Effects of pressure on electrical property of \( \text{BaIrO}_3 \)

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The in situ high-pressure measurements of electrical resistivity versus temperature for weak ferromagnetic \( \text{BaIrO}_3 \) have been performed, using a Cu–Be piston–cylinder-type apparatus up to 1.0 GPa at 80–300 K. The electrical resistivity is increasing with pressure. The pressure derivative of Curie temperature \( \Delta T_c / \Delta P \) is equal to \(-6.1(2) \) K/GPa, and the relative pressure dependence \( \delta \) in \( T_c / \Delta P \) is equal to \(-3.4(1)%/\)GPa, which indicates that \( \text{BaIrO}_3 \) is a weak itinerant ferromagnet.

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1. Introduction

At ambient pressure, \( \text{BaIrO}_3 \) crystallizes into the distorted 9R \( \text{BaRuO}_3 \) structure [1], with the space group \( C2/m \), due to a large tolerant factor (about 1.051) as calculated from the ion radii in Shannon Table [2]. The schematic view of the crystal structure is shown in Fig. 1. \( \text{BaIrO}_3 \) is a weak ferromagnet [3,4], with the Curie temperature \( T_c \) about 183 K. It is the first known ferromagnet that contains a 5d transition metal cation in a ternary oxide, which originates from spin polarization of Ir cations rather than spin canting [5,6]. The polycrystalline sample of \( \text{BaIrO}_3 \) is a semiconductor [7]. The obvious kink in the \( \rho–T \) curve corresponds to the Curie temperature \( T_c \). Blow \( T_c \), the electrical resistivity increases more rapidly with the decreasing temperature. For the single crystal, the temperature dependence of resistivity in the \( ab \)-plane is similar with that of the polycrystalline \( \text{BaIrO}_3 \), but the electrical resistivity at low temperature is much smaller than the corresponding value of polycrystal at the same temperature [5]. However, along the \( c \)-axis that is the high conductivity axis, \( \text{BaIrO}_3 \) transforms to a more insulating phase below \( T_c \), and then transforms to metallic and insulating states at 80 K and 26 K, respectively [5,6], which is different from the \( \rho–T \) curve of polycrystal. For \( \text{BaIrO}_3 \), the \( \rho_c \) is smaller than \( \rho_{ab} \), due to direct Ir–Ir interaction along the \( c \)-axis. This metal–insulator transition was ascribed to the charge density wave (CDW) formation in \( \text{BaIrO}_3 \), where the transition temperature \( T_{\text{CDW}} \), i.e. \( T_1 \) in [5], is equal to about 26 K. The CDW behavior is due to the distortion of IrO\(_6\) octahedron in the low symmetry quasi-one-dimensional chain-type structure of \( \text{BaIrO}_3 \), which reduces the bandwidth and enlarges the band gap.

Pressure is an important thermodynamical parameter to control the matter state. The knowledge about the pressure behavior is very helpful to fully understand the overall properties of materials. High pressure can affect the magnetic properties of oxide ruthenates, e.g. \( \text{SrRuO}_3 \) [8], \( \text{Ca}_2\text{RuO}_4 \) [9]. The \( T_c \) of \( \text{SrRuO}_3 \) is decreasing with increasing pressure by measuring electrical resistivity and AC magnetic susceptibility [8]. The pressure results and DC magnetization indicate that \( \text{SrRuO}_3 \) is a moderately weak itinerant ferromagnet. \( \text{Ca}_2\text{RuO}_4 \) becomes a ferromagnetic metal at 0.5 GPa from an antiferromagnetic Mott insulator, due to the phase transition from \( \text{S-Pbca} \) to \( \text{L-Pbca} \) structures under high pressure [9]. The discontinuity at 0.5 GPa in the relationship of electrical resistivity versus pressure indicates the first-order insulator–metal transition in \( \text{Ca}_2\text{RuO}_4 \). To our knowledge, there are no reports of high-pressure properties for oxide iridates so far. So it is interesting to learn how physical properties of iridates will evolve under pressure. Here we report the effects of pressure on electrical property of \( \text{BaIrO}_3 \), using in situ high-pressure measurements of resistivity versus temperature in a Cu–Be piston–cylinder-type apparatus.
2. Experimental

BaIrO$_3$ was synthesized by using the method of conventional solid-state chemical reaction. The starting materials were barium carbonate and iridium metal of 99.9% purity. Stoichiometric quantities of materials were mixed together, ground about 30 min in an agate mortar, and placed into an Al$_2$O$_3$ crucible. Then the powder was calcined for about 12 h at 900 °C in air. The calcined powder was reground, pressed into pellets at the pressure of 10 MPa, and sintered at 1000 °C for about 72 h in air with two intermediate re-grindings.

In order to obtain a high-quality BaIrO$_3$ bulk, we used a conventional cubic-anvil type high-pressure facility to perform the cold-pressing treatment. The BaIrO$_3$ powders were reground and pressed into pellets of 5.0 mm diameter, and then wrapped in silver foil to avoid contamination. The pellets were put into the hole of pyrophyllite, which was used as the pressure-transmitting medium. The pressure is calibrated by measuring the well known silicon oil and kerosene was used as the pressure-transmitting medium. The pressure was obtained using the four-probe method with Ag paste contacts at 0.0–1.0 GPa from the conventional cubic-anvil type high-pressure facility to perform the in situ high-pressure experiments.

The prepared sample was checked by the powder x-ray diffraction (XRD) with CuK$_\alpha$ 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°–120° and analyzed with Rietveld method by using the FullProf program [12]. The XRD pattern indicates that our BaIrO$_3$ sample is a single phase. The relationship between magnetic susceptibility and temperature was obtained using a SQUID magnetometer (Quantum Design, MPMS-5S) in the range 5–300 K. Data were collected under both zero-field-cooled (ZFC) and field-cooled (FC) conditions in an applied field of 0.1 T. The temperature dependence of electrical resistivity in the range 5–300 K at ambient pressure was obtained using the four-probe method with Ag paste contacts on an Oxford Maglab measuring system.

A piston–cylinder type apparatus, being made of the alloy of copper and beryllium, was used to perform the in situ high-pressure measurements of resistivity versus temperature. In order to keep a good hydrostatic environment, a kind of mixed silicon oil and kerosene was used as the pressure-transmitting medium. The pressure is calibrated by measuring the well known superconducting transition temperature $T_c$ of lead metal. The low-temperature experiments were carried out in a Dewar and the temperature was read from a NiCr–NiAl thermocouple. The electrical resistivity of sample was obtained by the conventional four-probe method with Ag paste contacts at 0.0–1.0 GPa from the liquid–nitrogen temperature to ambient.

3. Results and discussion

Fig. 2 shows the experimental (open circle) and fitted (line) x-ray diffraction patterns for BaIrO$_3$. 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. The inset shows the details of patterns in the range 70°–120°.

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magnetic susceptibility, respectively. The paramagnetic Curie temperature $\theta$ of 183.7(2) K is positive, which is consistent with the weak ferromagnetism of BaIrO$_3$. The effect magnetic moment per formula unit ($\mu_{\text{eff}}$) of 0.127(3) $\mu_B$, as obtained from C through the formula $\mu_{\text{eff}} = 2.83\sqrt{C}$, is approximately equal to the value in Ref. [5]. $\mu_{\text{eff}}$ is less than the theoretic value of about 1.73 $\mu_B$ calculated in the spin-only model for one unpaired 5d electron in the Ir$^{4+}$ cations. The small $\mu_{\text{eff}}$ indicates that the Ir$^{4+}$ cation loses partly local moment, which is attributed to the strong spin-orbit coupling in Ir cations and the improved itinerancy resulting from the direct interaction between two adjacent Ir cations in the Ir$_3$O$_{12}$ trioctahedron that lowers the magnetization of the sample.

Fig. 4 shows the temperature dependence of the electrical resistivity $\rho(T)$ (solid line) and the derivative $d(\log \rho)/d(1/T)$ (open circle) for BaIrO$_3$. The $\rho$–$T$ curve is similar with the previous result of polycrystalline sample [7]. It is clear that BaIrO$_3$ is a semiconductor, with the electrical resistivity about $10^5$Ω cm at 5 K. There is an obvious kink in the $\rho$–$T$ curve, corresponding to the Curie temperature $T_C$, which is indicated by the arrow in Fig. 3. The $T_C$ of ferromagnetism was defined as the turning point at the peak of $d(\log \rho)/d(1/T)$–$T$ curve as shown in Fig. 4. Using this definition, the $T_C$ is about 183.3 K for the sample, which is approximately equal to the value obtained from $\chi$–$T$ curve. While temperature is smaller than $T_C$, the electrical resistivity increases more rapidly with decreasing temperature, due to the gap open [5]. The electrical property of BaIrO$_3$ is closely related to its structure in terms of the IrO$_6$ octahedron connection. The Ir–Ir–Ir trimer in the trioctahedron of BaIrO$_3$ results in the novel electronic state. The wave function of the 5d orbitals is highly extended comparing with 3d ones, so the oxide iridates should be metallic, like the corresponding ruthenates. However, although the short Ir–Ir distance in the Ir$_3$O$_{12}$ trioctahedron is propitious to metallic behavior, BaIrO$_3$ is not a metal [5,7]. The twisting and distortion of the Ir$_3$O$_{12}$ trioctahedron reduce the bandwidth, and result in the non-metallic behavior in BaIrO$_3$ [5].

Fig. 5(a) shows the temperature dependence of electrical resistivity in the range 100–250 K at various pressures up to 1.0 GPa for BaIrO$_3$. The electrical resistivity is increasing with pressure in the experimental temperature range. When temperature is 200 K, electrical resistivity is 41.77 mΩ cm, 50.98 mΩ cm and 62.29 mΩ cm at 0.0 GPa, 0.5 GPa and 1.0 GPa, respectively. In the Ir$_3$O$_{12}$ trioctahedron of BaIrO$_3$, the direct Ir–Ir distances are shorter than the separation in iridium metal (2.72 Å) [1]. From the large bulk modulus of metal iridium [13], it could be deduced that there is a strong repulsion between the two neighboring Ir cations. Pressure strengthens the repulsion between Ir cations due to the shrinkage of crystal lattice, and then enhances the structural distortion, which enlarges the gap and results in the increase of electrical resistivity. Fig. 5(b) shows the temperature dependence of the derivative $d(\log \rho)/d(1/T)$ in the temperature range of 100–250 K at 0.0–1.0 GPa for BaIrO$_3$. According to the $d(\log \rho)/d(1/T)$–$T$ curves, the relationship of $T_C$ versus pressure is obtained, as shown in the inset of Fig. 5(a). The obtained Curie temperatures are 183.3 K, 180.4 K and 177.2 K at 0.0 GPa, 0.5 GPa and 1.0 GPa, respectively. $T_C$ is decreasing with increasing pressure. The suppression of ferromagnetism transition temperature of BaIrO$_3$ is similar with that of SrRuO$_3$ [8], which can be attributed to the augment of distortion under high pressure. For the Ba$_{1_x}$Sr$_x$IrO$_3$ series, $T_C$ is decreasing with the decreasing lattice parameter,
i.e. the increasing Sr content $x$ [14], which is consistent with the pressure effect in this paper. In the experimental pressure range, the pressure dependence of $T_c$ is roughly linear. The pressure derivative of the Curie temperature $\partial T_c / \partial P$ of $-6.1(2)$ K/GPa is approximately equal to the value of $-6.2 \pm 1.9$ K/GPa for SrRuO$_3$ [8].

According to the Wohlfarth theory [15,16], the relative pressure dependence $\partial \ln T_c / \partial P$ for an homogeneous ferromagnet can approximately be expressed as

$$\partial \ln T_c / \partial P = -\frac{\alpha}{T_c^2} + \frac{5}{3}\kappa,$$

(2)

where $\alpha$ is a slowly varying quantity and $\kappa$ is the compressibility. For the weak itinerant ferromagnet, the $\partial \ln T_c / \partial P$ is negative, because both $\alpha$ and $\kappa$ are positive, and the first term on the right-hand side in Eq. (2) is dominating comparing with the second term [15]. So the Curie temperature is decreasing with increasing pressure. The $\partial \ln T_c / \partial P$ of $-3.4(1)$%/GPa for BaIrO$_3$ is approximately equal to that of SrRuO$_3$ (about $-3.5%$/GPa) [8], but is much smaller than that of the Laves phase compound ZrZn$_2$ (about $-86%$/GPa) [17]. The small $\partial \ln T_c / \partial P$ supports that BaIrO$_3$ is a weak itinerant ferromagnet.

4. Conclusion

In summary, we observed the influence of pressure on the electrical property for BaIrO$_3$ through the in situ measurements of the temperature dependence of electrical resistivity at various pressures. The electrical resistivity is increasing with the increasing pressure and Curie temperature $T_c$ is depressed by high pressure. The small relative pressure dependence $\partial \ln T_c / \partial P$ shows the weak itinerant ferromagnetism of BaIrO$_3$.

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References