Coexisting charge and magnetic orders in the dimer-chain iridate Ba₅AlIr₂O₁₁

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We have synthesized and studied single-crystal Ba₅AlIr₂O₁₁ that features dimer chains of two inequivalent octahedra occupied by tetravalent Ir⁴⁺(5d⁵) and pentavalent Ir⁵⁺(5d⁶) ions, respectively. Ba₅AlIr₂O₁₁ is a Mott insulator that undergoes a subtle structural phase transition near Tₛ = 210 K and a magnetic transition at Tₘ = 4.5 K; the latter transition is surprisingly resistant to applied magnetic fields μ₀H ≤ 12 T but more sensitive to modest applied pressure (dTₘ/dp ≈ +0.61 K/GPa). All results indicate that the phase transition at Tₘ signals an enhanced charge order that induces electrical dipoles and strong dielectric response near Tₛ. It is clear that the strong covalency and spin-orbit interaction (SOI) suppress double exchange in Ir dimers and stabilize a novel magnetic state that is neither S = 3/2 nor J = 1/2, but rather lies in an “intermediate” regime between these two states. The novel behavior of Ba₅AlIr₂O₁₁ therefore provides unique insights into the physics of SOI along with strong covalency in competition with double-exchange interactions of comparable strength.

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I. INTRODUCTION

The 5d-electron-based iridates are distinguished by strong spin-orbit interaction (SOI) (≈ 0.4 eV) that is comparable to the on-site Coulomb interaction (U ≈ 0.5 eV), crystalline electric field interactions, and Hund’s rule coupling (J₉ ≈ 0.5 eV). This unique circumstance creates a delicate balance between interactions that generate novel magnetic states and dielectric behaviors. A profound manifestation of this competition is the “Jₙeff = 1/2 insulating state” first observed in Sr₂IrO₄ [1–4]. Indeed, in contrast to conventional wisdom, the iridates are much more likely to host a magnetic, insulating ground state with a very small magnetic moment [4–8] that is more strongly coupled to the lattice rather than other degrees of freedom [2,9–16].

Most studies of the iridates have focused on the tetravalent iridates since the Ir⁴⁺(5d⁵) ion provides four d electrons to fill the lower Jₐeff = 3/2 bands and one electron to partially fill the upper Jₐeff = 1/2 band that lies closest to the Fermi energy and therefore dominates underlying physical properties. Very limited studies have been devoted to iridates with pentavalent Ir⁵⁺(5d⁶) ions, in part because the strong SOI limit is expected to impose a nonmagnetic singlet ground state (J = 0). However, recent theoretical and experimental studies suggest that novel magnetic states in the iridates with pentavalent Ir⁵⁺(5d⁶) ions can also emerge from competitions between exchange interactions (0.05–0.10 eV) [12], noncubic crystal fields, singlet-triplet splitting (0.050–0.20 eV), and SOI [17–19].

Moreover, the vast majority of iridates studied thus far are either two- or three-dimensional systems [4]. Little work has been done on quasi-one-dimensional iridates, particularly those with dimers commonly found in other transition-metal materials and those in which the average number of electrons per transition metal is nonintegral, where double exchange is expected to play a critical role [20]. Double exchange occurs when one “extra” electron hops between neighboring transition-metal ions with localized spins, and the Hund’s rule J₉ coupling stabilizes the state with maximum possible (parallel) spin. This idea was first proposed by Zener for Mn dimers with average valence Mn⁵⁺⁺ [21] and has been applied successfully to many materials, such as colossal magnetoresistive manganites [22]. However, the strong SOI and covalency present in spin-dimer systems based on 5d electrons are expected to compete with the Hund’s rule coupling and double exchange, leading to new quantum phenomena. We show that such is indeed the case in Ba₅AlIr₂O₁₁.

In this paper, we report a novel magnetic state and dielectric behavior dictated by the joint action of a strong SOI and charge ordering in the dimer chain of Ba₅AlIr₂O₁₁. This newly synthesized, single-crystal iridate features both tetravalent Ir⁴⁺ and pentavalent Ir⁵⁺ ions that occupy dimers linked by AlO₄ tetrahedra lying along the b axis (see Fig. 1). Despite their one-dimensional character, the dimer chains undergo a second-order structural change or charge order at Tₛ = 210 K and a transition to magnetic order at Tₘ = 4.5 K. The antiferromagnetic state below Tₘ is highly anisotropic and resilient to strong magnetic field (up to 14 T) but is more susceptible to even modest hydrostatic pressure (up to 10 kbar). We propose that the charge order consists of an ordered arrangement of Ir⁴⁺ and Ir⁵⁺ ions within each dimer, which forms electrical dipoles and promotes the strong dielectric response that develops near Tₛ. Our studies suggest that a combined effect of both a strong SOI and covalent bonding overcomes double exchange and stabilizes coexisting antiferromagnetic and charge orders. The physical behavior of

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that the dimers are connected via AlO4 tetrahedra (yellow), forming dimer chains along the $b$ axis.

FIG. 1. (Color online) Crystal structure: The single-crystal structure generated based on the x-ray data for (a) the $ac$ plane, (b) the $ab$ plane, and (c) a representative single crystal of Ba$_5$AlIr$_2$O$_{11}$. Note that the dimers are connected via AlO4 tetrahedra (yellow), forming dimer chains along the $b$ axis.

The charge-ordered state we envision inevitably leads to formation of an electric dipole in each dimer. These electrical dipoles are parallel to each other within each dimer chain but are expected to orient antiparallel between dimer chains in order to minimize electrical energy, as schematically shown in Figs. 2(c) and 2(d), respectively. Each dimer consists of two face-sharing IrO$_6$ octahedra with two inequivalent, octahedral Ir2 and Ir1 sites occupied by tetravalent Ir$^{4+}$ ($5d^5$) and pentavalent Ir$^{5+}$ ($5d^3$) ions, respectively [see Fig. 1(b)]. The average Ir1-O bond distance $d_{[Ir1-O]} = 1.997$ Å, the average Ir2-O bond distance $d_{[Ir2-O]} = 2.013$ Å, and the average Ir-Ir distance $d_{[Ir-Ir]} = 2.7204(5)$ Å at $T = 100$ K and undergoes a sharp slope change at $T_S = 210$ K [Fig. 2(c)]. The fact that $d_{[Ir2-O]} > d_{[Ir1-O]}$ indicates that different oxidation states exist on the two Ir sites; that is, charge ordering occurs in this system. This is also consistent with the observation of two distinct IrO$_6$ octahedra volumes for the two inequivalent, octahedral Ir2 (Ir$^{4+}$) and Ir1 (Ir$^{5+}$) sites. The longer $d_{[Ir2-O]}$ is most likely due to the relatively large ionic radius $r$ of Ir$^{4+}$ ($r = 0.625$ and 0.570 Å for Ir$^{4+}$ and Ir$^{5+}$, respectively) and is assigned to the IrO$_6$ octahedra that are corner connected with the AlO$_4$ tetrahedra [Fig. 1(b)]. This is also consistent with the results of the band structure calculations justify the existence of the charge ordering [25], although it is not a complete one, which is common in transition-metal oxides [20]. A certain degree of order among the Ir$^{4+}$ and Ir$^{5+}$ ions in each dimer may already exist at room temperature; however, the anomalies in the lattice parameters (Fig. 2), electrical resistivity and dielectric constant (Fig. 3), and specific heat observed at $T_S = 210$ K (Fig. 6) signal an enhanced degree of order among the Ir$^{4+}$ and Ir$^{5+}$ ions, i.e., the formation of charge order. All Ir-O dimers are corner connected through AlO$_4$ tetrahedra, forming dimer chains along the $b$ axis, but the dimer chains are not connected along the $a$ and $c$ axes [see Figs. 1(a) and 2(b)]. This peculiar structural characteristic generates weak intrachain interactions via long Ir-O-O-Ir pathways and very small interchain interactions due to the lack of pathways between chains, which makes the observed long-range orders particularly unusual. All six Ir-O bond lengths in each octahedron are unequal, but the noncubic crystal field generated by these distortions is not a significant perturbation when compared to the SOI, as discussed below.

IV. RESULTS AND DISCUSSION

We first argue for the existence of charge order, which has important implications for the physical properties of Ba$_5$AlIr$_2$O$_{11}$. The electrical resistivity $\rho_b$ along the dimer chain direction increases by nearly nine orders of magnitude when temperature is lowered from 750 K (10$^5$Ω cm) to 80 K [10$^{11}$Ω cm; Fig. 3(a)]. More importantly, $\rho_b$ exhibits a distinct slope change near $T_S = 210$ K and follows an activation law reasonably well (better than power laws) in a temperature range of 200–750 K, which yields an activation energy gap $\Delta_a \approx 0.57$ eV [inset in Fig. 3(a)]. The more rapid increase in $\rho_b$ below $T_S = 210$ K indicates the charge-order transition is accompanied by increased localization of electronic states, as shown in Fig. 3(a). The dielectric constant $\varepsilon(T)$ and specific heat $C(T)$ (discussed below) are also consistent with a bulk transition to long-range order at $T_S$.

The charge-ordered state we envision inevitably leads to formation of an electric dipole in each dimer. These electrical dipoles are parallel to each other within each dimer chain but are expected to orient antiparallel between dimer chains in order to minimize electrical energy, as schematically...
illustrated in Fig. 4 (red arrows). This also explains the unusually large peak in dielectric response near $T_S = 210$ K, as shown in Fig. 3(b); the real parts $\varepsilon'_a(T)$ and $\varepsilon'_b(T)$ of the $a$-axis and $b$-axis dielectric constants, respectively, rise by two orders of magnitude and peak near $T_S$ due to lattice softening, an inevitable consequence of the structural phase transition. The observed strong peak in both $\varepsilon'_a(T)$ and $\varepsilon'_b(T)$ is stronger than that of well-known ferroelectrics such as BaMnF$_4$, BiMnO$_3$, HoMnO$_3$, and YMnO$_3$ [26–28]. In addition, two weaker anomalies occur near 130 and 30 K [inset in Fig. 3(b)]. The rapid decrease in $\varepsilon'_c(T)$ below 30 K implies the lattice stiffens as long-range magnetic order is approached at $T_M = 4.5$ K, as discussed below. Both $\varepsilon'_a(T)$ and $\varepsilon'_b(T)$ exhibit strong frequency dependencies that can signal relaxor behavior.

Given the quasi-one-dimensional nature of the crystal structure of Ba$_5$AlIr$_2$O$_{11}$, it is reasonable that three-dimensional correlations necessary for magnetic order are established at the rather low temperature $T_M = 4.5$ K. The $b$-axis magnetization $M_b$ exhibits a peak at $T_M$, whereas the $a$- and $c$-axis magnetizations, $M_a$ and $M_c$, rise below $T_M$ [Fig. 5(a)]. There is no discernable anomaly near $T_S$ (see inset in Fig. 5). The observed large magnetic anisotropy indicates that the SOI is significantly stronger than any possible noncubic crystal field due to the distortions in dimers, which would alter the effect of SOI, resulting in more isotropic magnetic behavior. We propose that the magnetic moments are aligned ferromagnetically within each dimer chain but antiferromagnetically between dimer chains to minimize magnetic dipole energy (see Fig. 4, black arrows). It needs to be pointed out that Fig. 4 is a simplified illustration, as it does not include possible canting of the magnetic moments. The fact that $M_a$ is greater than $M_c$, as evidenced in Fig. 5(a), suggests that the canting may be more tilted towards the $a$ axis than the $c$ axis. Nevertheless, it is curious that the magnetic susceptibility $\chi_b$ along the $b$ axis systematically decreases with applied field below $T_M$ [see Fig. 5(b)], indicating enhanced antiferromagnetic compensation or reduced moment fluctuations along the dimer chain direction. Moreover, the magnetic transition shifts only slightly in strong magnetic fields up to 12 T [Fig. 5(b)], which contrasts with the conventional expectation that a 12-T magnetic field should be strong enough to completely suppress $T_M$ ($= 4.5$ K at zero field). This behavior is also evidenced in the heat-capacity data obtained at a magnetic field of 9 T discussed below. Nevertheless, $T_M$ is more susceptible to hydrostatic pressure and shifts from 4.5 K at ambient pressure to 5 K at 8.2 kbar at the substantial rate of 0.61 K/GPa [see Fig. 5(c)], implying an enhanced magnetic interaction between the $5d$ electrons and a magnetoelastic effect. The weak field dependence coupled with the substantial pressure dependence of $T_M$ constitutes noteworthy characteristics of this dimer chain system.

![Fig. 2](image-url)
FIG. 3. (Color online) Temperature dependence of (a) the $b$-axis electrical resistivity $\rho_b$ and (b) the dielectric constant for the $a$ axis and $b$ axis, $\varepsilon'_a$ and $\varepsilon'_b$, respectively. The inset in (a) shows $\ln \rho_b$ vs $1/T$; the inset in (b) shows $\varepsilon'_b$ vs. $T$ for lower temperatures.

Data fits to the Curie-Weiss law for $50 < T < 320$ K yield a Curie-Weiss temperature $\theta_{\text{CW}} = -14$ K and effective moment $\mu_{\text{eff}} = 1.04\mu_B$/dimer, much smaller than the value $3.88\mu_B$ expected for an $S = 3/2$ system [see Fig. 5(a)]. The negative $\theta_{\text{CW}}$ implies antiferromagnetic coupling, whereas the reduced $\mu_{\text{eff}}$ results from the joint effect of the SOI and electron hopping between the two Ir1 and Ir2 sites [25]. The onset of long-range magnetic order is also corroborated by a sharp $\lambda$ peak in the specific heat $C(T)$ at $T_M = 4.5$ K, measured both at $\mu_0H = 0$ and 9 T [see Fig. 6(a)], which is consistent with the magnetization behavior shown in Fig. 5(b). An analysis of the $C(T)$ data yields an entropy removal below $T_M$ of approximately 1.00 J mole$^{-1}$ K$^{-1}$, which is well below the value 11.37 J mole$^{-1}$ K$^{-1}$ anticipated for an $S = 3/2$ system [Fig. 6(a)]. A portion of the magnetic entropy may be removed at higher temperatures by the transition at $T_S = 210$ K. Indeed, we observe a weak, but well-defined, anomaly in $C(T)$ near $T_S$.

FIG. 4. (Color online) A sketch of the proposed configurations of electrical dipoles ($E$, red arrows) and magnetic moments ($M$, black arrows) for (left) the $ac$ plane and (right) the $ab$ plane based on the data collected for this study. This is a simplified illustration that does not include possible magnetic moment canting.

FIG. 5. (Color online) Temperature dependence of (a) the magnetization for the $a$, $b$, and $c$ axes, $M_a$, $M_b$, and $M_c$, at $\mu_0H = 7$ T, (b) the $b$-axis magnetic susceptibility $\chi_b$ at various fields, and (c) $M_b$ at various pressures and $\mu_0H = 7$ T. The inset shows enlarged $M_b$ near $T_S$. 

J. TERZIC et al.  
PHYSICAL REVIEW B 91, 235147 (2015)
210 K, which decreases entropy, as shown in Fig. 6(b). This observation reinforces the remarkable trend that a very small entropy is removed at a well-defined magnetic transition in iridates studied so far [4, 15, 16, 19].

Our \textit{ab initio} calculations with the generalized gradient approximation (GGA; to be published elsewhere [25]) indicate that charge order is slightly more energetically favorable than the double-exchange state, although the charge order is incomplete (the charge disproportionation of \( \sim 0.3 \) electron) is approximately 0.3 electron. This is consistent with an exotic ground state in which antiferromagnetic and charge order coexist. The calculations (including GGA + SOI) result in a total effective moment \( \mu_{\text{eff}} \sim 1.04 \mu_B/\text{dimer} \) (compared to \( 2.0 \mu_B/\text{dimer} \) obtained in the GGA calculations without SOI), which is remarkably consistent with the experimental value discussed above and supports the importance of SOI. The combined effect of both SOI and electron hopping apparently alters the delicate balance between the competing energies and, as a result, weakens the Hund’s rule coupling \( J_H \) that tends to maximize the spin moment.

V. CONCLUSIONS

We have observed the coexisting charge and antiferromagnetic orders in a quasi-one-dimensional dimer system, Ba\(_3\)Al\(_2\)Ir\(_2\)O\(_{11}\). All our observations are consistent with a subtle ground state that is stabilized by an unusual interplay between charge disproportionation (due to the crystal structure), formation of molecular orbitals (due to strong covalency), a double-exchange mechanism (comparable \( J_{\text{DE}} \), and SOI.

While charge order is clearly manifested by the structural transition and anomalies in \( \rho(T) \) and \( C(T) \) at \( T_S = 210 \) K [Figs. 2, 3, and 6(b)], the charge disproportionation of \( \sim 0.3 \) electron is not fully developed but is sufficient to induce the strong anomalies observed in the dielectric constant (Fig. 3). The magnetic behavior at \( T_M = 4.5 \) K indicates an exotic, long-range order that is more sensitive to pressure than to magnetic fields (Fig. 5). It is plausible that the magnetic moments are aligned (along the \( b \) axis) ferromagnetically within each dimer chain but antiferromagnetically between dimer chains to minimize magnetic dipole energy (Fig. 4).

It is clear that a purely ionic model with strong SOI, which would support a \( J = 1/2 \) state in Ir\(^{5+} \) (5\( d^5 \)) ions and \( J = 0 \) state in Ir\(^{4+} \) (5\( d^4 \)) ions, is not entirely applicable here. The reduced total moment per dimer (1.04\( \mu_B/\text{dimer} \)) is evidence of depressed double exchange. These observations suggest covalency plays a role in formation of singlet molecular orbitals among some of the \( d \) orbitals [25, 29–32], but it alone cannot suppress Hund’s rule coupling \( J_H \) or double exchange. Indeed, both covalency and the SOI conspire to suppress the double exchange in Ir dimers and to stabilize a magnetic state that lies “in between” \( S = 3/2 \) and \( J = 1/2 \). Thus the combined action of strong covalency and the SOI overcomes double exchange and stabilizes a novel magnetic state.

The dimer chain Ba\(_3\)Al\(_2\)Ir\(_2\)O\(_{11}\) provides a unique paradigm for the investigation of SOI in the 4d/5d transition-metal oxides, especially mixed-valent 4d and 5d systems.

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