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Electronic structure and magnetic properties of Ca_2IrO_4, using first principles

Vijeta Singh*, J.J. Pulikkotil

Academy of Scientific & Innovative Research (AcSIR), CSIR-NPL, New Delhi 110012, India
Council of Scientific and Industrial Research, National Physical Laboratory, New Delhi 110012, India

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ABSTRACT

A comprehensive set of electronic structure calculations are performed to understand the origin of the insulating gap and magnetic properties of hexagonal Ca_2IrO_4. Although, isoelectronic with Sr_2IrO_4, the spin-orbit coupling driven J_{eff} model is anticipated to be less appropriate for Ca_2IrO_4 following its structural considerations. We find that the local density approximation (LDA), and those including the effects of Coulomb correlations and spin-orbit coupling fail to reproduce the experimental results. Moreover, the calculations employing the modified Becke-Johnson formalism seems to provide sufficiently good results, by predicting Ca_2IrO_4 to be an antiferromagnetic insulator. The origin of electronic gap is attributed to the antiferromagnetic ordering of Ir spins and the effects of spin-orbit coupling is found marginal. However, due to the anisotropy in the Ir−O bonding within the distorted IrO_6 octahedra we deduce large magneto-anisotropic energy in Ca_2IrO_4. Further, our analysis shows that Ca_2IrO_4 is an itinerant material, suggesting that band structure effects play an important role in determining the ground state properties of iridates.

1. Introduction

The length scales associated with crystal field interactions, Coulomb correlations and spin-orbit coupling (SOC) vary across the chemical periodic table. Interestingly, these interactions appear to balance for iridates, thereby yielding a plethora of novel quantum states [1–5]. In addition, the insulating ground state as exhibited by few iridates, such as Sr_2IrO_4, Ba_2IrO_4, Na_2IrO_3, $CaIrO_3$ and others [1–9] are also surprising. On conventional grounds, owing to the large spatial extend of their orbitals, iridates may be anticipated to be good conductors. However, from the physics of 3*d*-transition metal oxides it has been understood that octahedral distortions in oxides tend to narrow the bands, thereby facilitating Coulomb correlations and hence rendering an insulating ground state. However, in systems such as Sr_2IrO_4, the IrO_6 motifs possess a near cubic symmetry, while in $SrIrO_3$ they are relatively more distorted. Thus, given that iridates with octahedral motifs such as $SrIrO_3$ exhibit a conducting ground state and those with undistorted motifs are insulating suggests the prominence of an unconventional mechanism, beyond structural considerations, at play.

A fascinating model that explains the unconventional properties of iridates is the $J_{eff} = \frac{1}{2}$ model [1]. In this model, the crystal field split t_{2g} bands are further split by SOC into the $J_{eff} = \frac{3}{2}$ quartets and $J_{eff} = \frac{1}{2}$ doublet states. For iridates with Ir in a formal + 4 valence state (i.e., with an electronic configuration $5d^5$), the $J_{eff} = \frac{3}{2}$ would be fully filled with four electrons, leaving the $J_{eff} = \frac{1}{2}$ doublet singly occupied. Further, it is anticipated that Coulomb interactions would split the narrow $J_{eff} = \frac{1}{2}$ band into a lower and upper Hubbard band, thereby rendering iridates, such as Sr_2IrO_4, a SOC- driven $J_{eff} = \frac{1}{2}$ Mott state. The semimetallic ground state of $SrIrO_3$ also could be partly explained by the model, where an complete splitting of the J_{eff} bands is limited by strong Ir 5*d* - O 2*p* hybridization [10].

The basic assumption of the J_{eff} model is that the local IrO_6 motifs in iridates, possess an underlying cubic symmetry. Such symmetry considerations ensure a well separated t_{2g} and e_g bands of the Ir 5*d* manifold and that the three orbitals of the t_{2g} manifold remains degenerate. However, systems such as pPv-$CaIrO_3$, A_2IrO_3 (A = Li, Na), Sr_3IrCuO_6 are also found insulating, despite Ir having a formal + 4 valence state in an otherwise non-cubic crystal field. Furthermore, the SOC mediated J_{eff} model appears less successful to account for the insulating ground state of certain higher valence state systems. For instance, the charge neutrality condition for Sr_2YIrO_6 infers Ir to be in a 5+ valence state (i.e., $5d^4$) [2]. Therefore, the J_{eff} model would predict Sr_2YIrO_6 to be a nonmagnetic band insulator. However, experiments find Sr_2YIrO_6 to be an antiferromagnetic insulator with a transition temperature 1.3 K [2]. Also, the insulating and antiferromagnetic ordering in Ca_2NiIrO_6 also indicate towards an underlying unconventional mechanism [12].

* Corresponding author at: Academy of Scientific & Innovative Research (AcSIR), CSIR-NPL, New Delhi 110012, India.
E-mail address: vijeta.singh@nplindia.org (V. Singh).

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Certainly, SOC is dominant mechanism in Ca_2NiIrO_6 and also in pPv-$CaIrO_3$ as manifested by the large coercivity field displayed in the materials hysteresis loop [13].

Apart from the underlying cubic symmetry of the IrO_6 motifs, it also appears that dimensionality plays an important role in rendering iridates an insulating ground state [29]. For instance, in the Ruddlesden-Popper series $Sr_{n+1}Ir_nO_{3n+1}$, both $n = 1$ (Sr_2IrO_4) and $n = 2$ ($Sr_3Ir_2O_7$) are quasi-two dimensional systems, while $n = \infty$ ($SrIrO_3$) crystallizes in monoclinic and orthorhombic structures. The tetragonal structure of Sr_2IrO_4 and $Sr_3Ir_2O_7$ separates the IrO_6 octahedra along the crystallographic c-axis, with charge neutral −SrO− spacer layers. However, in $SrIrO_3$ the IrO_6 octahedra are interlinked along all crystallographic axes, thereby imparting a 3D structure. Despite being semi-metallic, the electronic structure of $SrIrO_3$ corroborate partly well with the $J_{eff} = \frac{1}{2}$ model [31]. From the first principles calculations, it follows that the t_{2g} and e_g manifold remain widely separated, and that SOC induces a pseudo-gap like feature in the density of states spectra [10,11]. The semi-metallic properties emerge from the incomplete splitting of the J_{eff} states, owing to the strong hybridization of the Ir 5d and O 2p orbitals. Thus, the clear distinction of the ground state properties of Sr_2IrO_4 and $SrIrO_3$ indicates to the detrimental role of the underlying crystal dimensionality.

In order to gain more insight into the interplay of crystal structure and various interactions at electronic level, we explore the physical properties of Ca_2IrO_4 [21]. Although isoelectronic with tetragonal Sr_2IrO_4, Ca_2IrO_4 crystallizes with an underlying $P\bar{6}2m$ hexagonal symmetry. The IrO_6 octahedra in Ca_2IrO_4, share edges with Ca ions in three different types of crystallographic sites, namely Ca(1) at the 2d Wyckoff position, Ca(2) at the 1a and Ca(3) at the 3g site positions of the hexagonal unit cell. Since these Ca ions have different coordination numbers and also smaller ionic radii compared to Sr and Ba counterparts, the IrO_6 octahedra in Ca_2IrO_4 are significantly distorted. Thus, Ca_2IrO_4 represents a non-cubic crystal field system with Ir ions in the + 4 valence state. However, given that Ca_2IrO_4 is an antiferromagnetic insulator [21,23] and that the IrO_6 motifs are significantly distorted [21], it may be well anticipated that prominent effects of SOC on the materials band structure may be drastically different from that of its isoelectronic Sr_2IrO_4 counterpart.

The equilibrium phase diagram of the ternary Ca−Ir−O systems were reported by McDaniel et al. [20]. It was found that $CaIrO_3$ when calcined at 1408 K, decomposes into Ca_2IrO_4 and Ir. A successful growth of Ca_2IrO_4 is also reported by Keawprak et al. [22], where a single phase was accomplished by solid state reaction techniques. The temperature dependence of electrical conductivity showed Ca_2IrO_4 to be a n-type semi-conducting material. Recently, Souri et al. [23], synthesized Ca_2IrO_4 thin-films by pulsed laser deposition. Quite differently from the bulk, the structural refinements of the films showed tetragonal symmetry which is quite similar to that of Sr_2IrO_4 [30]and Ba_2IrO_4. The magnitude of the band gap deduced from the resistivity curve was 120 meV which is comparable to that of Sr_2IrO_4 (250 meV) and Ba_2IrO_4 (190 meV) [23]. The authors attribute the origin of the gap to the SOC driven $J_{eff} = \frac{1}{2}$ splitting, despite finding strong distortions of the IrO_6 octahedra from their structural refinements. Hence, it becomes interesting to study the influence of cooperative mechanism involving SOC and Coulomb correlations, on the structural, electronic and magnetic properties of Ca_2IrO_4. Our interest in Ca_2IrO_4 is also motivated by the less explored debate that whether the electronic gap in iridates is purely SOC driven or by antiferromagnetic interactions [3,4]. We note that such controversies exist for pPv-$CaIrO_3$ systems as well, where despite strong IrO_6 octahedral distortions the origin of the electronic gap is attributed to SOC [24,25] and also to antiferromagnetic interactions [14,15].

To address these questions pertained to the origin of the electronic gap and magnetism in Ca_2IrO_4, we adopt the first-principles density functional theory based calculations. We find that both LDA and GGA are inappropriate approximations to match the experimental results. On the other hand, the LDA + U calculations with $U \simeq 3.5$ eV is found to open a small electronic band gap of magnitude 0.14 eV. It may be noted, that for iridates the magnitude of U deduced from experiments is not more than 1–2 eV [4,25]. Hence, the LDA + U method, with $U > 3$ eV also seems to be less appropriate methodology to describe the ground state properties of Ca_2IrO_4. Moreover, a much better consistency with the experiments are derived from the recently developed modified Becke-Johnson (mBJ) exchange potential [44]. In fact, it has been demonstrated earlier that mBJ calculations not only correctly predict an insulating state for a variety of systems but also find the magnitude of the gap to be in good agreement with the experiments [15–19]. Furthermore, as expected from the structural considerations SOC is found to have little or no role in the origin of electronic gap in Ca_2IrO_4. On the other hand, the computed high magneto-crystalline anisotropy in Ca_2IrO_4 is a clear manifestation of the SOC effects, which is partly due to a large structural $\frac{c}{a}$ ratio and anisotropy in the Ir−O bonding within the IrO_6 octahedra.

2. Computational details

To study the electronic structure and magnetic properties of Ca_2IrO_4, we adopt the full potential linearized augmented plane-wave (FP-LAPW) method as implemented in the WIEN2K code [36]. The experimental lattice parameters with $a = 9.42$ Å, and $c = 3.19$ Å were used [21]. The LAPW sphere radii for Ca, Ir and O were chosen as 2.25, 2.0 and 1.70 a.u., respectively. Prior to the charge self consistent calculations, the equilibrium ionic coordinates were determined using the force optimization technique [35]. For the total energy and the ground state electronic structure properties, well-converged basis sets were achieved with $R_{MT}K_{max} = 7$, were R_{MT} and K_{max} represents the smallest muffin-tin radius and the maximum size of the reciprocal lattice vectors, respectively. The Fourier-expanded charge density was truncated at $G_{max} = 24$ a.u.$^{-1}$and, the maximum value of the angular momentum was set as $l_{max} = 7$ for the wave function expansion inside the LAPW spheres. Additional local orbitals were also used to account for the semi-core Ir 5p states. A threshold energy of −8.0 Ry was used to separate the valence from the core states. The exchange correlation potential term in the crystal Hamiltonian was considered in the local density approximation (LDA)[37], LDA + U [34] and, in the recently developed modified Becke-Johnson (mBJ) [44] formalism. For the total energy calculations, the Brillouin Zone integration was carried out using the modified tetrahedron method with mesh of 400 k-points in its irreducible part. While the core states were treated relativistically, the SOC was included for the valence states through the second variational step with a scalar relativistic basis [39,40]. States up to 10 Ry above the Fermi energy (E_F) were included in the basis expansion.

3. Results and discussion

3.1. Crystal structure

The schematic representation of the Ca_2IrO_4 unit cell is shown in Fig. 1. By virtue of its underlying $P\bar{6}2m$ hexagonal symmetry, the six Ca atoms in the unit cell are distributed onto three inequivalent sites, namely the 2d: $\left(\frac{1}{3}, \frac{2}{3}, \frac{1}{2}\right)$, 1$a$: (0, 0, 0) and 3$g$: $\left(x, 0, \frac{1}{2}\right)$. Of three nonequivalent O atoms, the O(1) and O(2) atoms are distributed on to 3g sites while the O(3) atoms occupy the 6j (x, y, 0) sites. The Ir ions are positioned at the 3f: (x, 0, 0) sites. Note that from the nomenclature we follow, O(1) and O(2) ions lie in the a−b plane of the hexagonal unit-cell, while the O(3) is directed along the crystallographic c-axis. As evident, since the ionic coordinates of Ca(3), Ir and all O ions are not fixed by symmetry, we first determine the equilibrium coordinates using the force optimization algorithm The theoretical and experimental structural parameters, bond-distances and bond angles are shown in Tables 1. With the variance in the structural parameters being