

Density functional theory of resonant inelastic x-ray scattering in the quasi-one-dimensional dimer iridate $\text{Ba}_3\text{IrIr}_2\text{O}_9$

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We have investigated the electronic structure of $\text{Ba}_3\text{IrIr}_2\text{O}_9$ within the density-functional theory using the generalized gradient approximation while considering strong Coulomb correlations (GGA + U) in the framework of the fully relativistic spin-polarized Dirac linear muffin-tin orbital band-structure method. We have studied resonant inelastic x-ray scattering (RIXS) spectra of $\text{Ba}_3\text{IrIr}_2\text{O}_9$ at the Ir L_3 edge for the monoclinic $C2/c$ and hexagonal $P6_3/mmc$ crystal structures. The calculated results are in good agreement with experimental data. The RIXS spectrum at the Ir L_3 edge possesses several sharp features below 2 eV, corresponding to transitions within the Ir t_{2g} levels. The excitation located from 2 to 5 eV is due to $t_{2g} \rightarrow e_g$ transitions. The wide structure situated at 5–12 eV appears due to charge transfer transitions. The influence of the momentum transfer vector and incident photon energy on the Ir L_3 RIXS spectrum has been investigated. Also, we have calculated the RIXS spectra of $\text{Ba}_3\text{IrIr}_2\text{O}_9$ at the Ir K , M_3 , M_5 , N_3 , N_5 , and N_7 edges to study the influence of core states on the resulting Ir RIXS spectra. The theoretical RIXS spectrum at the oxygen K edge has also been analyzed.

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I. INTRODUCTION

In $5d$ transition metal compounds, the energy scale of the spin-orbit coupling (SOC) is comparable with the on-site Coulomb interaction and the crystal-field energy. Due to the strong competition between these interactions, fascinating electronic states can arise. SOC in such systems splits the t_{2g} orbitals into a quartet ($J_{\text{eff}} = \frac{3}{2}$) and a doublet ($J_{\text{eff}} = \frac{1}{2}$) [1–3]. In $5d^5$ (Ir^{4+}) iridium oxides, such as Sr_2IrO_4 , the quartet $J_{\text{eff}} = \frac{3}{2}$ is fully occupied, and the relatively narrow $J_{\text{eff}} = \frac{1}{2}$ doublet, occupied by one electron, can be splitted by moderate Hubbard U_{eff} with opening a small band gap called the relativistic Mott gap [4–7]. Iridates have been at the center of intensive research in recent years for novel phenomena, such as topological insulators [8–11], Mott insulators [4,5,12,13], Weyl semimetals [14–16], and quantum spin liquids [17–19].

The specific features of the systems with spin and orbital degeneracy strongly depend on the local geometry. The most typical cases, widely discussed in the literature, are those with MO_6 octahedra (M is a transition-metal ion) sharing a common oxygen (or a common corner), such as the LaMnO_3 perovskite or layered systems as La_2CuO_4 , and with neighboring octahedra sharing two common oxygen (octahedra with a common edge), met in many layered systems with triangular lattices, such as NaCoO_2 and LiNiO_2 . The features of spin-orbital systems in both these cases were studied in detail; see,

e.g., Ref. [20]. However, there exists yet one more typical geometry, which is also very often met in many real materials: the case of octahedra with a common face (three common oxygen). This case has relatively small attention in the literature. Actually, there are many transition-metal compounds with the face-sharing geometry [21]. Such materials include, for example, hexagonal crystals such as BaCoO_3 [22], BaVS_3 [23], or CsCuCl_3 [24]. Many other similar systems have finite face-sharing blocks, e.g., BaIrO_3 [25], BaRuO_3 [26,27], or $\text{Ba}_4\text{Ru}_3\text{O}_{10}$ [28,29] with blocks of three such face-sharing octahedra, connected between themselves by common corners; or blocks of two such octahedra as in a large series of systems with the general formula $A_3\text{BM}_2\text{O}_9$ [30–37], where A is Ba, Ca, Sr, Li, or Na, and the face-sharing MO_6 octahedra of transition metals are separated by BO_6 octahedra (which have common corners with MO_6). Such systems have very diverse properties: some of them are metallic [38]; others are insulators [30] or undergo a metal-insulator transition [31]. Materials of this family with magnetic B sites have been shown to exhibit quantum spin-liquid behavior, in particular, $\text{Ba}_3\text{NiSb}_2\text{O}_9$ [39–41] and $\text{Ba}_3\text{IrTi}_2\text{O}_9$ [42], while others, $\text{Ba}_3\text{CuSb}_2\text{O}_9$ [43–45] and $\text{Ba}_3\text{ZnIr}_2\text{O}_9$ [46], exhibit possible quantum spin-orbital liquids. Furthermore, $\text{Ba}_3\text{CoSb}_2\text{O}_9$ has allowed for some of the first studies on the magnetization process of a truly triangular spin- $\frac{1}{2}$ antiferromagnet [47–51].

The series of perovskites $\text{Ba}_3\text{M}\text{Ir}_2\text{O}_9$ (M = an alkaline-earth, transition metal, or rare-earth element) is also rather interesting because a wide range of compounds with a variety of Ir oxidation states can be obtained by changing component M . The nominal oxidation state of Ir can be 5.5+ (for $M = \text{Li}^+$, Na^+ [52]), 5+ (for $M = \text{Zn}^{2+}$, Mg^{2+} , Ca^{2+} , Cd^{2+} [53]), 4.5+ (for $M = \text{Y}^{3+}$, Sc^{3+} , In^{3+} , Lu^{3+} [53,54]), and 4+ (for $M = \text{Ti}^{4+}$, Zr^{4+} [53]). There are several experimental studies

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on the $6H$ $Ba_3M\text{Ir}_2\text{O}_9$ compounds with $M = \text{Zn, Mg, Ca, Sr, Y, Sc, and In}$ [46,53,55–58], which show diverse ground-state properties. For instance, $Ba_3\text{ZnIr}_2\text{O}_9$ was reported to exhibit a spin-orbital liquid state, with an effective magnetic moment of $\sim 0.26 \mu_B/\text{Ir}$ site [46]. Closely related $Ba_3\text{CdIr}_2\text{O}_9$ [58] and $Ba_3\text{MgIr}_2\text{O}_9$ [56] were seen to exhibit no long-range magnetic order down to the lowest measured temperature. However, $Ba_3\text{CaIr}_2\text{O}_9$ and $Ba_3\text{SrIr}_2\text{O}_9$ were observed to exhibit weak-dimer-like and ferromagnetic (FM)-like features in the magnetic susceptibility, respectively, though these transitions could not be identified in heat capacity measurements [56].

Materials with a fractional oxidation state of Ir are especially very interesting because such an oxidation state (accompanied by a unique crystallographic site) can lead to fascinating ground states. Such materials have been less explored theoretically, despite the fact that their experimental magnetic response reveals several peculiarities. There are three holes per dimer in $Ba_3M^{3+}\text{Ir}_2^{4.5+}\text{O}_9$ compounds. At high temperatures, where the mixed-valence dimers can be seen as isolated, the magnetic susceptibility deviates from the conventional Curie-Weiss behavior [53,59,60], suggesting nontrivial temperature evolution of the local magnetic moment. At low temperatures, interactions between the dimers become important, and signatures of frustrated magnetic behavior [61], including possible formation of a spin-liquid ground state, have been reported [57]. The linear fit to the high-temperature part produces the effective moments of $1.53 \mu_B/\text{f.u.}$ (for $M = \text{Ir}$) and $1.79 \mu_B/\text{f.u.}$ (for $M = \text{Sc}$) that were interpreted as the $S = 1$ state of the mixed-valence dimer [53]. $Ba_3\text{YIr}_2\text{O}_9$ undergoes long-range magnetic ordering at 4.5 K [62,63] but $Ba_3\text{ScIr}_2\text{O}_9$ does not show any long-range magnetic order down to at least 2 K [62]. At the same time, according to thermodynamic measurements, nuclear magnetic resonance, and muon spin resonance, $Ba_3\text{In}^{3+}\text{Ir}_2^{4.5+}\text{O}_9$ shows persistent spin dynamics down to 20 mK without any long-range magnetic order [57]. This can point toward a possible gapless spin-liquid ground state in this perovskite.

Here we report a theoretical investigation of the electronic and magnetic structures of the $Ba_3\text{InIr}_2\text{O}_9$ perovskite. The structure of this compound consists of InO_6 and IrO_6 octahedra. The latter octahedra share a face and develop along the crystallographic c axis, so-called Ir_2O_9 dimers, which are connected through corners with the InO_6 octahedra and form an edge-shared triangular lattice in the ab plane. Therefore, such a compound would become geometrically frustrated in the presence of the antiferromagnetic (AFM) interaction. Novel properties are expected from this structural arrangement in addition to those driven by SOC.

In this article, we focus our attention on the RIXS properties of $Ba_3\text{InIr}_2\text{O}_9$. Since the first publication by Kao *et al.* on NiO [64], the RIXS method has shown remarkable progress as a spectroscopic technique to record the momentum and energy dependence of inelastically scattered photons in complex materials. RIXS rapidly became the forefront of experimental photon science [65,66]. RIXS combines spectroscopy and inelastic scattering to probe the electronic structure of materials. This method is an element- and orbital-selective x-ray spectroscopy technique, based on a two-step, two-photon resonant process. It combines x-ray emission spectroscopy (XES) with x-ray absorption spectroscopy (XAS) by measuring the

coherent x-ray emission at incident x-ray photon energy within the near edge x-ray absorption spectrum. In the first step (x-ray absorption), an electron of the absorbing atom is resonantly excited from a core level to an empty state. The resulting state, called the intermediate state, carries a core hole with a very small lifetime. In the second step (x-ray emission), the system radiatively decays into a final state in which the core hole is filled by another electron accompanied by photon-out emission. The polarization of the incoming and outgoing light and the resonant energy are involved in the RIXS process, making RIXS a simultaneous spectroscopy and scattering technique. RIXS has a number of unique features in comparison with other spectroscopic techniques. It covers a large scattering phase space and requires only small sample volumes. It is also bulk sensitive and polarization dependent, as well as element and orbital specific [65]. A detail comparison with other spectroscopic techniques can be found in recent review article [66]. Spectral broadening owing to a short core hole lifetime can be reduced to produce the RIXS spectra with high resolution. It permits direct measurements of phonons, plasmons, single-magnon, and orbitons as well as other many-body excitations in strongly correlated systems, such as cuprates, nickelates, osmates, ruthenates, and iridates, with complex low-energy physics and exotic phenomena in the energy and momentum space.

There has been great progress in the RIXS experiments over the past decade. Most calculations of the RIXS spectra of various materials have been carried out using the atomic multiplet approach with some adjustable parameters and the number of theoretical first-principle calculations of RIXS spectra is extremely limited. In this paper, we report a theoretical investigation from the first principles of the RIXS spectra of $Ba_3\text{InIr}_2\text{O}_9$. Recently, the RIXS measurements have been successfully performed at the Ir L_3 edge in $Ba_3\text{InIr}_2\text{O}_9$ by Revelli *et al.* [67] in the energy range up to 5.5 eV. In addition to the elastic peak centered at zero energy loss, the spectrum consists of several peaks below 2 eV with a high-energy shoulder at ~ 1.8 eV and a peak at 4 eV.

We carry out here a detailed study of the electronic structure and RIXS spectra of $Ba_3\text{InIr}_2\text{O}_9$ in terms of the density functional theory. Our study sheds light on the important role of band structure effects and transition metal $5d$ – oxygen $2p$ hybridization in the spectral properties of $5d$ oxides. We use the *ab initio* approach using the fully relativistic spin-polarized Dirac linear muffin-tin orbital (LMTO) band-structure method. Both the generalized gradient approximation (GGA) and the GGA + U approach are used to assess the sensitivity of the RIXS results to different treatment of the correlated electrons.

The paper is organized as follows. The crystal structure of $Ba_3\text{InIr}_2\text{O}_9$ and computational details are presented in Sec. II. Section III presents the electronic and magnetic structures of $Ba_3\text{InIr}_2\text{O}_9$. In Sec. IV, the theoretical investigations of the XAS and x-ray magnetic circular dichroism (XMCD) spectra of $Ba_3\text{InIr}_2\text{O}_9$ at the Ir $L_{2,3}$ edges and the RIXS spectra at the Ir K , L_3 , M_3 , M_5 , N_3 , N_5 , and N_7 edges are presented. Also, we present here the results of comprehensive theoretical calculations of the RIXS spectrum at the oxygen K edge. The theoretical results are compared with experimental measurements. Finally, the results are summarized in Sec. V.

II. COMPUTATIONAL DETAILS

A. RIXS

In the direct RIXS process [65], the incoming photon with energy $\hbar\omega_{\mathbf{k}}$, momentum $\hbar\mathbf{k}$, and polarization ϵ excites the solid from ground state $|g\rangle$ with energy E_g to intermediate state $|I\rangle$ with energy E_I . During relaxation, an outgoing photon with energy $\hbar\omega_{\mathbf{k}'}$, momentum $\hbar\mathbf{k}'$ and polarization ϵ' is emitted, and the solid is in state $|f\rangle$ with energy E_f . As a result, an excitation with energy $\hbar\omega = \hbar\omega_{\mathbf{k}} - \hbar\omega_{\mathbf{k}'}$ and momentum $\hbar\mathbf{q} = \hbar\mathbf{k} - \hbar\mathbf{k}'$ is created. Our implementation of the code for the calculation of the RIXS intensity uses Dirac four-component basis functions [68] in the perturbative approach [69]. RIXS is a second-order process, and its intensity is given by

$$I(\omega, \mathbf{k}, \mathbf{k}', \epsilon, \epsilon') \propto \sum_f \left| \sum_I \frac{\langle f | \hat{H}'_{\mathbf{k}'\epsilon'} | I \rangle \langle I | \hat{H}'_{\mathbf{k}\epsilon} | g \rangle}{E_g - E_I} \right|^2 \times \delta(E_f - E_g - \hbar\omega), \quad (1)$$

where the RIXS perturbation operator in the dipole approximation is given by the lattice sum $\hat{H}'_{\mathbf{k}\epsilon} = \sum_{\mathbf{R}} \hat{\alpha}\epsilon \exp(-i\mathbf{k}\mathbf{R})$, where $\hat{\alpha}$ are the Dirac matrices. The sum over intermediate states $|I\rangle$ includes the contributions from different spin-split core states at the given absorption edge. The matrix elements of the RIXS process in the frame of the fully relativistic Dirac LMTO method were presented in Ref. [70].

B. Crystal structure

The Rietveld refinement of room-temperature (300 K) neutron diffraction data for $\text{Ba}_3\text{InIr}_2\text{O}_9$ obtained by Dey *et al.* [57] reveals the hexagonal crystal structure (space group $P6_3/mmc$, No. 194). At 3.4 K, the symmetry is reduced to the monoclinic structure ($C2/c$ space group No. 15). The corresponding lattice parameters and Wyckoff positions are presented in Table I. The mixed-valence $\text{Ba}_3\text{InIr}_2\text{O}_9$ shows a high degree of structural order. Dey *et al.* [57] were able to obtain reasonable atomic displacement parameters in fully ordered models of both the hexagonal and monoclinic structures, however, a weak site-mixing scenario was observed with $\sim 2.8\%$ In-Ir intersite mixing.

Both structures feature a single crystallographic position of Ir, suggesting the intermediate-valence Ir 4.5+ state. This is different from, e.g., $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$, where two sites of the Ir_2O_9 dimer belong to two different crystallographic positions, thus making possible charge redistribution within the dimer [71]. The structure consists of Ir_2O_9 dimers, which are IrO_6 face-shared octahedra along the crystallographic c axis, connected through corners with InO_6 octahedra and forming an edge-shared triangular lattice in the ab plane, with Ba ions sitting in typical for normal perovskites 12-fold coordination sites (see Fig. 1). $\text{Ba}_3\text{InIr}_2\text{O}_9$ contains two formula units and hence two structural dimers in the unit cell, which are connected via O-In-O paths along the c axis.

The Ir - O_1 and Ir - O_2 interatomic distances for the hexagonal $P6_3/mmc$ structure are equal to 2.034 and 1.962 Å, respectively. The corresponding Ir - O_1 , Ir - O_2 , Ir - O_3 , Ir - O_4 , and Ir - O_5 distances for the monoclinic $C2/c$ structure are equal to 2.056, 2.023, 1.951, 2.017, and 1.958 Å,

TABLE I. The Wyckoff positions (WPs) for the hexagonal $P6_3/mmc$ and monoclinic $C2/c$ crystal structures of $\text{Ba}_3\text{InIr}_2\text{O}_9$ (lattice constants $a = 5.8316$ Å, $c = 14.4877$ Å for the $P6_3/mmc$ structure and $a = 5.8152$ Å, $b = 10.0680$ Å, $c = 14.4619$ Å, and $\beta = 90.854^\circ$ for the $C2/c$ structure) [57].

Structure	WP	Atom	x	y	z
$P6_3/mmc$	$2b$	Ba ₁	0	0	0.25
	$4f$	Ba ₂	0.3333	0.6667	0.0889
	$2a$	In	0	0	0
	$4f$	Ir	0.3333	0.6667	0.1590
	$6h$	O ₁	0.4867	0.5133	0.25
	$12k$	O ₂	0.1715	0.3430	0.0841
	$4e$	Ba ₁	0	0.0010	0.25
	$8f$	Ba ₂	0.0049	0.3360	0.0889
	$4a$	In	0	0	0
	$8f$	Ir	-0.0081	0.3334	0.8397
$C2/c$	$8f$	O ₁	0	0.4918	0.75
	$8f$	O ₂	0.2300	0.2573	0.7541
	$8f$	O ₃	-0.0180	0.1717	0.9140
	$8f$	O ₄	0.2260	0.4158	0.9251
	$8f$	O ₅	-0.2630	0.4144	0.9079

respectively. The In - O_2 interatomic distance in InO_6 octahedra for the hexagonal $P6_3/mmc$ structure is equal to 2.118 Å. The corresponding In - O_3 , In - O_4 , and In - O_5 distances for the monoclinic $C2/c$ structure are equal to 2.132, 2.105, and 2.101 Å, respectively. The low-temperature monoclinic distortion is primarily related to the tilting of IrO_6 and InO_6 octahedra. It has nearly no effect on relative positions of Ir atoms.

Note that in our electronic structure calculations, we rely on experimentally measured atomic positions and lattice constants because they are well established for this material and still more accurate than those obtained from DFT.

C. Calculation details

The details of the computational method are described in our previous papers [70,72–74] and here we mention several aspects. The band structure calculations were performed using the fully relativistic LMTO method [75,76]. This implementation of the LMTO method uses four-component basis functions constructed by solving the Dirac equation inside an atomic sphere [68]. The exchange-correlation functional of a GGA type was used in the version of Perdew *et al.* [77]. The Brillouin zone integration was performed using the improved tetrahedron method [78]. The basis consisted of Ir and Ba s , p , d , and f ; and In and O s , p , and d LMTOs.

To consider the electron-electron correlation effects, we used the relativistic generalization of the rotationally invariant version of the GGA + U method [79], which considers that, in the presence of spin-orbit coupling, the occupation matrix of localized electrons becomes nondiagonal in spin indexes. Hubbard U was considered an external parameter and varied from 0.65 to 3.65 eV. We used in our calculations the value of exchange Hund's coupling $J_H = 0.65$ eV obtained from constrained LSDA calculations [80,81]. Thus, the parameter $U_{\text{eff}} = U - J_H$, which roughly determines the splitting

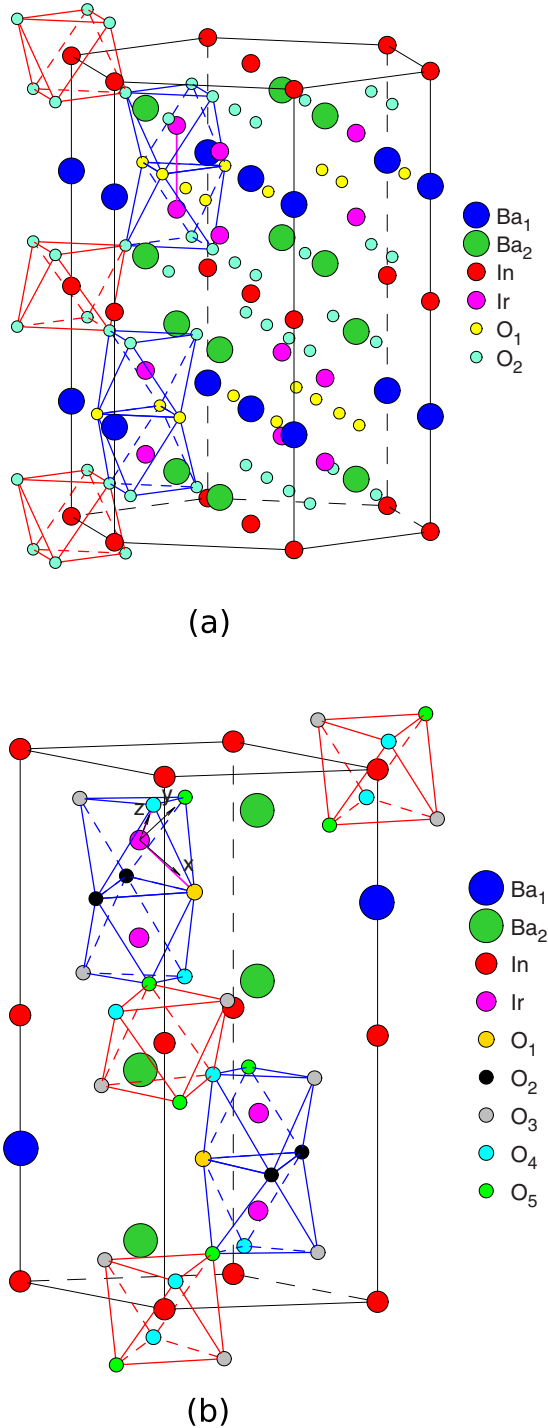


FIG. 1. The schematic representation of $\text{Ba}_3\text{InIr}_2\text{O}_9$ in the hexagonal $P6_3/mmc$ (a) and monoclinic $C2/c$ (b) crystal structures.

between the lower and upper Hubbard bands, varied between 0 and 3.0 eV. We adjusted the value of U to achieve the best agreement with the experiment.

In the RIXS process, an electron is promoted from a core level to an intermediate state, leaving a core hole. As a result, the electronic structure of this state differs from that of the ground state. To reproduce the experimental spectrum, the self-consistent calculations should be carried out, including a core hole. Usually, the core-hole effect has no impact on the

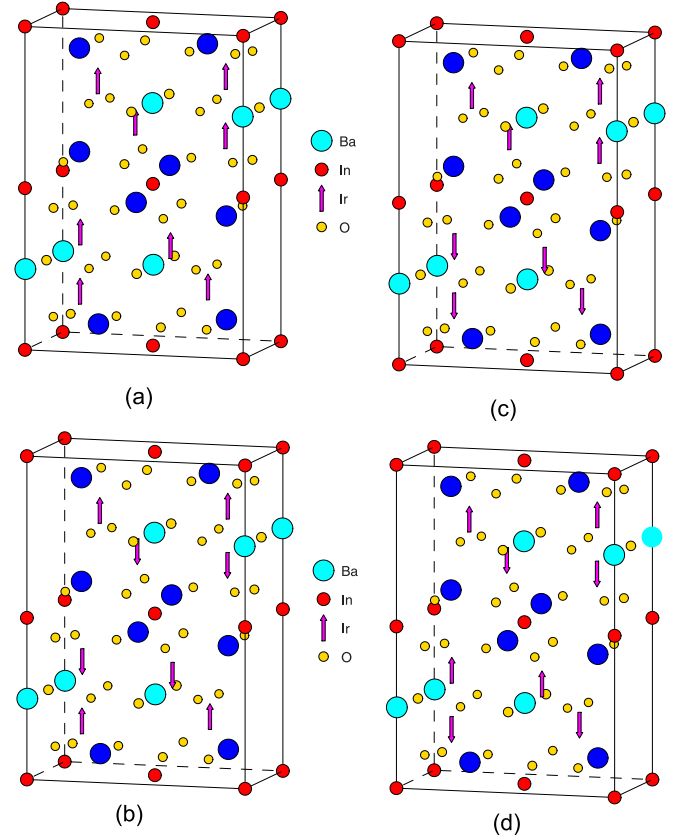


FIG. 2. Different magnetic ordering in $\text{Ba}_3\text{InIr}_2\text{O}_9$: ferromagnetic (a), antiferromagnetic AFM_1 (b), AFM_2 (c), and AFM_3 (d) for the monoclinic $C2/c$ crystal structure.

shape of XAS at the $L_{2,3}$ edges of $5d$ systems and just a minor effect on the XMCD spectra at these edges [76]. However, the core hole has a strong effect on the RIXS spectra in transition metal compounds [70,82]; therefore, we consider it in our calculations.

III. ELECTRONIC AND MAGNETIC STRUCTURES

We performed GGA, GGA + SO, and GGA + SO + U calculations of the electronic and magnetic structures of $\text{Ba}_3\text{InIr}_2\text{O}_9$ for the experimental crystal structure [57] (see Table I). To understand the magnetic properties of the system, four different magnetic configurations, namely, FM (both the intra- and interdimer couplings are FM), AFM_1 (both the intra- and interdimer couplings are AFM), AFM_2 (the intradimer coupling is FM and the inter-dimer coupling is AFM), and AFM_3 (the intradimer coupling is AFM and the interdimer coupling is FM) have been simulated (see Fig. 2). The calculations show that the AFM_2 state has the lowest energy (Table II). A similar magnetic ground state was obtained by Panda *et al.* for $\text{Ba}_2\text{YIr}_2\text{O}_9$ [63] and Nag *et al.* for $\text{Ba}_2\text{ZnIr}_2\text{O}_9$ [46].

The difference in total energy between the magnetic and nonmagnetic solutions (with considering SOC and Hubbard correlations) is relatively large and equals to 1.682 eV per formula unit. However, between the different magnetic solutions it is very small. Probably, it may explain the fact that

TABLE II. The total energy E_{total} per atom (in meV) in $\text{Ba}_3\text{InIr}_2\text{O}_9$ calculated in the GGA+SO+ U approach ($U_{\text{eff}} = 2.3$ eV) for the FM, AFM₁, AFM₂, and AFM₃ configurations for the monoclinic $C2/c$ crystal structure.

FM	AFM ₁	AFM ₂	AFM ₃
0.232	3.375	0	4.273

$\text{Ba}_3\text{InIr}_2\text{O}_9$ possesses no long-range magnetic order down to very low temperatures and points out on possible spin-liquid behavior of local moments below 1 K in this perovskite [57]. We also found several noncollinear AFM solutions but with significantly higher total energy than the solutions with FM and AFM ordering along the c direction.

According to the experimental measurements of Revelli *et al.* [67], the real part of the conductivity is $\sigma \sim 10^{-6}/\Omega \text{ cm}$, which firmly indicates insulating character of $\text{Ba}_3\text{InIr}_2\text{O}_9$. This conclusion is also supported by the observation that the dielectric loss ε'' is much smaller than the permittivity ε' , as usually expected for an insulator [67].

In Fig. 3, the plots of orbital resolved partial density of states (DOS) for $\text{Ba}_3\text{InIr}_2\text{O}_9$ are presented. The crystal field (CF) at the Ir site ($C1$ point symmetry) causes the splitting of $5d$ orbitals into five singlets d_{3z^2-1} , $d_{x^2-y^2}$, d_{xy} , d_{xz} , and d_{yz} . The largest bonding-antibonding splitting corresponds to d_{3z^2-1} orbitals. The rightmost peak in Fig. 3 (the upper panel) corresponds to the antibonding d_{3z^2-1} orbital at 0.2 eV, while the antibonding d_{xy} states lie from -0.4 to 0.1 eV (the lower panel of Fig. 3). Due to the strong distortion of IrO_6 octahedra the t_{2g} orbitals are strongly mixed. Although in $\text{Ba}_3\text{InIr}_2\text{O}_9$ there is a tendency of forming a dimer structure by two face-shared IrO_6 octahedra (see Fig. 1), it does not lead to

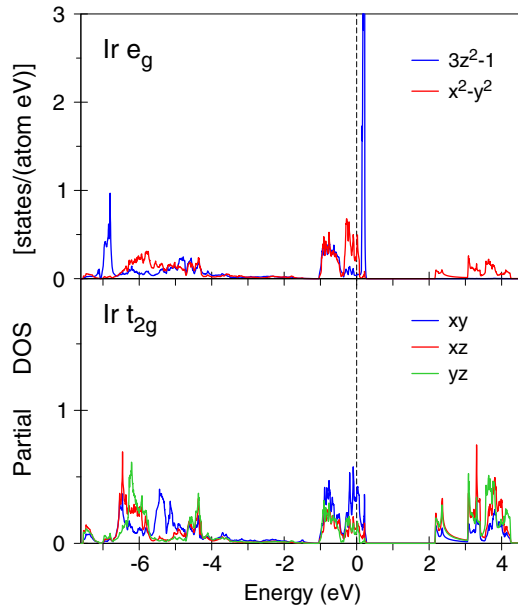


FIG. 3. The orbital resolved partial density of states (DOS) [in states/(atom eV)] for $\text{Ba}_3\text{InIr}_2\text{O}_9$ calculated in GGA for the monoclinic $C2/c$ crystal structure.

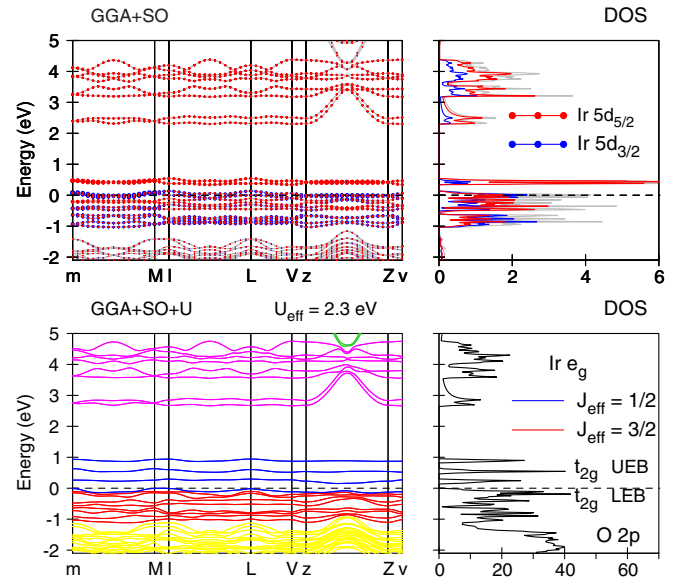


FIG. 4. Upper panel: The energy band structure of the monoclinic phase of $\text{Ba}_3\text{InIr}_2\text{O}_9$ calculated in the fully relativistic Dirac GGA + SO approximation. The bands crossing the Fermi level which have almost pure $d_{5/2}$ character (open red circles) are formed by t_{2g} states with $J_{\text{eff}} = 1/2$ (lower panel). The energy bands calculated in the GGA + SO + U approximation with $U_{\text{eff}} = 2.3$ eV.

a dielectric ground state, as it was, for example, in the high pressure honeycomb-based $5d^5$ iridate $\beta\text{-Li}_2\text{IrO}_3$ [6,83,84].

Figure 4 (the upper panel) shows the fully relativistic GGA + SO bands presented by circles proportional in size to their orbital character projected onto the basis set of Ir $d_{3/2}$ (the relativistic quantum number $\kappa = 2$, the blue curve) and $d_{5/2}$ ($\kappa = -3$, the red curve) states. In the strong SOC limit, the t_{2g} band splits into effective total angular momentum $J_{\text{eff}} = 1/2$ doublet and $J_{\text{eff}} = 3/2$ quartet bands. The functions of the $J_{\text{eff}} = 3/2$ quartet are dominated by $d_{3/2}$ states with some weight of $d_{5/2}$ ones. The $J_{\text{eff}} = 1/2$ functions are almost completely given by the linear combination of $d_{5/2}$ states (the lower panel of Fig. 4). The GGA + SO approach gives a metallic ground state in $\text{Ba}_3\text{InIr}_2\text{O}_9$. It is in contradiction with experiment. To obtain a dielectric ground state one has to take into account strong Coulomb correlations. Hubbard U applied to the Ir $5d$ states in the frame of the GGA + SO + U method produces a dielectric ground state with three narrow empty peaks just above the Fermi level (lower panel of Fig. 4).

Figure 5 shows the Ir $5d$ partial DOS for $\text{Ba}_3\text{InIr}_2\text{O}_9$ for the energy interval from -8 to 5 eV calculated in the GGA + SO, GGA + U , and GGA + SO + U approaches. The GGA and GGA + SO approaches give a metallic ground state in $\text{Ba}_3\text{InIr}_2\text{O}_9$. The calculations show that the energy gap is already formed in the GGA + U approximation without SOC. $\text{Ba}_3\text{InIr}_2\text{O}_9$ can be classified as a Mott insulator, since it was expected to be metallic from GGA band structure calculations. We found that the best agreement between the calculated and experimentally measured RIXS spectra at the Ir L_3 edge can be achieved for $U_{\text{eff}} = 2.3$ eV (see Sec. IV). Figure 5(d) shows the Ir $5d$ partial DOS for $\text{Ba}_3\text{InIr}_2\text{O}_9$ for the high temperature

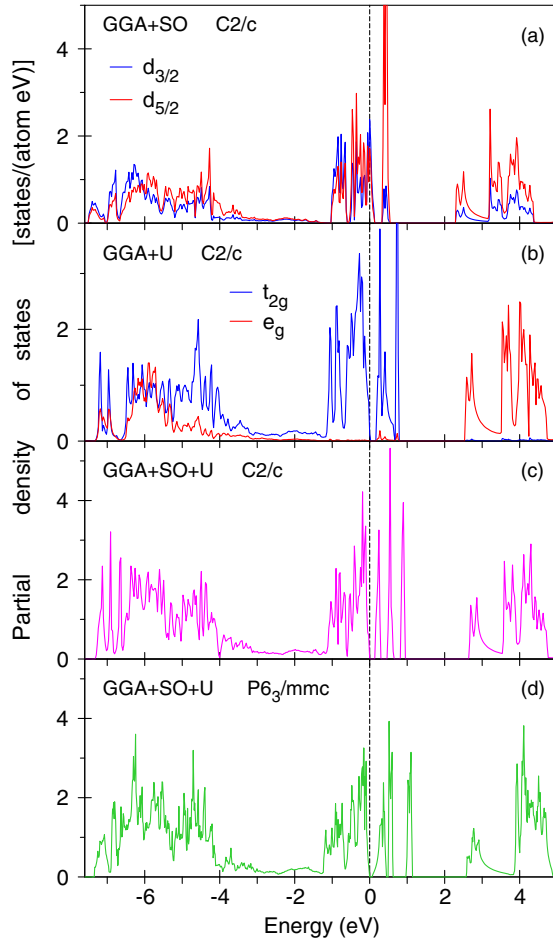


FIG. 5. The Ir 5d partial density of states (DOS) [in states/(atom eV)] for $\text{Ba}_3\text{InIr}_2\text{O}_9$ calculated in the GGA + SO (a), GGA + U (b), and GGA + SO + U ($U_{\text{eff}} = 2.3$ eV) (c) approaches for the monoclinic $C2/c$ crystal structure. (d) Ir 5d partial DOS for the hexagonal $P6_3/mmc$ structure calculated in GGA + SO + U ($U_{\text{eff}} = 2.3$ eV).

hexagonal $P6_3/mmc$ structure calculated in GGA + SO + U ($U_{\text{eff}} = 2.3$ eV). The partial DOS is very similar to the corresponding states for the monoclinic $C2/c$ crystal structure [Fig. 5(c)]. There are some minor differences in the energy positions, widths, and relative intensities of three empty t_{2g} states above the Fermi level. There are also small variations in the shape of the e_g states and the energy distribution of the Ir 5d states ≤ -6.5 eV. Such minor differences lead to visible differences in the corresponding RIXS spectra (see Sec. IV B).

Figure 6 presents a phase diagram in the $U_{\text{eff}} - \text{SOC}$ plane for two different crystal structures of $\text{Ba}_3\text{InIr}_2\text{O}_9$ in comparison with Sr_2IrO_4 [85]. To obtain this diagram, we tuned the SOC term for the Ir 5d orbitals. A scaling factor λ in the SOC term of the Hamiltonian is introduced in the second variational step [86]. In this way, we can enhance the effect of SOC by taking $\lambda > 1$ or reduce it by taking $\lambda < 1$. For $\lambda = 0$ there is no SOC at all, while $\lambda = 1$ refers to the self-consistent reference value.

The green solid-circled, blue solid-circled, and red solid-circled curves separate metal (under the curves) and Mott insulator (above the curves) states connected via a first-order phase transition for hexagonal $\text{Ba}_3\text{InIr}_2\text{O}_9$, monoclinic

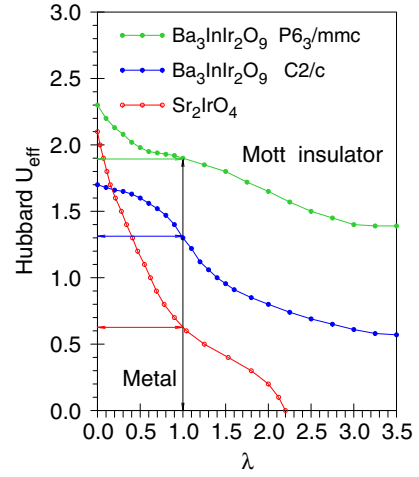


FIG. 6. The phase diagram in the $U_{\text{eff}} - \text{SOC}$ plane for $\text{Ba}_3\text{InIr}_2\text{O}_9$ for the hexagonal $P6_3/mmc$ (the green curve) and monoclinic $C2/c$ (the blue curve) crystal structures in comparison with Sr_2IrO_4 [85] (the red curve). The curves separate metal (under the curves) and Mott insulator (above the curves) states connected via a first-order phase transition. The horizontal lines indicate the values of Hubbard U_{eff} for which the energy band gap is opened for hexagonal $\text{Ba}_3\text{InIr}_2\text{O}_9$ (the green line), monoclinic $\text{Ba}_3\text{InIr}_2\text{O}_9$ (the blue line), and Sr_2IrO_4 (the red line).

$\text{Ba}_3\text{InIr}_2\text{O}_9$, and Sr_2IrO_4 , respectively. In the case of Sr_2IrO_4 , the energy gap opens up for $\lambda = 0$ with $U_{\text{eff}}^c = 2.1$ eV and for $\lambda = 2.2$ with $U_{\text{eff}}^c = 0$ eV; the greater the value of U_{eff} , the lower the value of λ is for the phase transition. For monoclinic $C2/c\text{Ba}_3\text{InIr}_2\text{O}_9$, the energy gap opens up for $\lambda = 0$ with $U_{\text{eff}}^c = 1.7$ eV, however, there is no dielectric solution for $U_{\text{eff}} \leq 0.63$ eV with any value of λ . Even for very large λ , the curve does not cross the abscissa axis. We can conclude that $\text{Ba}_3\text{InIr}_2\text{O}_9$ in the $C2/c$ crystal structure is a less strong Mott dielectric than Sr_2IrO_4 because it possesses a smaller $U_{\text{eff}} - \text{SOC}$ Mott-dielectric phase space in comparison with Sr_2IrO_4 . The high temperature phase of $\text{Ba}_3\text{InIr}_2\text{O}_9$ in the hexagonal $P6_3/mmc$ crystal structure shows even smaller Mott-dielectric properties. For this structure modification of $\text{Ba}_3\text{InIr}_2\text{O}_9$, the energy gap opens up for $\lambda = 0$ with $U_{\text{eff}}^c = 2.3$ eV and there is no dielectric solution for $U_{\text{eff}} \leq 1.39$ eV. The points on the curves at $\lambda = 1$ define the values of corresponding Hubbard U_{eff} for which the energy band gap is opened. These values are equal to 1.9, 1.31, and 0.62 eV for the hexagonal $\text{Ba}_3\text{InIr}_2\text{O}_9$, monoclinic $\text{Ba}_3\text{InIr}_2\text{O}_9$, and Sr_2IrO_4 iridates, respectively (the values are indicated by corresponding horizontal lines in Fig. 6).

Figures 7 and 8 present the energy band structure and partial DOS, respectively, in $\text{Ba}_3\text{InIr}_2\text{O}_9$ for the AFM₂ solution calculated in the GGA + SO + U approach with $U_{\text{eff}} = 2.3$ eV for the monoclinic $C2/c$ crystal structure. The occupied t_{2g} states [the low energy band (LEB)] are situated in the energy interval from -1.2 eV to E_F and can be subdivided into two band groups from -1.2 to -0.6 eV and from -0.6 eV to E_F . The empty t_{2g} states [the upper energy band (UEB)] consist of three narrow single peaks divided by energy gaps and occupy the energy range from 0.07 to 0.88 eV. There is a significant amount of Ir 5d DOS located at the bottom of

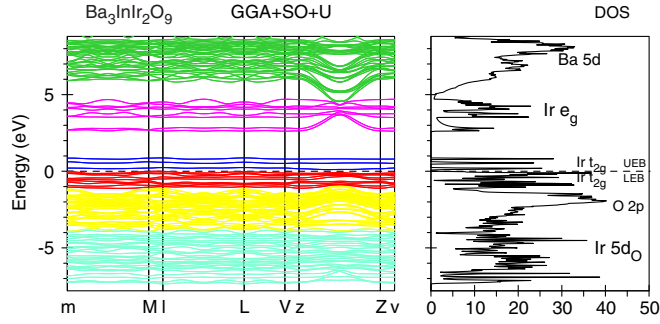


FIG. 7. The energy band structure and total density of states (DOS) [in states/(cell eV)] for $\text{Ba}_3\text{InIr}_2\text{O}_9$ calculated in the GGA + SO + U approach ($U_{\text{eff}} = 2.3$ eV) for the monoclinic $C2/c$ crystal structure.

oxygen $2p$ states from -7.35 to -4.05 eV below the Fermi energy. These so-called Ir $5d_O$ states are provided by the tails of oxygen $2p$ states inside the Ir atomic spheres and play an

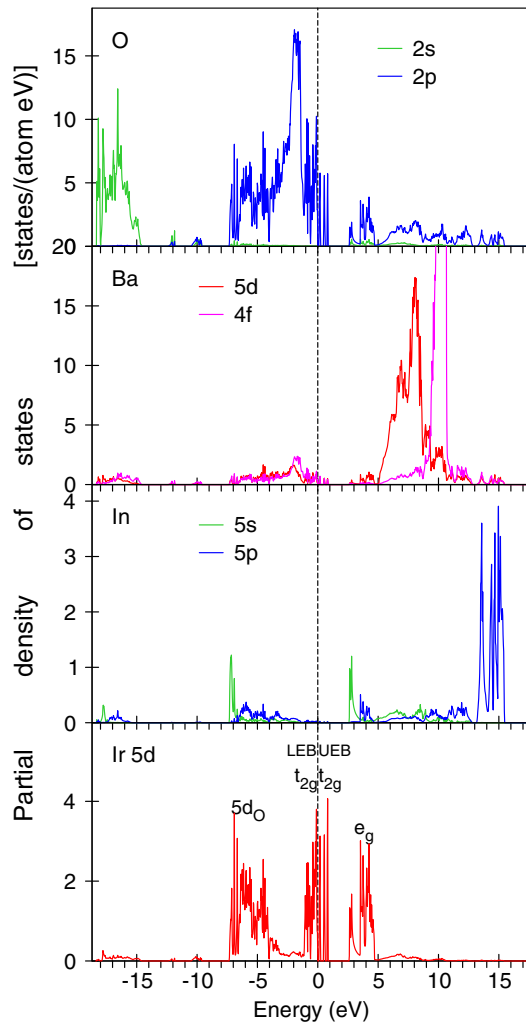


FIG. 8. The partial density of states (DOS) [in states/(atom eV)] for $\text{Ba}_3\text{InIr}_2\text{O}_9$ calculated in the GGA + SO + U approach ($U_{\text{eff}} = 2.3$ eV) for the monoclinic $C2/c$ crystal structure.

TABLE III. The theoretically calculated in the GGA+SO+ U approach ($U_{\text{eff}} = 2.3$ eV) spin M_s , orbital M_l , and total M_{tot} magnetic moments (in μ_B) in $\text{Ba}_3\text{InIr}_2\text{O}_9$ for the AFM₂ solution for the monoclinic $C2/c$ crystal structure.

atom	M_s	M_l	M_{tot}
Ba ₁	0.0415	-0.0020	0.0395
Ba ₂	0.0141	0.0056	0.0197
In	0	0	0
Ir	0.3903	0.1393	0.5296
O ₁	0.1188	0.0397	0.1585
O ₂	0.0386	0.0054	0.0440
O ₃	0.0513	0.0133	0.0646
O ₄	0.0430	0.0015	0.0445
O ₅	0.0667	0.0131	0.0798

essential role in the RIXS spectrum at the Ir L_3 edge (see Sec. IV).

The In $5p$ states are mostly situated above the Fermi level from 13.2 to 15.5 eV and consist of four separated energy peaks. The Ba $5d$ states occupy the energy region from 5.1 to 9.2 eV above the Fermi energy. A narrow and intensive DOS peak of Ba $4f$ states is located just above the Ba $5d$ states from 9.2 to 10.8 eV. The oxygen $2s$ states are situated far below the Fermi level from -18.3 to -14.6 eV. The occupied O $2p$ states are localized from -7.35 eV to E_F . They are strongly hybridized with Ir $5d$ states from -7.35 to -4.05 eV and from -1.2 eV to E_F . The empty oxygen $2p$ states are strongly hybridized with Ir t_{2g} UEB just above the Fermi level and with the Ir e_g states from 2.6 to 4.7 eV. They are also hybridized with Ba $5d$ and $4f$ states as well as In $5p$ states.

Table III presents the theoretically calculated in the GGA + SO + U approach ($U_{\text{eff}} = 2.3$ eV) spin M_s , orbital M_l , and total M_{tot} magnetic moments in $\text{Ba}_3\text{InIr}_2\text{O}_9$ for the AFM₂ solution. The spin and orbital moments at the Ir site equal to 0.3903 and 0.1393 μ_B , respectively. They are in the same direction, as Ir $5d$ states are more than half filled.

IV. XAS, XMCD, AND RIXS SPECTRA

A. Ir $L_{2,3}$ XAS and XMCD spectra

Figure 9 presents the XAS (the upper panel) and XMCD spectra (the lower panel) at the Ir $L_{2,3}$ edges for $\text{Ba}_3\text{InIr}_2\text{O}_9$ calculated in the GGA + SO + U ($U_{\text{eff}} = 2.3$ eV) approach. The isotropic XAS spectra are dominated by empty e_g states with a smaller contribution from empty t_{2g} orbitals at lower energy. The XMCD spectra, however, mainly come from the t_{2g} orbitals. This results in a shift between the maxima of the XAS and XMCD spectra.

Due to the importance of SOC effects in iridates, it is natural to quantify the strength of the SO interaction in these compounds. XAS provides one of the methods for this. Van der Laan and Thole showed that the so-called branching ratio $\text{BR} = I_{L_3}/I_{L_2}$ ($I_{L_{2,3}}$ is the integrated intensity of isotropic XAS at the $L_{2,3}$ edges) is an important quantity associated with SOC [87]. The BR is directly related to the ground-state expectation value of the angular part of the spin-orbit coupling $\langle \mathbf{L} \cdot \mathbf{S} \rangle$ through $\text{BR} = (2 + r)/(1 - r)$, where $r = \langle \mathbf{L} \cdot \mathbf{S} \rangle / n_h$

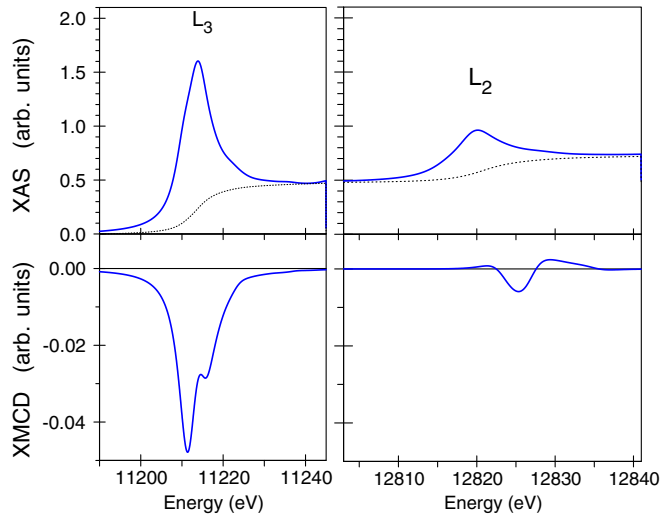


FIG. 9. The theoretically calculated x-ray absorption (the upper panel) and XMCD spectra (the lower panel) at the Ir $L_{2,3}$ edges in $\text{Ba}_3\text{InIr}_2\text{O}_9$ for the monoclinic $C2/c$ crystal structure in the GGA + SO + U approach ($U_{\text{eff}} = 2.3$ eV). The dotted black curves in the upper panel show the background scattering intensity.

and n_h is the number of holes in $5d$ states [87]. As a result, XAS provides a direct probe of SOC, which is complementary to other techniques such as the magnetic susceptibility, electron paramagnetic resonance, and Mössbauer spectroscopy (which probe SOC through the value of the Lande g -factor). In the limit of negligible SOC effects, the statistical branching ratio value $\text{BR} = 2$ takes place, and the L_3 white line is twice the size of the L_2 feature [87]. The theoretically calculated BR in $\text{Ba}_3\text{InIr}_2\text{O}_9$ is 3.64 for the Ir site in the GGA + SO + U ($U_{\text{eff}} = 2.3$ eV) approach. It is even larger than the theoretically calculated BR of 3.56 for Sr_2IrO_4 with strong SOC [85]. A strong deviation from 2 indicates a strong coupling between the local orbital and spin moments in $\text{Ba}_3\text{InIr}_2\text{O}_9$.

B. Ir L_3 RIXS spectra

The experimental RIXS spectrum at the Ir L_3 edge was measured by Revelli *et al.* [67] in the energy range up to 5.5 eV. In addition to the elastic peak centered at zero energy loss, the spectrum consists of several peaks below 2 eV, a strong peak at 3.9 eV, and a fine structure above 4.4 eV. We found that the fine structure situated below 2 eV corresponds to intra- t_{2g} excitations. These peaks are very sensitive to the value of the energy gap in $\text{Ba}_3\text{InIr}_2\text{O}_9$ and the relative position of t_{2g} LEBs and UEBs (Fig. 7). Figure 10 shows the experimental RIXS spectrum measured by Revelli *et al.* [67] compared with the theoretical spectra calculated for $t_{2g} \rightarrow t_{2g}$ transitions in the GGA + SO + U approach for the AFM₂ solution for different U_{eff} values. The best agreement was found for $U_{\text{eff}} = 2.3$ eV. The GGA + SO calculations (not shown) as well as the GGA + SO + U approach with smaller U_{eff} do not produce adequate agreement with the experimental data. The larger values of U_{eff} shift the RIXS spectrum towards higher energies.

Figure 11(a) shows the theoretical RIXS spectrum at the Ir L_3 edge for the $t_{2g} \rightarrow t_{2g}$ transitions in $\text{Ba}_3\text{InIr}_2\text{O}_9$ compared

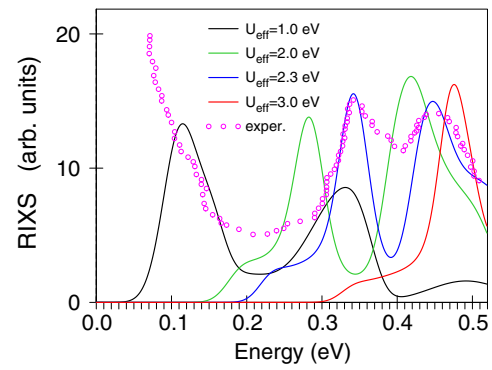


FIG. 10. The experimental RIXS spectrum (open magenta circles) measured by Revelli *et al.* [67] at 10 K for π polarization of incident photons with the energy of 11215 eV and with the momentum transfer vector $\mathbf{Q} = (0.3, 0, 14)$ in reciprocal lattice units (r.l.u.) at the Ir L_3 edge in $\text{Ba}_3\text{InIr}_2\text{O}_9$ compared with the theoretically calculated one in the GGA + SO + U approach for different U_{eff} for the monoclinic $C2/c$ crystal structure for π polarization, the incident energy of 11215 eV, and vector $\mathbf{Q} = (0, 0, 15)$ r.l.u.

with the measurements of Revelli *et al.* [67]. The Ir L_3 spectrum for the $t_{2g} \rightarrow t_{2g}$ transitions has quite a rich fine structure with at least 12 well-separated peaks from A to L below 2 eV. The appearance of multiple peaks in the RIXS spectrum is a direct consequence of a strong noncubic CF splitting originating from the distorted octahedral environment of the Ir ions. The CF splitting leads to a very specific energy band structure of Ir t_{2g} states presented in Fig. 12. There are nine t_{2g} bands below E_F (from 1 to 9) and three empty bands α , β , and γ separated by energy gaps. The interband transitions between these nine occupied and three empty bands produce 27 peaks. Some of these peaks are quite small. As a result, the structure of the Ir L_3 RIXS spectrum below 2 eV consists of at least twelve well distinguished peaks. The corresponding interband transitions are presented in Fig. 11(b). The low-energy peaks A, B, and C are due to the transitions from the first, second, and third occupied bands (the red, green, and blue bands in Fig. 12) into the low-energy empty band (the blue band with DOS peak α). The other peaks from D to L are due to many interband transitions, which are presented in Fig. 11(b).

The experimental RIXS spectra at the Ir L_3 edge measured by Revelli *et al.* [67] present a clear shoulder at ~ 0.12 eV [see Fig. 3 in Ref. [67] especially for the momentum transfer vector $\mathbf{Q} = (0.3, 0, 19.6)$ in r.l.u.]. This fine structure is absent in our first-principles RIXS calculations. Most probably, this structure belongs to a magnon excitation. It is interesting to note that the reference iridate Sr_2IrO_4 also possesses a low-energy peak at 0.1 eV, which is considered in Ref. [88] as a magnon excitation in agreement with scanning tunneling microscope measurements [89]. The theoretical description of magnon and exciton spectra demands a many-body approach beyond the one-particle approximation, such as the Bethe-Salpiter equation for exciton spectra and calculations of the magnon dispersion and the electron-magnon interaction for magnon spectra.

Figure 13(a) presents the theoretically calculated and experimentally measured RIXS spectra at the Ir L_3 edge for $\text{Ba}_3\text{InIr}_2\text{O}_9$ [67] in a wide energy interval up to 14 eV. As we

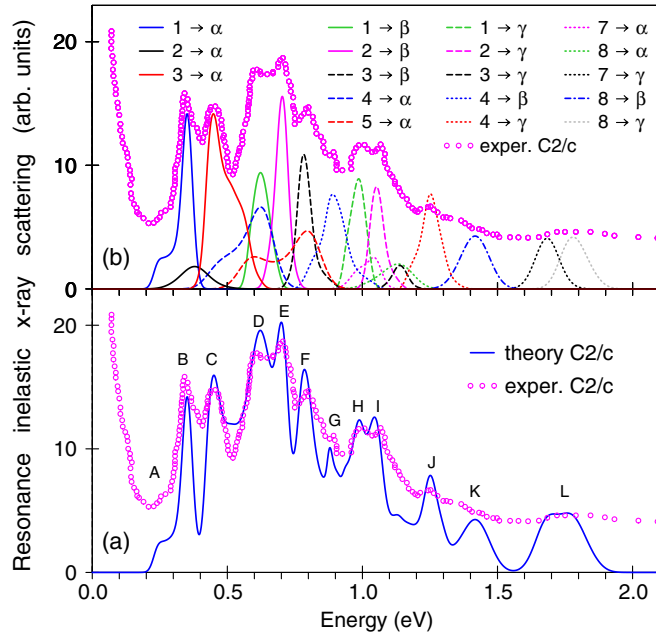


FIG. 11. (a) The experimental RIXS spectrum (open magenta circles) for the monoclinic $C2/c$ crystal structure measured by Revelli *et al.* [67] at 10 K for π polarization of incident photons with the energy of 11215 eV and with the momentum transfer vector $\mathbf{Q} = (0.3, 0, 14)$ in reciprocal lattice units (r.l.u.) at the Ir L_3 edge in $Ba_3InIr_2O_9$ and the theoretically calculated Ir L_3 spectrum (the blue curve) for the $t_{2g} \rightarrow t_{2g}$ transitions calculated in the GGA + SO + U approach ($U_{\text{eff}} = 2.3$ eV) for the monoclinic $C2/c$ crystal structure for π polarization, the incident energy of 11215 eV, and vector $\mathbf{Q} = (0, 0, 15)$ r.l.u.; (b) the partial contributions from different transitions between the energy bands presented in Fig. 12 in comparison with the experiment [67] (open magenta circles) for the monoclinic $C2/c$ crystal structure.

mentioned above, the peaks situated below 2 eV correspond to intra- t_{2g} excitations [the blue curve in Fig. 13(a)]. The peak located at ~ 4 eV was found to be due to $t_{2g} \rightarrow e_g$ transitions (the green curve). The increase of the intensity above 4.5 eV can be associated with charge-transfer excitations $5d_O \rightarrow t_{2g}$ (the black curve). These transitions also contribute into the major peak at 4 eV. The strong fine structure at ~ 9 eV (the magenta curve) is due to $5d_O \rightarrow e_g$ transitions. The theoretical calculations are in good agreement with the experimental data.

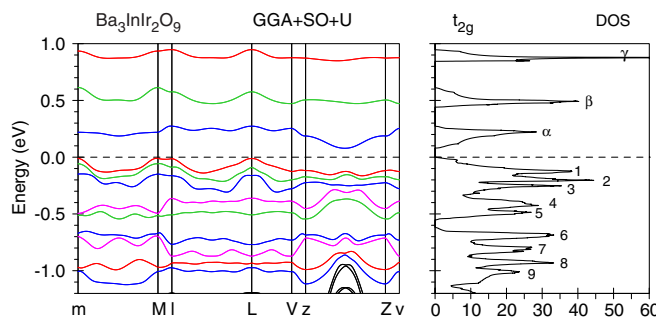


FIG. 12. The energy band structure of Ir t_{2g} states calculated for $Ba_3InIr_2O_9$ in the GGA + SO + U approach ($U_{\text{eff}} = 2.3$ eV) for the monoclinic $C2/c$ crystal structure.

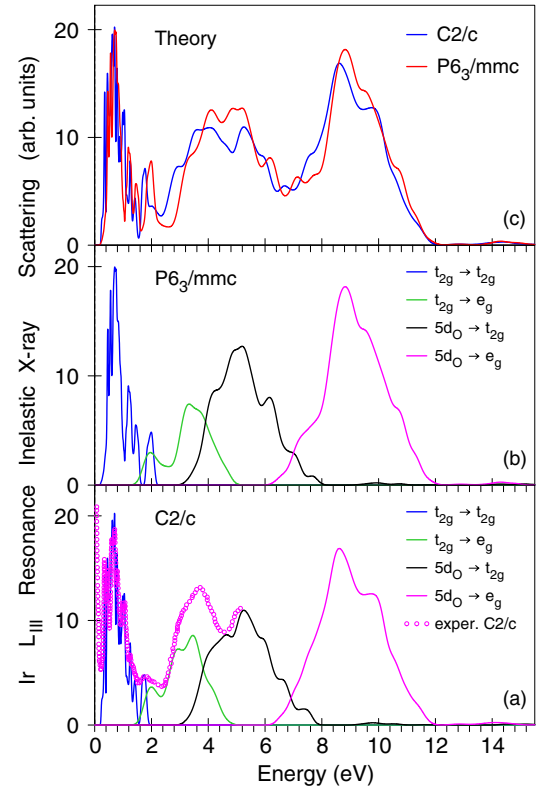


FIG. 13. (a) The experimental RIXS spectrum (open magenta circles) measured by Revelli *et al.* [67] at the Ir L_3 edge at 10 K for π polarization of incident photons with the energy of 11215 eV, and with the momentum transfer vector $\mathbf{Q} = (0.3, 0, 14)$ in reciprocal lattice units (r.l.u.) for the monoclinic $C2/c$ crystal structure of $Ba_3InIr_2O_9$ compared with the theoretically calculated one in the GGA + SO + U approach ($U_{\text{eff}} = 2.3$ eV) for the monoclinic $C2/c$ crystal structure for π polarization, for the incident energy of 11215 eV, and vector $\mathbf{Q} = (0, 0, 15)$ r.l.u. in a wide energy range; (b) partial contributions from different interband transitions calculated in the GGA + SO + U approach ($U_{\text{eff}} = 2.3$ eV) for the hexagonal $P6_3/mmc$ crystal structure for π polarization, the incident energy of 11215 eV, and vector $\mathbf{Q} = (0, 0, 15)$ r.l.u.; (c) the theoretically calculated Ir L_3 RIXS spectra for the monoclinic $C2/c$ (the blue curve) and hexagonal $P6_3/mmc$ (the red curve) structures.

Figure 13(b) presents the theoretically calculated partial contributions into the Ir L_3 spectrum of $Ba_3InIr_2O_9$ for the high temperature hexagonal $P6_3/mmc$ crystal structure. Figure 13(c) presents the comparison of the theoretically calculated Ir L_3 RIXS spectra for the monoclinic $C2/c$ (the blue curve) and hexagonal $P6_3/mmc$ (the red curve) structures. The spectra are very similar, although, there are some minor differences in relative intensities and energy positions of some fine structures.

It is widely believed that $d-d$ excitations show only small momentum transfer vector $\mathbf{Q}$ dependence in $5d$ transition metal compounds [90,91]. As we see in the upper panel of Fig. 14, the RIXS spectra show small dependence as a function of Q_x with the momentum transfer vector $\mathbf{Q} = (Q_x, 0, 15)$ in reciprocal lattice units (r.l.u.) for incident photon energy $\hbar\omega_{\text{in}} = 11215$ eV in the energy interval up to 12 eV. The lower panel of Fig. 14 shows the RIXS spectra at the Ir L_3

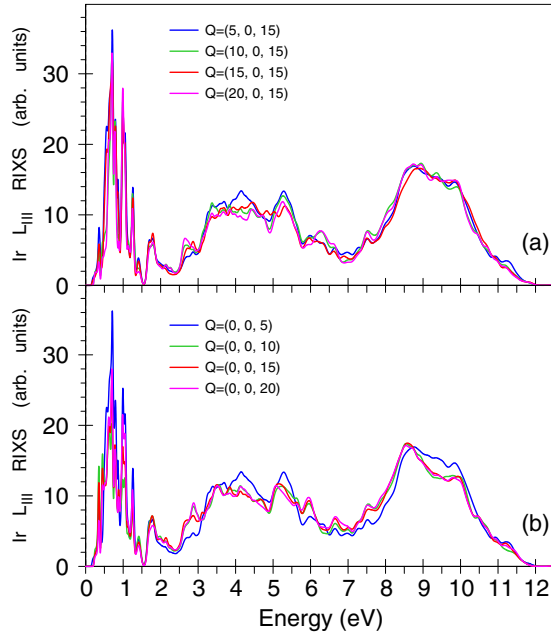


FIG. 14. The theoretically calculated RIXS spectra at the Ir L_3 edge in $\text{Ba}_3\text{InIr}_2\text{O}_9$ in the monoclinic $C2/c$ structure for π polarization calculated as a function of Q_x with the momentum transfer vectors $\mathbf{Q} = (Q_x, 0, 15)$ in reciprocal lattice units (the upper panel) and Q_z with $\mathbf{Q} = (0, 0, Q_z)$ in reciprocal lattice units (the lower panel) for incident photon energy $\hbar\omega_{in} = 11215$ eV.

edge in $\text{Ba}_3\text{InIr}_2\text{O}_9$ calculated as a function of Q_z with the momentum transfer vector $\mathbf{Q} = (0, 0, Q_z)$ r.l.u. We found that the RIXS spectrum possesses an oscillation character. With increasing Q_z from 5 to 10, 15, and 20 r.l.u. the low-energy structure, which reflects the $t_{2g} \rightarrow t_{2g}$ transitions, is increased then decreased, again increased and after that decreased. The high-energy fine structures above 3 eV are changed insignificantly with the increase of Q_z . Similar dependence of the RIXS spectrum on Q_z was detected experimentally by Revelli *et al.* [67], namely, they found that the low-energy RIXS spectrum below 1.5 eV shows an oscillation character for the momentum transfer vector $\mathbf{Q} = (0.3, 0, Q_z)$. It is increased with the changing of Q_z from 11.2 to 14.0, then decreased for $Q_z = 16.8$, and increased for $Q_z = 19.6$ r.l.u. Although, the peaks above 3 eV were found to be almost insensitive to the changing of Q_z . Analyzing Fig. 14, we can conclude that the momentum dependence of the excitations in $\text{Ba}_3\text{InIr}_2\text{O}_9$ is rather small, as earlier observed in other iridates, such as $\text{Sr}_3\text{CuIrO}_6$ [90], $\text{In}_2\text{Ir}_2\text{O}_7$ [91], or Sr_2IrO_4 [7].

Figure 15 shows the Ir L_3 RIXS spectrum as a function of incident photon energy E_i above the corresponding edge with the momentum transfer vector $\mathbf{Q} = (0, 0, 15)$. We found that the low-energy fine structure corresponding to the intra- t_{2g} excitations steadily decreases when the incident photon energy changes from 11215 to 11223 eV, whereas the energy peak corresponding to the $t_{2g} \rightarrow e_g$ transitions firstly increases, when the incident photon energy changes from 11215 to 11219 eV, and after that decreases. The same behavior occurs for the high-energy peak between 7 and 12 eV, which corresponds to the charge transfer transitions $5d_O \rightarrow e_g$.

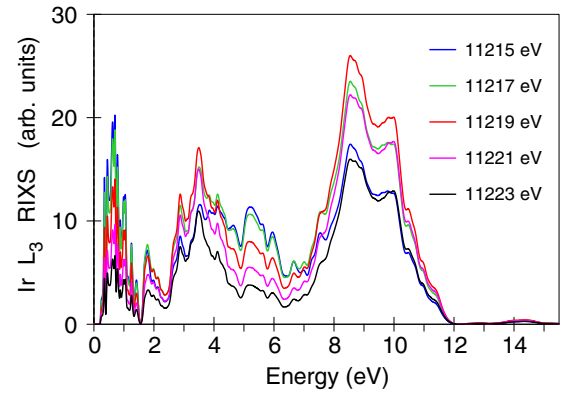


FIG. 15. The theoretically calculated RIXS spectra at the Ir L_3 edge in $\text{Ba}_3\text{InIr}_2\text{O}_9$ in the monoclinic $C2/c$ structure for π polarization calculated as a function of incident photon energy E_i in the monoclinic $C2/c$ structure with the momentum transfer vector $\mathbf{Q} = (0, 0, 15)$ in reciprocal lattice units.

C. Ir K , M and N , and O K RIXS spectra

At the core level, RIXS is not only element-specific but also orbital specific. For $3d$ transition metals, the electronic states can be probed by K , $L_{2,3}$, and $M_{2,3}$ x-ray absorption and emission spectra, whereas for $5d$ transition metals, one can use K , $L_{2,3}$, $M_{2,3}$, $M_{4,5}$, $N_{2,3}$, $N_{4,5}$, $N_{6,7}$, and $O_{2,3}$ spectra. For unpolarized absorption spectra, only transitions with $\Delta l = \pm 1$, $\Delta j = 0, \pm 1$ are allowed (the dipole selection rules). Therefore, only the electronic states with appropriate symmetry contribute to the absorption and emission spectra under consideration (Table IV).

To investigate the influence of core states on the resulting Ir RIXS spectra, we calculated the RIXS spectra of $\text{Ba}_3\text{InIr}_2\text{O}_9$ at the Ir K , M_3 , M_5 , N_3 , N_5 , and N_7 edges. Figure 16 presents the theoretically calculated RIXS spectra at the Ir M_3 , N_3 , and N_7 edges in the GGA + SO + U approach. We found a systematic decrease in the intensity of the RIXS spectra in the row $L_3 - M_3 - N_3$ edges. Although, the RIXS spectrum at the N_7 edge is significantly increased in comparison with the M_3 and N_3 spectra and becomes comparable with the RIXS spectrum at the L_3 edge, at least at the low-energy part of the spectrum ≤ 2 eV. The shapes of the Ir M_3 and N_3 RIXS spectra

TABLE IV. Angular momentum symmetry levels indicating the dipole-allowed transitions from core states to unoccupied valence states in $5d$ metals.

Spectra	K	L_2	L_3	M_4	M_5	N_6	N_7
		M_2	M_3				
		N_2	N_3	N_4	N_5		
		O_2	O_3				
Core level	$1s_{1/2}$	$2p_{1/2}$	$2p_{3/2}$				
		$3p_{1/2}$	$3p_{3/2}$	$3d_{3/2}$	$3d_{5/2}$	$4f_{5/2}$	$4f_{7/2}$
		$4p_{1/2}$	$4p_{3/2}$	$4d_{3/2}$	$4d_{5/2}$		
		$5p_{1/2}$	$5p_{3/2}$				
Valence states	$p_{1/2}$	$s_{1/2}$	$s_{1/2}$	$p_{1/2}$	$p_{3/2}$	$d_{3/2}$	$d_{5/2}$
	$p_{3/2}$	$d_{3/2}$	$d_{3/2}$	$p_{3/2}$	$f_{5/2}$	$d_{5/2}$	$g_{7/2}$
			$d_{5/2}$	$f_{5/2}$	$f_{7/2}$	$g_{7/2}$	$g_{9/2}$

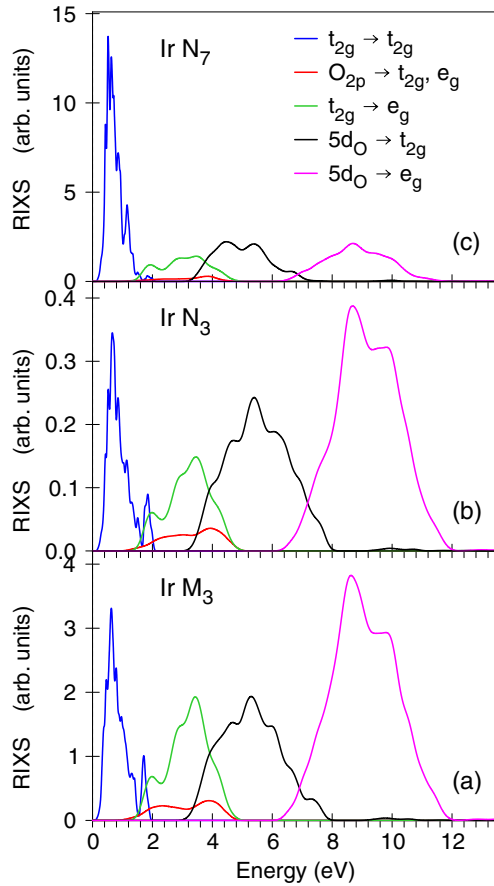


FIG. 16. The theoretically calculated RIXS spectra at the Ir M_3 , N_3 , and N_7 edges in $\text{Ba}_3\text{InIr}_2\text{O}_9$ in the GGA + SO + U approach ($U_{\text{eff}} = 2.3$ eV) for π polarization and vector $\mathbf{Q} = (0, 0, 15)$ r.l.u. for the monoclinic $C2/c$ structure.

are very similar to the corresponding RIXS spectrum at the L_3 edge. However, the $t_{2g} \rightarrow t_{2g}$ transitions are narrower for the N_7 edge in comparison with the L_3 , M_3 , and N_3 spectra. Besides, these transitions are relatively much stronger than other partial contributions to the N_7 spectrum. The Ir L_3 , M_3 , and N_3 RIXS spectra are derived from the absorption and emission of the $d_{3/2}$ and $d_{5/2}$ empty and occupied states, respectively. On the other hand, only the $d_{5/2}$ states contribute to the Ir N_7 RIXS spectrum, as can be seen from Table IV (the contributions from the $g_{7/2}$ and $g_{9/2}$ states are negligible). It explains why the $t_{2g} \rightarrow t_{2g}$ transitions are narrower in the N_7 RIXS spectrum in comparison with the L_3 , M_3 , and N_3 ones. We should mention that because of a relatively small spin-orbit splitting of core Ir $4f$ states (~ 3.3 eV), the N_6 and N_7 RIXS spectra would have an appreciable overlap. For this reason, the N_7 spectrum contributes to some extent to the structure of the total $N_{6,7}$ spectrum in the region of the N_6 edge. To decompose a corresponding experimental $N_{6,7}$ spectrum into its N_6 and N_7 parts will therefore be quite difficult in general.

The RIXS spectroscopy of Ir atoms in the ultrasoft x-ray energy range at the $N_{6,7}$ edges may be a very useful tool for the investigation of the electronic structure of magnetic materials.

Figure 17 shows the theoretically calculated RIXS spectra at the Ir K , M_5 , and N_5 edges in $\text{Ba}_3\text{InIr}_2\text{O}_9$ in the GGA + SO + U approach. The exchange splitting of the initial $1s$ core

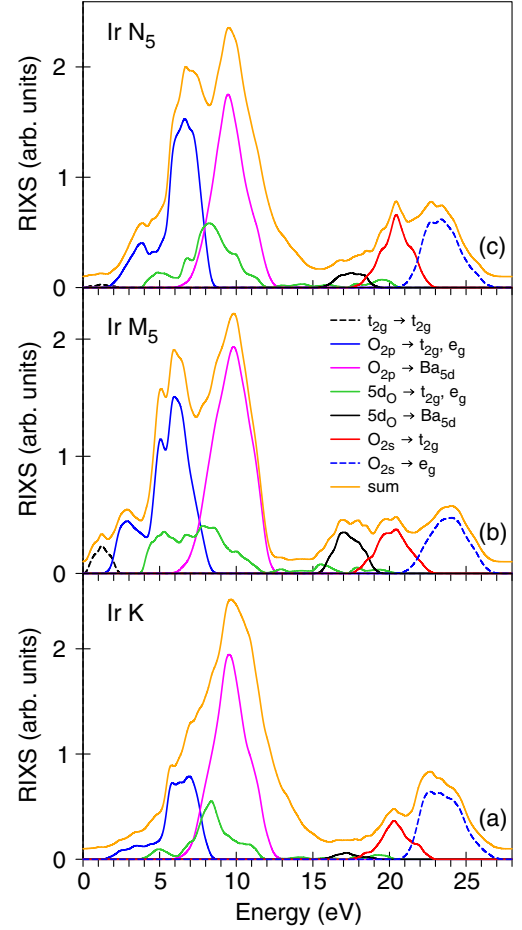


FIG. 17. The theoretically calculated RIXS spectra at the Ir K , M_5 , and N_5 edges in $\text{Ba}_3\text{InIr}_2\text{O}_9$ in the GGA + SO + U approach ($U_{\text{eff}} = 2.3$ eV) for π polarization and vector $\mathbf{Q} = (0, 0, 15)$ r.l.u. for the monoclinic $C2/c$ structure.

state is extremely small [76,92], therefore only the exchange and spin-orbit splitting of $6p$ states is responsible for the observed RIXS spectrum at the Ir K edge. The Ir K RIXS spectrum consists of two major peaks at 2–15 and 18–27 eV. The low-energy peak is due to the interband transitions from the Ir $6p$ states which are hybridized with oxygen $2p$ states (O_{2p}) to the Ir $6p$ states which are hybridized with Ir t_{2g} and e_g states [the blue curve in Fig. 17(a)] and the states derived from the hybridization with Ba $5d$ states (the magenta curve). The transitions $5d_O \rightarrow (t_{2g}, e_g)$ also contribute to the major low-energy peak (the green curve). The two-peak high-energy fine structure is due to the interband transitions between the Ir $6p$ states which are hybridized with oxygen $2s$ states (O_{2s}) and Ir t_{2g} and e_g states (the red and dashed blue curves, respectively).

Ir M_5 and N_5 spectra can be, to some extent, considered as an analog of the K spectrum. The Ir K RIXS spectrum reflects the energy distribution of the $6p_{1/2}$ and $6p_{3/2}$ energy states (Table IV). The M_5 (N_5) RIXS spectrum due to the dipole selection rules occurs for the transitions from the $3d_{3/2}$ ($4d_{3/2}$) core states to the $6p_{3/2}$, $5f_{5/2}$, and $5f_{7/2}$ states. The results of our theoretical calculations of the RIXS spectra at the M_5 and N_5 edges of Ir in $\text{Ba}_3\text{InIr}_2\text{O}_9$ are shown in Figs. 17(b) and 17(c). Comparing these spectra with the corresponding

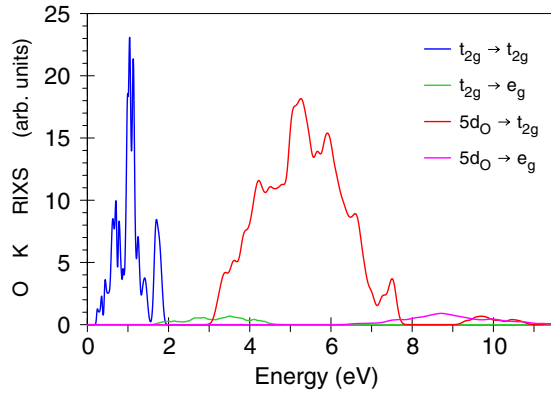


FIG. 18. The theoretically calculated in the GGA + SO + U approach ($U_{\text{eff}} = 2.3$ eV) RIXS spectrum at the O K edge of $\text{Ba}_3\text{InIr}_2\text{O}_9$ in the monoclinic $C2/c$ structure for π polarization.

RIXS spectrum at the Ir K edge, one can see an obvious resemblance between them. The major difference is seen from 0 to 7 eV. In comparison with the Ir K spectrum, both the M_5 and N_5 RIXS spectra possess a larger contribution from the $\text{O}_{2p} \rightarrow (t_{2g}, e_g)$ transitions. In addition, the M_5 RIXS spectrum shows visible $t_{2g} \rightarrow t_{2g}$ transitions at the 0 – 2 eV energy interval [the dashed black curve in Fig. 17(b)] and $5d_{\text{O}} \rightarrow \text{Ba}_{5d}$ transitions at 15 – 19 eV (the full black curve). The difference between the Ir K and M_5 and N_5 spectra can be attributed to an additional contribution of the $5f_{5/2,7/2}$ energy states to the M_5 and N_5 spectra and to the difference in the radial matrix elements ($1s \rightarrow 6p_{1/2,3/2}$ in the K spectrum and $3d_{5/2} \rightarrow 6p_{3/2}$ and $4d_{5/2} \rightarrow 6p_{3/2}$ in the M_5 and N_5 spectra, respectively). Although the latter plays a minor role due to the fact that radial matrix elements are smooth functions of energy [76].

Figure 18 shows the theoretically calculated RIXS spectrum at the O K edge of $\text{Ba}_3\text{InIr}_2\text{O}_9$ in the GGA + SO + U approach. We found that the $t_{2g} \rightarrow t_{2g}$ transitions (the blue curve), which are situated below 2 eV, are quite intensive and even exceed the $5d_{\text{O}} \rightarrow t_{2g}$ transitions (the red curve). This is quite unusual because the latter transitions in some other transition metal oxides, such as Sr_2IrO_4 [7] and $\text{Ca}_3\text{Ru}_2\text{O}_7$ [93], are dominant. The $t_{2g} \rightarrow e_g$ (the green curve) and $5d_{\text{O}} \rightarrow e_g$ transitions (the magenta curve) are rather small.

Experimental measurements of the RIXS spectra at the Ir K , M_3 , M_5 , N_3 , N_5 , N_7 , and O K edges in $\text{Ba}_3\text{InIr}_2\text{O}_9$ are highly desirable.

V. CONCLUSIONS

To summarize, we have investigated the electronic and magnetic structures of $\text{Ba}_3\text{InIr}_2\text{O}_9$ in the frame of the fully relativistic spin-polarized Dirac approach. We have also presented comprehensive theoretical calculations of the RIXS spectra at the Ir L_3 and oxygen K edges.

The delicate interplay between electron correlations, SOC, intersite hopping, and a crystal field splitting leads to a strongly competing ground state in $\text{Ba}_3\text{InIr}_2\text{O}_9$. We found that the ground magnetic state in $\text{Ba}_3\text{InIr}_2\text{O}_9$ is AFM₂ with the FM intradimer and AFM interdimer coupling. The GGA

and GGA + SO approaches give a metallic ground state in $\text{Ba}_3\text{InIr}_2\text{O}_9$. It is in contradiction with electric conductivity and energy loss measurements, which firmly indicate an insulating character of $\text{Ba}_3\text{InIr}_2\text{O}_9$. After taking into account the Coulomb correlations in the frame of the GGA + SO + U method, we obtained the energy gap for the AFM ground state in the monoclinic $C2/c$ crystal structure. The calculations show that the energy gap is already formed in the GGA + U approximation without SOC. $\text{Ba}_3\text{InIr}_2\text{O}_9$ can be classified as a Mott insulator, since it was expected to be metallic from GGA band structure calculations. We found that the best agreement between the calculated and experimentally measured RIXS spectra at the Ir L_3 edge in $\text{Ba}_3\text{InIr}_2\text{O}_9$ can be achieved for $U_{\text{eff}} = 2.3$ eV.

We calculated a phase diagram in the $U_{\text{eff}} - \text{SOC}$ plane for two different crystal structures of $\text{Ba}_3\text{InIr}_2\text{O}_9$. We found that $\text{Ba}_3\text{InIr}_2\text{O}_9$ in both crystallographic modifications possesses a smaller $U_{\text{eff}} - \text{SOC}$ Mott-dielectric phase space in comparison with the typical strongly correlated Sr_2IrO_4 iridate. The energy band gap for $\lambda = 1$ is opened at Hubbard U_{eff} , equal to 1.9 and 1.31 eV for hexagonal and monoclinic $\text{Ba}_3\text{InIr}_2\text{O}_9$, respectively. For monoclinic $C/2c\text{Ba}_3\text{InIr}_2\text{O}_9$, the energy gap opens up for $U_{\text{eff}}^c = 1.7$ eV for $\lambda = 0$, however, there is no dielectric solution for $U_{\text{eff}} \leq 0.63$ eV with any value of λ . Even for very large λ , the curve does not cross the abscissa axis. For the hexagonal $P6_3/mmc$ crystal structure, the energy gap opens up for $U_{\text{eff}}^c = 2.3$ eV for $\lambda = 0$ and there is no dielectric solution for $U_{\text{eff}} \leq 1.39$ eV.

Although in $\text{Ba}_3\text{InIr}_2\text{O}_9$ there is a tendency of forming a dimer structure by two face-shared IrO_6 octahedra, the insulating state in $\text{Ba}_3\text{InIr}_2\text{O}_9$ is not driven by dimerization as it happens, for example, in the high pressure honeycomb-based $5d^5$ iridate $\beta\text{-Li}_2\text{IrO}_3$ [6,83,84]. The gap in $\text{Ba}_3\text{InIr}_2\text{O}_9$ is opened only with taking into account strong Coulomb correlations.

The theoretically calculated Ir L_3 RIXS spectrum is in good agreement with the experiment. We found that the low-energy part of the RIXS spectrum ≤ 2 eV corresponds to intra- t_{2g} excitations. It has quite a rich fine structure with at least 12 well-separated peaks. Such a shape of the RIXS spectrum can be explained by a specific energy band structure of Ir t_{2g} states with nine DOS peaks below E_F and three empty narrow DOS peaks separated by energy gaps. The interband transitions between these nine occupied and three empty bands produce the rich structure of the Ir L_3 RIXS spectrum below 2 eV. The appearance of multiple peaks in the RIXS spectrum is a direct consequence of a strong noncubic crystal field splitting originating from the distorted octahedral environment of the Ir ions. The RIXS peak located at ~ 4 eV was found to be due to $t_{2g} \rightarrow e_g$ transitions with some additional contributions from $5d_{\text{O}} \rightarrow t_{2g}$ transitions. The strong fine structure at ~ 9 eV is due to $5d_{\text{O}} \rightarrow e_g$ transitions.

We found rather small momentum dependence of the excitations in $\text{Ba}_3\text{InIr}_2\text{O}_9$, which is typical for $5d$ transition oxides. Our investigation of the Ir L_3 RIXS spectrum as a function of incident photon energy E_i shows that the intra- t_{2g} excitations steadily decrease with increasing the incident photon energy, whereas the high-energy peaks corresponding to the $t_{2g} \rightarrow e_g$ transitions and the charge transfer transitions

$5d_O \rightarrow t_{2g}$ possess oscillation dependence on the incident photon energy.

To investigate the influence of core states on the resulting Ir RIXS spectra, we calculated the RIXS spectra of $\text{Ba}_3\text{IrIr}_2\text{O}_9$ at the Ir K , M_3 , M_5 , N_3 , N_5 , and N_7 edges. We found a systematic decrease in the intensity of the RIXS spectra in the row $L_3 - M_3 - N_3$ edges. Although, the RIXS spectrum at the N_7 edge is significantly increased in comparison with the M_3 and N_3 spectra and becomes comparable with the RIXS spectrum at the L_3 edge. The shapes of the Ir M_3 and N_3 RIXS spectra are very similar to the corresponding RIXS spectrum at the L_3 edge.

The exchange splitting of the initial $1s$ core state is extremely small, therefore only the exchange and spin-orbit splitting of $6p$ states is responsible for the observed RIXS spectrum at the Ir K edge. Ir M_5 and N_5 spectra can be to some extent considered as an analog of the K spectrum. There is a resemblance between the calculated Ir M_5 and N_5 spectra and the Ir K spectrum in $\text{Ba}_3\text{IrIr}_2\text{O}_9$. However, both the M_5

and N_5 RIXS spectra possess a larger contribution from the $\text{O}_{2p} \rightarrow (t_{2g}, e_g)$ transitions in comparison with the Ir K spectrum.

We also calculated the RIXS spectrum at the oxygen K edge in $\text{Ba}_3\text{IrIr}_2\text{O}_9$. We found that the $t_{2g} \rightarrow t_{2g}$ transitions, which are situated below 2 eV, are rather intensive and even exceed the $5d_O \rightarrow t_{2g}$ transitions. This is quite unusual because the latter transitions in some other transition metal oxides, such as Sr_2IrO_4 and $\text{Ca}_3\text{Ru}_2\text{O}_7$, are dominant.

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DATA AVAILABILITY

No data were created or analyzed in this study.

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