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Influence of structural distortions on the Ir magnetism in $\text{Ba}_{2-x}\text{Sr}_x\text{YIrO}_6$ double perovskites



Brendan F. Phelan*, Elizabeth M. Seibel, Daniel Badoe Jr., Weiwei Xie, R.J. Cava

Department of Chemistry, Princeton University, Princeton, NJ 08540, United States

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ABSTRACT

We explore the relative strengths of spin orbit coupling and crystal field splitting in the Ir^{5+} compounds $\text{Ba}_{2-x}\text{Sr}_x\text{YIrO}_6$. In the case of strong spin orbit coupling and regular Ir^{5+} octahedra, one expects a non-magnetic $J=0$ state; in the case of distorted octahedra where crystal field effects dominate, the t_{2g} manifold splits into a magnetic ground state. We report the results of continuously transitioning from the cubic Ba_2YIrO_6 double perovskite with ideal octahedra to the monoclinic Sr_2YIrO_6 double perovskite with distorted octahedra. We see no emergence of an enhanced Ir^{5+} magnetic moment in the series on increasing the structural distortions, as would have been the case for significant crystal field splitting. The near-constant magnetic moment observed through the $\text{Ba}_{2-x}\text{Sr}_x\text{YIrO}_6$ series reinforces the notion that spin-orbit coupling is the dominant force in determining the magnetism of iridium-oxygen octahedra in perovskite-like structures.

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1. Introduction

Spin-orbit coupling (SOC) continues to be an important factor to consider when predicting and understanding the electronic and magnetic properties of strongly correlated materials that include heavy metals. It has proven to play an important role in the emergence of materials properties such as insulating antiferromagnets, superconductors, and topological insulators [1–12]. Of particular interest have been extended systems of IrO_6 octahedra with iridium in a formal oxidation state of $4+$. In these octahedral- $[\text{Xe}]5d^5$ systems, the five valence electrons occupy the triply degenerate t_{2g} manifold. It is widely accepted that strong spin-orbit coupling will split this degenerate t_{2g} manifold into a doublet $J_{\text{eff}}=1/2$ and a quartet $J_{\text{eff}}=3/2$ band. The completely filled, lower energy $J_{\text{eff}}=3/2$ and the half-filled, higher energy $J_{\text{eff}}=1/2$ bands give rise to an overall $J=1/2$ system. Much of the work studying these systems has focused on advanced spectroscopic techniques such as inelastic x-ray scattering. These studies point to the existence of a complex interplay between competing spin-orbit coupling and crystal field splitting, the latter of which is also able to break the degeneracy of the t_{2g} manifold [13–20]. With increasing distortion of the octahedra it is to be expected that the strength of crystal field will become a more important factor in determining the electronic structure of these compounds.

However, little work has focused on how far a crystal structure based on IrO_6 octahedra can be distorted from ideal geometry before the magnetism is affected due to the influence of the crystal field. For this purpose, systems featuring isolated Ir^{5+} octahedra whose size or shape can be continuously varied are useful. Compared to systems featuring Ir^{4+}O_6 ($J_{\text{eff}}=1/2$) octahedra, those featuring Ir^{5+}O_6 ($J_{\text{eff}}=0$) octahedra remain scarcely studied through the lens of SOC. The expected spin state of these compounds should be zero in the point-charge picture and, as a result, small deviations of the crystal field resulting from structural distortions have the potential to leverage large changes in magnetic behavior.

For this reason we designed a study based on two previously reported compounds: Sr_2YIrO_6 [21] and Ba_2YIrO_6 [22]. Ba, Sr, Y and O ions are all non-magnetic (they have closed electron shells) in this type of system. The former compound is monoclinic with significantly distorted and tilted IrO_6 octahedra, while the latter is a cubic compound with undistorted octahedra (in Fig. 1a and b, bond angles and lengths are taken from Ref. [23], as are the structural parameters included in Fig. 4). The structural characteristics of the $\text{Ba}_{2-x}\text{Sr}_x\text{YIrO}_6$ solid solution between these two end-member compounds have been reported in detail [23], and are not repeated here: they provide the crystallographic framework for the current work. By tracking the changes in the magnetic moment per Ir as the crystal structure becomes increasingly distorted, we can determine whether the structural distortions

* Corresponding author.

E-mail address: bfp@princeton.edu (B.F. Phelan).

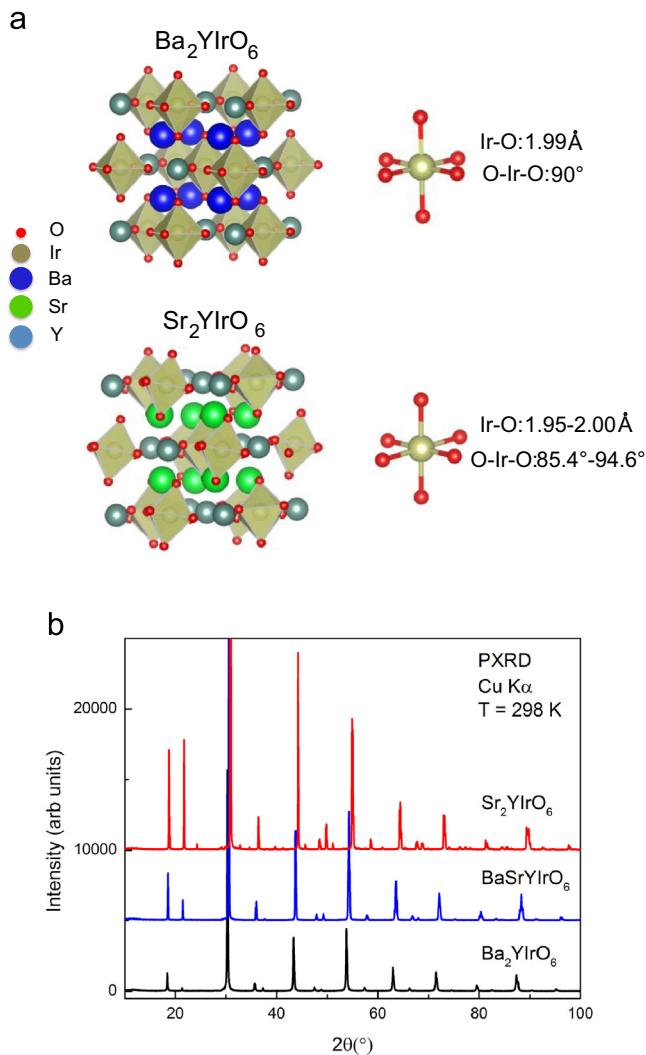


Fig. 1. (a) The crystal structures of Ba_2YIrO_6 and Sr_2YIrO_6 . The IrO_6 octahedra in Ba_2YIrO_6 are regular, with 6 Ir–O bond lengths of 1.99 Å and O–Ir–O angles of 90° [22,23]. The IrO_6 octahedra of Sr_2YIrO_6 are significantly distorted, with Ir–O bond lengths between 1.95–2.00 Å, and O–Ir–O angles of $85.4\text{--}94.6^\circ$ [21,23]. (b) Representative powder X-ray diffraction patterns of Ba_2YIrO_6 , BaSrYIrO_6 and Sr_2YIrO_6 .

increase the crystal field enough to overcome the influence of the SOC and cause a significant change in the electronic structure.

2. Materials and methods

Polycrystalline samples of $\text{Ba}_{2-x}\text{Sr}_x\text{YIrO}_6$ ($0 \leq x \leq 2$, $\Delta x = 0.25$) were prepared by solid-state synthetic methods. Powdered samples were prepared from dried BaCO_3 (powder, 99.99%, Alfa Aesar), dried SrCO_3 (powder, 99.99%, Alfa Aesar), Y_2O_3 (nanopowder, 99.99%, Sigma-Aldrich) and Ir metal (powder, 99.95%, Alfa Aesar). Mixtures of starting materials were homogenized with mortar and pestle and then heated to 1200°C under flowing O_2 for 36 h. Samples were reground and heated again to 1300°C under flowing O_2 for 36 h. Samples were characterized using powder X-ray diffraction (PXRD) using a Bruker D8 ECO Advance with Cu $K\alpha$ radiation and LYNXEYE-XE detector [24].

Temperature dependent magnetizations (M) were measured with a Quantum Design Magnetic Property Measurement System (MPMS). Measurements of the M vs. applied magnetic field ($\mu_0 H$)

were linear up to applied fields of 1.5 T, and thus χ was defined as $\chi = M/\mu_0 H$, at an applied field of 1 T. Zero-field cooled (ZFC) measurements were performed on heating from 2 K to 300 K in a magnetic field of 1 T.

3. Calculations

Theoretical calculations on hypothetical model compounds in the $\text{Ba}_{2-x}\text{Sr}_x\text{YIrO}_6$ solid solution, using experimental Ba_2YIrO_6 structural data for $x = 0\text{--}1.0$ [22], and experimental Sr_2YIrO_6 structural data and for $x = 1.25\text{--}2$ [21]. Calculations were carried out using the Vienna Ab-initio Simulation Package (VASP) with the plane wave cutoff energy of 500 eV, and a set of $7 \times 7 \times 7$ k and $7 \times 7 \times 5$ k points for the irreducible Brillouin zones of the cubic Ba_2YIrO_6 – model and the monoclinic Sr_2YIrO_6 – model, respectively. Exchange and correlation were treated by the generalized gradient approximation. To consider the effect of on-site repulsion for the 5d element, Ir, LSDA calculations were performed with and without U , with $U = 4.7$ eV and $J = 0.7$ eV. The density of states (DOS) and band structure calculations for the compounds were performed by employing the Tight-binding Linear-Muffin-Tin-Orbital Atomic Sphere Approximation (TB-LMTO-ASA) using Stuttgart codes. Exchange and correlation were treated by the local density approximation (LDA) and the local spin-density approximation (LSDA). In the ASA method, space is filled with overlapping Wigner–Seitz (WS) spheres. The symmetry of the potential is considered spherical inside each WS sphere, and a combined correction is used to take into account the overlapping parts of the charge density. Empty spheres are necessary for this structure type, and the overlap of WS spheres is limited to no larger than 16%.

4. Results and discussion

The solid solution of the type $\text{Ba}_{2-x}\text{Sr}_x\text{YIrO}_6$ ($0 \leq x \leq 2$, $\Delta x = 0.25$) was successfully prepared as single phase materials by the method described [23]. The X-ray powder diffraction patterns for the end members (Ba_2YIrO_6 and Sr_2YIrO_6) and one intermediate composition BaSrYIrO_6 are shown as examples in Fig. 1c and are in agreement with previous work [23]. In order to experimentally determine the effective moment (μ_{eff}) per iridium for the members of the solid solution, we measured the zero field cooled (ZFC) magnetization versus temperature at an applied field of 1 T from 2 to 300 K. The temperature dependent magnetic susceptibilities (χ) are shown in Fig. 2, plotted in different ways. Fig. 2 shows the general behavior of the susceptibility on a linear scale; it can immediately be seen that there is no dramatic increase in χ as the IrO_6 octahedra and the inter-octahedra bond angles become more distorted with increasing x . Thus the raw data show that the system does not become substantially more magnetic with increasing structural distortion. The inset to Fig. 2 shows the measured susceptibilities at high temperatures for all samples studied. From these data we later extract the raw susceptibility at 250 K as a measure of the overall paramagnetism of each material. At high T this is dominated by a temperature independent term (χ_0) that is extracted from the low temperature fits, as described.

Because the magnetic moments in the system are small and weakly interacting, the low temperature magnetic susceptibilities best reflect the magnetic state of the Ir and its interactions. Fig. 3 shows that there are two regions in the $1/(\chi - \chi_0)$ plot. At high temperatures, the curves turn over, and somewhat higher moments and higher apparent Curie Weiss temperatures could be inferred for the whole series. However, this high temperature

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