becomes an orthorhombic perovskite with the space group *Pnma*, which can be quenched to ambient pressure as a metastable phase.⁸ The perovskite-type SrIrO₃ is denoted to 3C since it has the cubic perovskite nature. In the oxide iridates, the orthorhombic SrIrO₃ perovskite is the only compound with the GeFeO₃-type structure.

The ambient phase of SrIrO₃ is the first known paramagnetic metal in the ternary oxide iridates. Liu *et al.* prepared the SrIrO₃ films by laser ablating method and measured the electrical properties.¹⁰ With increasing oxygen pressure, it gradually transfers to a metal from a semiconductor, which indicates that the oxygen content enhances the metallicity. Up to now, there are very few reports about the properties of orthorhombic SrIrO₃ perovskite except that reported by Longo *et al.* more than 30 years ago, who carried out measurements at liquid nitrogen and found that SrIrO₃ is a paramagnetic metal.⁸ In order to investigate more details about the physical property of SrIrO₃, especially its low temperature behavior, we synthesized the orthorhombic SrIrO₃ perovskite by treating the ambient pressure phase with high-temperature and high-pressure method and investigated in detail the structural, magnetic, and electrical properties. A positive magnetoresistance (PMR) effect at low temperature as well as a metal insulator transition was observed in the orthorhombic SrIrO₃ perovskite.

II. EXPERIMENT

The ambient phase of SrIrO₃ was synthesized by using the method of conventional solid-state chemical reaction. The starting materials were 99.99% SrCO₃ and 99.9% iridium metal. Stoichiometric quantities of materials were mixed together, ground about 30 min in an agate mortar, and placed into an Al₂O₃ crucible. Then the powder was calcined for about 12 h at 900 °C in air. The calcined powder was reground, pressed into a pellet at the pressure of 10 MPa, and sintered at 1000 °C for about 72 h in air with two intermediate grindings.

A conventional cubic-anvil-type high-pressure facility was used to perform the high-pressure and high-temperature experiments. The ambient phase of SrIrO₃ was pressed into a pellet of 5.0 mm diameter and then wrapped with gold foil to avoid contamination. The pellet was put into an *h*-BN sleeve which was in turn inserted into a graphite tube heater. Pyrophyllite was used as the pressure-transmitting medium. The treating process was carried out at 5.0 GPa and 1000 °C for about 30 min, followed by a quench in air from high temperature before pressure release. When the electric current in

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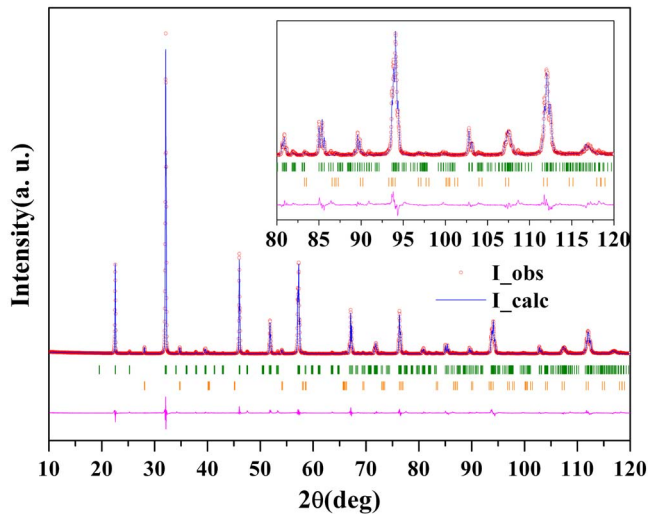


FIG. 1. (Color online) The experimental (open circle) and fitted (line) XRD patterns for the orthorhombic SrIrO₃ perovskite. The difference plot between observed and calculated patterns is shown at the bottom. The positions of the Bragg reflections are shown by the vertical lines. Inset: the enlargement in the range 80°–120°.

graphite tube heater is cut, the temperature of sample will be about 30 °C after one minute, due to the small volume of heater. The product adopted the orthorhombic perovskite structure, which was a black and hard polycrystal bulk.

The structure of our sample was checked by the powder x-ray diffraction (XRD) with Cu *K*α radiation at room temperature, using a Rigaku diffractometer (MXP-AHP18). The experimental data were collected in 2θ steps of 0.02° and 3 s counting time in the range $10^\circ \leq 2\theta \leq 120^\circ$ and analyzed with Rietveld method using the FULLPROF program.¹¹ The relationships of magnetic susceptibility versus temperature at different magnetic fields were obtained using a superconducting quantum interference device magnetometer (Quantum Design, MPMS-5S) in the range of 5–300 K. Data were collected under both zero-field-cooled (ZFC) and field-cooled (FC) conditions. The magnetic field dependence of magnetization was measured at 5 K from –1 to 1 T. The temperature dependences of electrical resistivity in the range of 3–300 K at different magnetic fields and field dependences of electrical resistivity in the range of 0–7 T at different temperatures were obtained using the four-probe method on an Oxford Maglab measuring system.

III. RESULTS AND DISCUSSION

Figure 1 shows the observed and fitted XRD patterns of the orthorhombic SrIrO₃ perovskite, and the inset shows the enlargement in the range of 80°–120°. The lower vertical lines in Fig. 1 are the Bragg reflections of IrO₂. According to

the refined results, the content of IrO₂ is about 3% in the whole sample. IrO₂ is a paramagnetic metal with very small electrical resistivity and magnetic susceptibility in a large temperature range.^{12,13} Because of this, the effects of impurity for our experimental data presented below are small. The data are analyzed with the Rietveld method. The obtained R_p , R_{wp} , and R_{exp} factors are 7.24%, 10.3%, and 4.21%, respectively, which indicated the good consistency of the refined results. The lattice parameters are refined to be $a = 5.5909(1)$ Å, $b = 7.8821(1)$ Å, and $c = 5.5617(1)$ Å, respectively. The shrinkage of volume per one chemical formula unit is equal to about 3.6%, comparing with the ambient phase of SrIrO₃.⁸ Table I lists the Wyckoff notation, coordinates, and thermal parameters. The average Sr–O and Ir–O distances are 2.809(14) and 2.021(9) Å, respectively. So the tolerance factor calculated from the bond distances is 0.983(9), being close to the theoretical value of 0.992. The O(1)–Ir–O(2) angles deviate from 90°, which indicates that the IrO₆ octahedron is distorted from the ideal one. The Ir–O–Ir angles are 156.49(8)° and 153.7(5)°, which are close to those in Sr₂IrO₄ and Sr₃Ir₂O₇,^{14,15} so the exchange interactions between Ir cations through the O anions are not linear.

Figure 2(a) shows the temperature dependences of magnetic susceptibility of the orthorhombic SrIrO₃ perovskite at different magnetic fields. There is no obvious deviation between ZFC and FC curves, indicating the compound is basically not ferromagnetic, so Fig. 2(a) only shows the ZFC modes. The inset shows the enlargement in the range of 100–300 K. There is an obvious turning point at about 170 K, being indicated with T^* in the inset, which may be attributed to the transition from paramagnetism to another magnetism (local magnetic order) at higher temperature. T^* does not change with increasing magnetic field. This transition temperature is consistent with that in the ρ - T curve in the following discussion. Figure 2(b) shows the magnetic field dependence of magnetization at 5 K. There is no hysteresis phenomenon in the M - H curve, which indicates no long-range ferromagnetic order. The concave downward curvature at low field in the M - H curve indicates the exchange-enhanced paramagnetism.¹⁶

The magnetic susceptibility data below about 150 K can be fitted to the modified Curie–Weiss law

$$\chi = \frac{C}{T - \theta} + \chi_0, \quad (1)$$

where C , θ , and χ_0 are the Curie constant, paramagnetic Curie temperature, and temperature independent magnetic susceptibility, respectively. The effective magnetic moment per Ir cation (μ_{eff}) is obtained from Curie constant C through the formula $\mu_{\text{eff}} = 2.83\sqrt{C}$. The μ_{eff} is equal to 0.117(7) μ_B ,

TABLE I. Atomic coordinates for the orthorhombic SrIrO₃ perovskite.

Atom	Site	x	y	z	B (Å ²)
Sr	4c	0.4901(7)	0.25	0.5085(7)	0.12(3)
Ir	4b	0	0	0.5	0.94(1)
O(1)	4c	0.073(2)	0.25	0.506(5)	3.5(2)
O(2)	8d	0.714(2)	0.044(1)	0.292(2)	1.1(2)

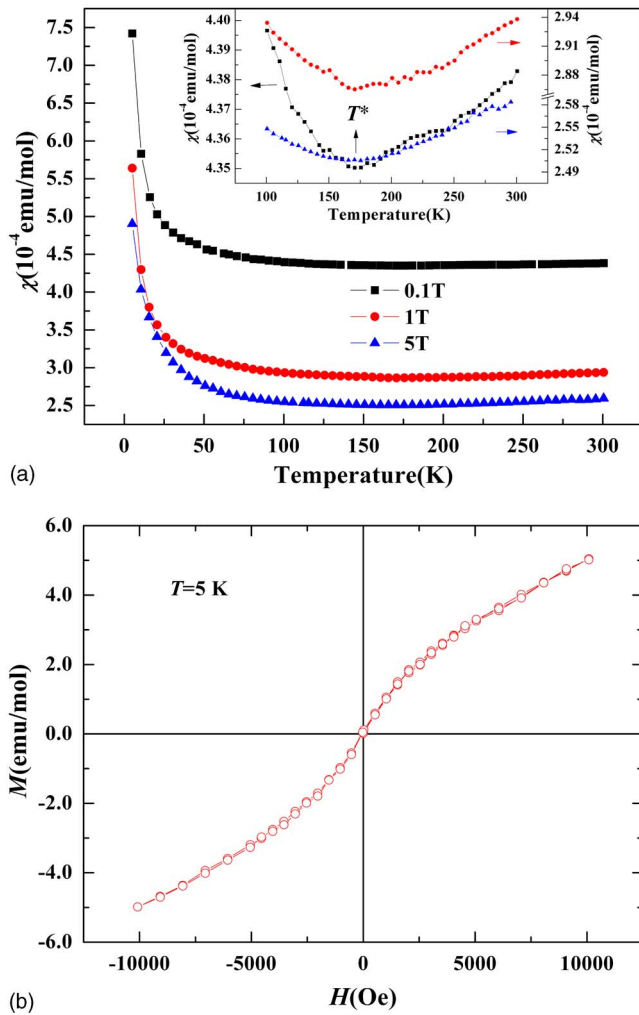


FIG. 2. (Color online) (a) Temperature dependences of magnetic susceptibility of the orthorhombic SrIrO₃ perovskite at different magnetic fields. Inset: the enlargements in the range of 100–300 K. (b). Magnetic field dependence of magnetization at 5 K.

0.119(7) μ_B , and 0.151(2) μ_B for the 0.1, 1 and 5 T curves, respectively. The μ_{eff} is less than the theoretical Hund's-rule value of about 1.73 μ_B /Ir for one unpaired 5*d* electron in the Ir⁴⁺ cation, as calculated through the formula $\mu_{\text{eff}} = 2\sqrt{S(S+1)}$, where $S=1/2$. The small Ir moments are also found for the Ir⁴⁺ cation in the ferromagnetic "9R" BaIrO₃ (0.13 μ_B /Ir), Sr₂IrO₄ (0.05 μ_B /Ir) and Sr₃Ir₂O₇ (0.69 μ_B /Ir).^{3,17,18} The value of μ_{eff} indicates that the Ir⁴⁺ cation partly loses the local moment, which is contributed to the strong hybridization between Ir and O ions, due to the large extension of *d*-electron orbitals, which enhances crystal field splittings and the 5*d* 2*p* hybridization between Ir and O ions.¹⁷ The temperature independent magnetic susceptibility χ_0 is equal to 4.234(4) × 10⁻⁴, 2.766(3) × 10⁻⁴, and 2.29(1) × 10⁻⁴ emu/mol at 0.1, 1, and 5 T, respectively. Although the material is paramagnetic, the magnetic susceptibility is decreasing with increasing magnetic field. The paramagnetic Curie temperature θ is approximately equal to zero, which indicates that the magnetic interaction between the two electronic spins on the nearest-neighbor Ir sites is negligible. However, for most iridates, there is ferromagnetic interaction between the adjacent electronic spins. For example, the "9R"

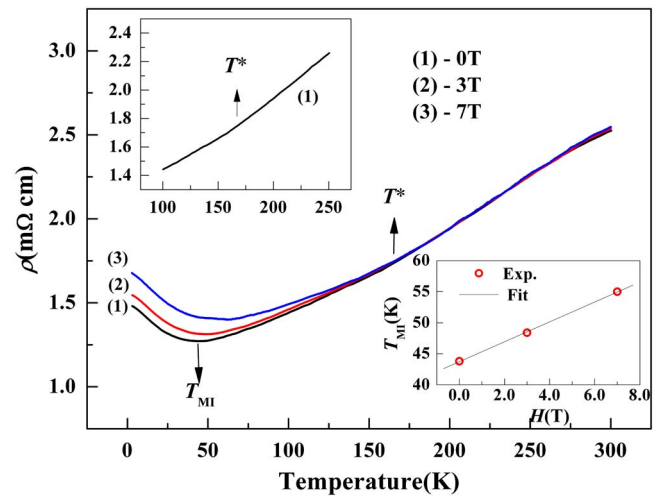


FIG. 3. (Color online) Temperature dependences of electrical resistivity of the orthorhombic SrIrO₃ perovskite at different magnetic fields. Inset in the top left corner: the enlargement at 0 T in the range of 100–250 K. Inset in the bottom right corner: the relationship of MIT temperature T_{MI} vs magnetic field.

BaIrO₃ and the Ruddlesden–Popper series of Sr₂IrO₄ and Sr₃Ir₂O₇ are weak ferromagnetic.^{3,17,18} Unlike the quasi-one-dimensional chain type structure of the "9R" BaIrO₃ and the two-dimensional structure of Sr₂IrO₄ and Sr₃Ir₂O₇, the orthorhombic SrIrO₃ perovskite adopts unique three-dimensional perovskite structure in the oxide iridates. Compared with the Sr₂IrO₄ and Sr₃Ir₂O₇, there is the larger distortion in the IrO₆ octahedra of the orthorhombic SrIrO₃ perovskite, which weakens the superexchange interaction between adjacent electronic spins of Ir cations, so the orthorhombic SrIrO₃ perovskite is paramagnetic. The similar phenomenon also exists in the oxide ruthenates. For example, the perovskite SrRuO₃ is a ferromagnet, but the isostructural and isoelectronic compound CaRuO₃ is paramagnetic, due to the large structural distortion in the latter.^{19,20}

The temperature dependence of electrical resistivity in the range of 3–300 K of the orthorhombic SrIrO₃ perovskite is shown in Fig. 3. The resistivity of about 2.5 mΩ cm at room temperature is close to that in Ref. 8. It is clear that the orthorhombic SrIrO₃ perovskite is a metal at high temperature and becomes insulatorlike at lower temperature, with the metal-insulator transition (MIT) temperature T_{MI} about 44 K. There is no obvious anomaly in the χ -*T* curve at T_{MI} , which indicates that the MIT transition in the orthorhombic SrIrO₃ perovskite is not due to the magnetic order change. But, there is a slight kink at T^* (~170 K) in the ρ -*T* curve, as shown in the inset in the top left corner, which coincides with the turning point in the χ -*T* curve in the aforementioned magnetic properties. The wave function of the 5*d* orbitals is highly extended comparing with that of the 3*d* ones, so the oxide iridates should be metallic, like the corresponding ruthenates. However, the ρ -*T* curve of the orthorhombic SrIrO₃ perovskite behaves insulatorlike below about 44 K. The distortion of IrO₆ octahedron results in the decreasing metal-oxygen-metal orbital overlap and the gap formation, which can explain the unusual electrical property of the orthorhombic SrIrO₃ perovskite at low temperature. We performed the

XRD diffraction experiments down to 10 K and did not find any obvious structural phase transition at low temperature (the results are not shown). So the MIT in the orthorhombic SrIrO₃ perovskite is related to the electronic phase transition. The spoonlike ρ - T curve and MIT at low temperature are very similar with those of the 9R BaRuO₃, which shows a pseudogap phenomenon in transport, magnetic, and optical properties.²¹ In the 9R BaRuO₃, there is an indirect gap near the Fermi surface,²² which results in its novel physical properties. According to the band calculation, there is also a gap of about 1 eV near the Fermi face at the Γ point of band structure in the orthorhombic SrIrO₃ perovskite.²³ The bands that are cross through Fermi surface are not filled completely, so it is metallic at high temperature. While temperature is lower than T_{MI} , the gap opens, which makes the orthorhombic SrIrO₃ perovskite transfer to a band insulator, like the 9R BaRuO₃ or the “9R” BaIrO₃.^{21,24}

In order to study the influence of magnetic field to the orthorhombic SrIrO₃ perovskite, we measured the temperature dependences of electrical resistivity at different fields, with the results being shown in Fig. 3. Under high magnetic field, the resistivity does not change above 170 K, but is increasing below 170 K. Therefore there is a PMR behavior in the orthorhombic SrIrO₃ perovskite, while the onset temperature of the MR is 170 K, which corresponds to the transition temperature T^* in the ρ - T and χ - T curves. The unknown magnetism above 170 K results in the loss of magnetoresistance effect. The inset in the bottom right corner shows the relationship of T_{MI} versus magnetic field. T_{MI} is increasing with magnetic field, and the value of $\partial T_{MI}/\partial H$ is equal to 1.60(3) K/T. Figure 4(a) shows the relationships of MR [$MR=(\rho_H-\rho_0)/\rho_0$] versus temperature at different magnetic fields, as obtained from Fig. 3. There is no abnormal change near the T_{MI} in the MR- T curves and the maximum MR is at 20 K. We consequently investigated the PMR in the orthorhombic SrIrO₃ perovskite by calculating the relationships of MR versus magnetic field at different temperatures, with the results being shown in Fig. 4(b). The solid lines are linear fits to the data at high fields. The relationships of MR versus H^2 at different temperatures are not linear. We obtain the maximum MR at 20 K, which is consistent with that from MR- T curves. While temperature is higher than T^* , the electrical resistivity does not change at all with increasing magnetic field, and the MR- H line is almost parallel with the H axis. The PMR effect exists in many compounds and is a universal physical phenomenon.²⁵ However, the electrical resistivity of most ternary oxide iridates is insensitive to the magnetic field up to 10 T, e.g., the “9R” BaIrO₃ and Sr₂IrO₄.^{4,17} The PMR effect exists also in Sr₃Ir₂O₇ below 15 K in a field of 0.05 T.¹⁸ While the magnetic field is larger than 0.05 T, the MR of Sr₃Ir₂O₇ becomes negative, which is attributed to the magnetization reversal at low temperature. The orthorhombic SrIrO₃ perovskite is an exceptional compound among the known iridates in terms of its unusual PMR. This is believed to resulting from its special three-dimensional GdFeO₃-type perovskite structure.

For the ordinary magnetoresistance (OMR), the MR is proportional to the square of magnetic field at low field within the band theory, which arises from curved orbits in a

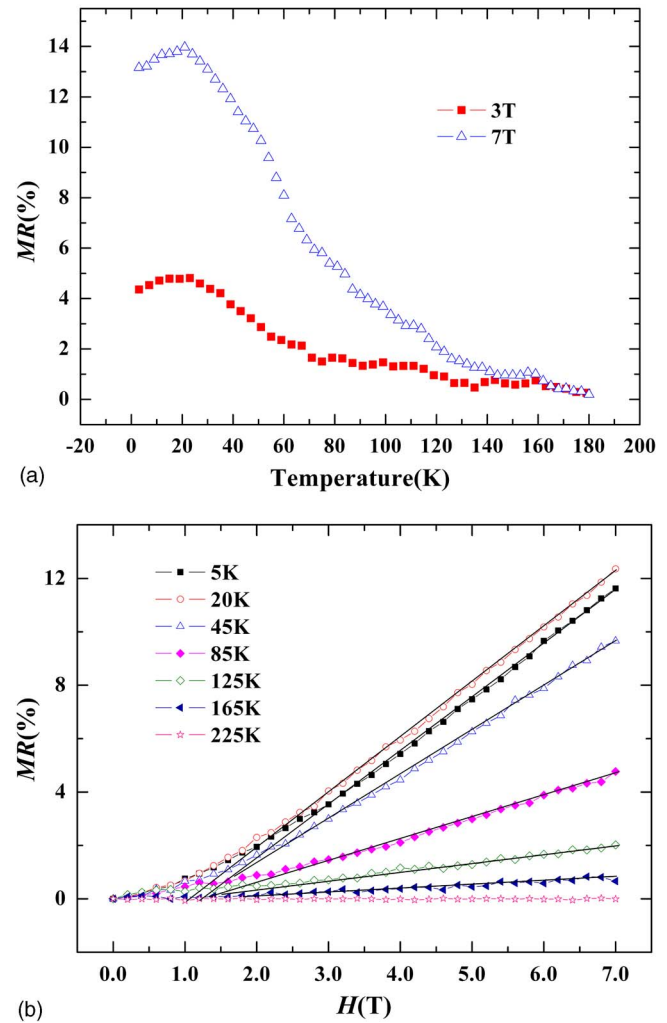


FIG. 4. (Color online) (a) Temperature dependences of MR of the orthorhombic SrIrO₃ perovskite at different magnetic fields. (b). Magnetic field dependences of MR at different temperatures. The solid lines are linear fits to the data at high magnetic field.

magnetic field caused by Lorentz force.²⁶ The OMR is always positive and proportional to $(\omega_c\tau)^2$ when the product of ω_c and τ is smaller than 1, where $\omega_c(=eB/m^*)$ is the cyclotron frequency and τ is the relaxation time that is determined by the carrier mean-free-path l . The orthorhombic SrIrO₃ perovskite is paramagnetic below 170 K, so the PMR effect should be attributed to the energy band shifts. However, the MR is proportional to the magnetic field, i.e., $\omega_c\tau$, not to $(\omega_c\tau)^2$. The linear field dependence of MR was firstly found by Kapitza through measuring the electrical transposition properties under high magnetic field of the single-crystal bismuth and other polycrystalline metals in the 1920s.^{27,28} Lifshitz and Peschanskii gave a reasonable explanation to the linear MR according to a classical treatment of electron trajectories in a magnetic field because many metals have open Fermi surfaces.²⁹ Recently, Yang *et al.* found a giant linear PMR in the electrodeposited single-crystal bismuth thin films that are semimetals, with the maximum value of 380,000% at 5 K in a field of 5 T, due to the small effective mass m^* in Bi and large mean-free-path l for the single-crystal sample.³⁰ Xu *et al.* found that the nonstoichiometric silver chalcogenides that are nonmagnetic semiconductors behave the lin-

ear PMR effects under high magnetic field,³¹ which can be explained to quantum MR by Abrikosov.^{32,33} The linear MR is related to the gap. In the orthorhombic SrIrO₃ perovskite, large distortion in the IrO₆ octahedra results in the formation of a pseudogap near the Fermi face in the aforementioned discussion. The linear magnetoresistance can be attributed to this pseudogap.

IV. CONCLUSIONS

In summary, the orthorhombic phase of SrIrO₃ was synthesized by using the high-pressure technique, and the XRD pattern, magnetic susceptibility, and electrical resistivity were measured. The magnetic and electrical properties showed that the orthorhombic SrIrO₃ perovskite is paramagnetic below 170 K and is metallic above 44 K before a band type metal insulator transition appeared. The orthorhombic SrIrO₃ perovskite behaves novel PMR effect. Under high magnetic fields, the electrical resistivity is increasing below 170 K and does not change at higher temperature.

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