Spin-Orbit Mott State in the Novel Quasi-2D Antiferromagnet \( \text{Ba}_2\text{IrO}_4 \)

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Abstract. The spin-orbit Mott state in the novel quasi-2D iridate \( \text{Ba}_2\text{IrO}_4 \) was studied on crystal structure, electrical resistivity, magnetic susceptibility, and \( \mu \)SR experiments. \( \text{Ba}_2\text{IrO}_4 \) crystallizes in a \( \text{K}_2\text{NiF}_4 \)-type structure (\( \text{I}4/\text{mmm}, a = 4.030(1) \text{ Å} \) and \( c = 13.333(4) \text{ Å} \)) which includes \( \text{IrO}_2 \) square planar lattices with straight \( \text{Ir-O-Ir} \) bonds. The minimal Mott-gap size is \( \sim 70 \text{ meV} \). The magnetic ground state is antiferromagnetic long-range order (\( T_N \sim 240 \text{ K} \)) without spin canting. The magnetic moment (\( \mid \mu \mid \sim 0.34 \mu_B/\text{Ir} \)) is much reduced by a low-dimensional quantum spin fluctuation with a large intra-plane correlation \( \mid J \mid \). The critical exponent (\( \beta \sim 0.18 \)) suggests that the magnetic state is classified into 2-D \( X-Y \) or (anisotropic) Heisenberg spin systems with weak 3-D interlayer coupling \( \mid J' \mid \).

1. Introduction

Recently, extensive studies have carried out on the layered-perovskite iridium oxide \( \text{Sr}_2\text{IrO}_4 \). This compound includes \( \text{Ir}^{4+} \) ions with five valence electrons in the \( 5d \) \( t_{2g} \) orbital. Since \( 5d \) orbitals are spatially more extended than \( 3d \) and \( 4d \) orbitals, the \( 5d \) bandwidth (\( W \)) should be comparatively broad. The \( 5d \) system is thus expected to have a metallic state. However, on the contrary to the naïve expectation, \( \text{Sr}_2\text{IrO}_4 \) actually shows insulating behavior with canted antiferromagnetic long-range order below 240 K [1]. It has been recently found that the insulating state could be attributed to cooperation of onsite Coulomb (\( U \)) and spin-orbit (SO) interactions [2-4]. The iridium \( 5d \) \( t_{2g} \) orbital splits into a half-filled \( J_{\text{eff}} = 1/2 \) doublet and a \( J_{\text{eff}} = 3/2 \) quadruplet due to large SO coupling. The onsite Coulomb interaction further splits the \( J_{\text{eff}} = 1/2 \) band into upper and lower Hubbard bands, forming the novel Mott insulating state.

It has been proposed that the unconventional \( J_{\text{eff}} = 1/2 \) magnetic ground state originates from the strong SO coupling in the Mott state [2, 3]. In the strong SO coupling limit, the \( J_{\text{eff}} = 1/2 \) state can be
expressed as \( J_{\text{eff}} = \pm 1/2, m_{J_{\text{eff}}} = \pm 1/2 \) \( \frac{1}{\sqrt{3}} \left( xy, x\sigma \pm z\sigma \right) \), where \( |\pm\sigma\rangle \) and \( |-\sigma\rangle \) denote spin-up and spin-down states, respectively. This equation indicates that the \( J_{\text{eff}} = 1/2 \) state is much different from \( d \)-orbital states in 3d or 4d systems. In 3d or 4d systems, the electronic state is mainly depends on the crystal field, where the real wavefunctions can be described by the \( t_{2g} (xy, yz, \text{and } zx) \) and \( e_g (x^2-y^2 \text{ and } 3z^2-r^2) \) orbitals. In contrast, the \( J_{\text{eff}} = 1/2 \) state is a considerably complex state hybridizing spin \( (\pm \sigma) \) and orbital \( (xy, yz, \text{and } zx) \) degrees of freedom. Therefore, investigation of this state may give a new insight into \( d \)-electron physics, and it may lead to possible unusual cooperative phenomena such as anisotropic superconductivity.

In this paper, we review electronic and magnetic states in Ba\(_2\)IrO\(_4\), which is a new isostructural compound recently found by the present authors [5]. Through the analyses of the crystal structure, electrical resistivity, magnetic susceptibility, and \( \mu \)SR experiments, we discuss the nature of the spin-orbit Mott state in Ba\(_2\)IrO\(_4\).

2. Experimental
Pure polycrystalline samples of Ba\(_2\)IrO\(_4\) were prepared from the solid-state reaction of a stoichiometric mixture of BaO\(_2\) and Ir-metal powder, using a high-pressure synthesis technique at 1,500 °C under 6 GPa. The detailed procedure of the synthesis has been reported in Ref. 5. Crystal structure of Ba\(_2\)IrO\(_4\) was studied by electron and powder X-ray diffractions. The electron diffraction patterns were taken using a transmission electron microscope (TEM, JEM-4010; JEOL) operated at 400 kV. The X-ray diffraction data were taken using a diffractometer with Cu K\(_\alpha\) radiation (RINT2000; Rigaku). The structural parameters were refined by the Rietveld method. Electrical resistivity was measured by the standard dc four-probe method using a commercial apparatus (PPMS; Quantum Design). Magnetic data were collected using a SQUID magnetometer (MPMS-XL; Quantum Design).

Zero-field \( \mu \)SR experiments were performed using the D1 instrument at MUSE (Muon Science Establishment) in J-PARC, Tokai, Japan. Nearly 100% spin-polarized positive muons with a momentum of 28 MeV/c were implanted into the polycrystalline samples. The time-dependent muon spin polarization was measured using positron detectors. Temperature was controlled by a cryostat.

3. Results and discussion

3.1. Crystal Structure
Electron diffraction patterns indicated that Ba\(_2\)IrO\(_4\) has a unit cell with \( |a| = |b| \sim 2.5 \text{ nm}^{-1} \) and \( |c| \sim 4.0 \text{ Å} \) and \( |e| \sim 0.75 \text{ nm}^{-1} \) (\( |c| \sim 13.3 \text{ Å} \)). The extinctions were \( h+k=2n (hh0), h+l=2n (h0l), \) and \( l=2n (hhl), (00l) \). Possible space groups are \( I4/mmm \), \( I4/m \), and their related non-centrosymmetric space groups. High-resolution transmission electron microscopy observation revealed that the IrO\(_2\) mono layer and the BaO double layers are alternately stacked along the \( c \)-axis, and that the IrO\(_2\) (or BaO) layer forms the square lattice in the \( a-b \) plane. A resultant crystal-structure model is a conventional K\(_2\)NiF\(_4\)-type one. The structure has no rotational distortion of the IrO\(_6\) octahedra. The inversion symmetry in the IrO\(_2\) plane gives rise to absence of the Dzyaloshinsky-Moriya (D-M) interaction.

Powder X-ray diffraction pattern was analyzed using the Rietveld method. The refined structure parameters of the \( I4/mmm \) model are \( x=y=1/2, z=0.14485(7), \) and \( B=0.172(2) \text{ Å}^2 \) for Ba (4e); \( x=y=z=0, \) and \( B=0.152(2) \) for Ir (2a); \( x=z=0, y=1/2, \) and \( B=1.3(2) \) for O1 (4c); and \( x=y=z=0.1616(6), \) and \( B=0.6(2) \) for O2 (4e). The lattice constants are \( a=4.030(1) \text{ Å} \) and \( c=13.333(4) \text{ Å} \). The reliability factors are \( R_p=0.0898, R_f=0.0392, \) and \( R_p=0.0241 \). The Ir-O1 (in-plane) length is 2.015 Å, which is consistent with the typical value 2.025 Å expected from the Shannon’s ionic radii (Ir\(^{4+}\) (VI): 0.625 Å, O\(^{2-}\) (VI): 1.40 Å [6]). In contrast, for Sr\(_2\)IrO\(_4\), the in-plane Ir-O length is 1.981 Å [1]. It suggests that Ba\(_2\)IrO\(_4\) is spatially more tolerant than Sr\(_2\)IrO\(_4\). This may be the reason for no octahedral rotation in Ba\(_2\)IrO\(_4\). For Ba\(_2\)IrO\(_4\), the Ir-O2 (apical) length (2.155 Å) is longer than the Ir-O1 (in-plane) length (2.015 Å), indicating that the IrO\(_6\) octahedra are tetragonally distorted. The tetragonal crystal field may split the \( J_{\text{eff}} = 1/2 \) and the \( J_{\text{eff}} = 3/2 \) bands furthermore.

2
3.2. Electrical resistivity
Temperature ($T$) dependence of electrical resistivity ($\rho$) of Ba$_2$IrO$_4$ is shown in Fig. 1. This indicates that Ba$_2$IrO$_4$ behaves like a semiconductor. The activation energy is ~70 meV, which is almost the same as that of Sr$_2$IrO$_4$ (~60 meV) [7]. It seems that Ba$_2$IrO$_4$ is essentially analogous to Sr$_2$IrO$_4$ in terms of electronic structure near the Fermi level. The energy gap was caused by the energy-band splitting probably due to the cooperation of the large SO coupling and the on-site Coulomb repulsion of the 5$d$ electrons, implying that Ba$_2$IrO$_4$ belongs to spin-orbit Mott insulators.

3.3. Magnetic susceptibility
Magnetic susceptibility ($\chi$) data are plotted as a function of temperature in Fig. 1. No difference between the zero-field cool (ZFC) and field cool (FC) data was observed. No signal enhancement due to spontaneous magnetization was observed at all the temperature range measured. The inset shows an $M$-$H$ curve taken at 5 K. No magnetic saturation was observed. These results clearly indicate that there is no ferromagnetic order in Ba$_2$IrO$_4$, which is great contrast to the case of Sr$_2$IrO$_4$ [1].

The most characteristic feature in regard to the magnetic susceptibility is that at $T > 240$ K, the susceptibility gradually decreases with decreasing temperature. This contribution is from the intrinsic spin susceptibility of the iridium moment. The upturned signal in the low-temperature range is due to extrinsic spins such as lattice imperfections and/or small amounts of magnetic impurities. $\chi$ includes a $T$-independent part due to the closed-shell diamagnetic susceptibility and the orbital susceptibility such as the van-Vleck susceptibility. From the Curie-Weiss analysis, the amount of the extrinsic spins are estimated to be ~1.1%, if $S = 1/2$. The $T$-independent part is $\sim 1.2 \times 10^{-5}$ emu/mol. The remaining part is the spin susceptibility. It was found that as the temperature decreases, the spin susceptibility exponentially decays and becomes less than $\sim 1 \times 10^{-5}$ emu/mol around 200 K. This behavior is characteristic of a low-dimensional antiferromagnetic spin order of the Heisenberg spin system.

Figure 1. Temperature ($T$) dependence of electrical resistivity ($\rho$) and magnetic susceptibility ($\chi$) of polycrystalline Ba$_2$IrO$_4$. The $\chi$ data were measured in the magnetic field ($H$) of 1 T. The inset shows an $M$-$H$ curve at $T = 5$ K.

Figure 2. Temperature dependence of the muon-spin precession frequency ($f$) of Ba$_2$IrO$_4$. Inset is a zero-field $\mu$SR (ZF-$\mu$SR) time spectrum measured at 181 K. The oscillatory signal was observed at all temperatures below 240 K.

3.4. $\mu$SR studies
Figure 2 (inset) shows a zero-field $\mu$SR (ZF-$\mu$SR) time spectrum measured at 181 K in Ba$_2$IrO$_4$. Such a muon-spin precession was observed at all temperatures below 240 K. This is clear evidence that there exists a coherent internal magnetic field induced by long-range ordered spins. The $\mu$SR signal arises from the majority of muon sites in the sample. Since no spontaneous magnetization was observed in the magnetic susceptibility data (Fig. 2), the magnetic state is an antiferromagnetic long-
range order. In Fig. 2 (inset), the solid wavy curve indicates numerical data analysis using a damped oscillator model for polycrystalline samples.

Figure 2 (main panel) shows temperature dependence of the precession frequency $f$. In the magnetic ordered state, $f$ is proportional to the static internal field $B_{\mu}$ (i.e., $f = \gamma B_{\mu}/2\pi = 135.54$ (MHz/T) $\times B_{\mu}$) and consequently to the sublattice magnetization $M_{\text{s}}$. This result clearly indicates that the antiferromagnetic long-range order transition occurs at $T_N \sim 240$ K. Since $f$ is the order parameter of the transition around $T_N$ ($T \leq T_N$), $f$ can be expressed as $f(T) = f(0)[1 - T/T_N]^\beta$, where $f(0)$ is the precession frequency at $T = 0$ K and $\beta$ is the critical exponent of the transition. In Fig. 2, the solid curve is the best fit of the data with this equation. The obtained parameters are $f(0) = 2.67(6)$ MHz ($B_{\mu} = 197$ G), $T_N = 243(1)$ K, and $\beta = 0.18(1)$. This obtained $\beta$ value (0.18) is close to the theoretical value (0.23) expected for 2-D $X$-$Y$ or (anisotropic) Heisenberg spin systems with weak 3-D interlayer coupling $J'$ [8].

An effective magnetic moment of the iridium ions in the antiferromagnetic ordered state of Ba$_2$IrO$_4$ was estimated using a dipolar-field model, with an internal field of $B_{\mu} = 197$ G at the muon ($\mu^+$) site. In the present case, the hyperfine field $B_{\text{dip}}$ is negligible, so the local field approaches the dipolar field; i.e., $B_{\mu} \sim B_{\text{dip}}$. The dipolar field $B_{\text{dip}}$ is given by $B_{\text{dip}}(r) = (\mu_0/4\pi) \mu_{\text{i}}((\mathbf{\mu} \cdot \mathbf{n}) n_i - \mu_{\text{i}})(r - r_i)^3$, where $\mu_{\text{i}}$ is the effective magnetic moment of the $i$-th Ir$^{4+}$ ion at $r_i$, $r$ is the $\mu^+$ site, $n_i = ((r - r_i)/|r - r_i|)$ is the unit vector from the $i$-th Ir$^{4+}$ ion to $\mu^+$, and $\mu_0$ is magnetic permeability of free space. For the calculation of the moment $\mu_{\text{i}}$, we assumed that the implanted positive muons ($\mu^+$) stop at the most electronegative point around the O2 site and form (Omu) bonds with the O2 ion. The $\mu^+$ site was determined from Madelung calculation using the structural parameters. It was also assumed that the antiferromagnetic staggered moments are directed to the [110] or [-1-10] direction at the iridium sites.

As a result, the amplitude of the iridium moment at $T = 0$ K is $|\mu_{\text{i}}| = 0.34(4)$ $\mu_B$/Ir.

The Ir$^{4+}$ (5$d^5$, $S(J_{\text{eff}}) = 1/2$) moment (0.34 $\mu_B$) in Ba$_2$IrO$_4$ is much smaller than the integer moment 1 $\mu_B$ of $S = 1/2$. This moment reduction is attributed to a low-dimensional quantum spin fluctuation with large intra-plane antiferromagnetic correlation $|J|$. This result is consistent to the magnetic susceptibility data in Fig. 1, in which the spin susceptibility is significantly reduced to the small value ($< 1 \times 10^{-5}$ emu/mol) around $T_N \sim 240$ K. A similar moment reduction is reported for parent materials of high-$T_c$ cuprate superconductors. For example, in La$_2$CuO$_4$ the moment size of the Cu$^{2+}$ (3$d^9$, $S = 1/2$) ion is estimated to be 0.2 $\sim$ 0.6 $\mu_B$ from neutron scattering experiments [9, 10]. The moment size (0.34 $\mu_B$) in Ba$_2$IrO$_4$ is in good agreement with the values (0.2 $\sim$ 0.6 $\mu_B$) in La$_2$CuO$_4$. Therefore, the magnetic state in Ba$_2$IrO$_4$ is interesting in terms of an analogy to high-$T_c$ cuprate superconductors.

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