

Electronic structure of BaIrO₃: A first-principles study using the local spin density approximation

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We investigate the electronic structure of BaIrO₃, an interesting compound exhibiting charge density wave transition in its insulating phase and ferromagnetic transition at the same temperature, using full potential linearized augmented plane wave method within the local spin density approximations. The ferromagnetic ground state could exactly be described in these calculations and the calculated spin magnetic moment is found to be small as observed in the magnetic measurements. Interestingly, no signature of exchange splitting is observed in the density of states corresponding to Ir 5*d* and/or any other electronic states. The small spin moment appears essentially due to unequal population of the up- and down-spin Ir 5*d* bands. Comparison of the valence band density of states with the experimental spectral functions suggests that a rigid shift of the Fermi level towards higher energies in the calculated density of states provides a good description of the experimental spectra. This indicates that the intrinsic oxygen nonstoichiometry leads to electron doping in the system and plays the primary role in determining the electronic structure rather than the electron correlation effects as often observed in other systems. The calculated results for Ba 5*p* core levels show that the Madelung potential of one of the three nonequivalent Ba atoms is different from that of other two as predicted in the recent experiments.

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I. INTRODUCTION

The compound, BaIrO₃ has drawn significant attention in the recent time due to the observation of charge density wave (CDW) transition despite insulating transport observed above and below the CDW transition temperature ($T_c \approx 185$ K).¹ Interestingly, it also exhibits a ferromagnetic transition at the same temperature (185 K) where CDW ground state sets in. The saturation magnetic moment in the ferromagnetic phase, however, is found to be very small ($\sim 0.03 \mu_B$) compared to that expected from the t_{2g}^5 electronic configuration corresponding to Ir⁴⁺.

The crystal structure of BaIrO₃ is monoclinic (space group $B2/m$; unique axis c). In this structure, IrO₆ octahedra form Ir₃O₁₂ trimers by face sharing as shown in Fig. 1. The Ir₃O₁₂ trimers are interlinked by corner-sharing to form columns parallel to the a axis. The axis of the connecting trimers are marginally tilted ($\sim 12^\circ$) as shown in Fig. 1.² This leads to the monoclinic structure with the crystallographic angle, $\gamma = 103.27^\circ$. This typical structure makes it a quasi-one-dimensional system as has clearly been manifested in the anisotropic transport, magnetic, and optical properties.¹ The structure becomes more complex due to the twisting and buckling of the trimers resulting in the multiplicity of Ir–O and Ba–O bond distances, thereby creating four types of Ir and three types of Ba sites.^{3,4} Different nonequivalent Ir atoms are represented by Ir1, Ir2, Ir3, and Ir4 in the figure. Interestingly, each trimer consists of two nonequivalent Ir atoms. For example, if Ir2 forms the central octahedron of a trimer, it is connected by face sharing to the other two octahedra formed by Ir1. Similarly, the neighboring Ir₃O₁₂ trimer is formed by Ir3 and Ir4, where Ir4 forms the central octahedron and Ir3 forms the other two octahedra. Thus, the inter-trimer link is established along the a direction via (Ir1)–O–(Ir3) connectivity.

Despite very short intratrimer Ir–Ir distances compared to Ir-metal and Ir–O–Ir angle close to 180° for intertrimer connections, BaIrO₃ exhibits insulating transport behavior. In addition, there are multiple metal-insulator (MI) transitions within the CDW ground state. While the occurrence of CDW transitions in the insulating phase is surprising, a recent high resolution photoemission study⁵ reveals the signature of finite density of states at the Fermi level, ϵ_F , at room temperature and it was shown that the CDW ground state evolves by opening a soft gap at ϵ_F across the CDW transition temperature. Interestingly, the intensity at ϵ_F in the photoemission spectra at room temperature ($T > T_c$) is significantly small

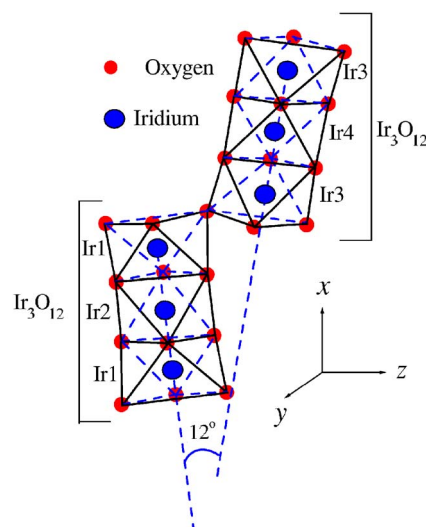


FIG. 1. (Color online) Schematic diagram of the Ir₃O₁₂ trimers in the monoclinic structure of BaIrO₃ (space group $B2/m$). The trimers are connected by corner sharing and their long axis are tilted by 12° .

consistent with the observation of very small electronic specific heat coefficient¹ (~ 1 mJ/mole K²). In contrast, previous theoretical study using extended Hückel tight-binding electronic band structure calculations⁶ exhibits large intensity at ϵ_F as expected for a t_{2g} electronic configuration corresponding to Ir⁴⁺. In addition, the analysis of the core level spectra in the photoemission measurements⁵ predicts the existence of two different kinds of Ba sites at room temperature, which become similar before the onset of CDW ground state. All these anomalies¹⁻⁸ in the transport, magnetic, and spectroscopic data reveal that BaIrO₃ is truly an exotic material.

Since, the $5d$ orbitals in $5d$ transition metal oxides are highly extended compared to that in $3d$ or $4d$ systems, it is expected that the electron correlation strength will be significantly weak and that the *ab initio* approaches will be successful to describe the electronic properties in this system. In this study, we therefore, investigate the electronic structure of BaIrO₃ using *state-of-the-art ab initio* approaches. The calculations for various magnetic configurations suggest that the ground state of BaIrO₃ is ferromagnetic exhibiting small magnetic moments consistent with the experimental observations.¹ The analysis of the valence band density of states in comparison to the experimental photoemission results⁵ suggests that the small intensity at ϵ_F in the photoemission spectra and the insulating transport behavior are presumably related to the pinning of ϵ_F at the upper edge of t_{2g} band due to the intrinsic nonstoichiometry of the samples³ and these edge states are localized due to disorder/crystallographic distortions.^{9,10} The calculations for the Ba $4p$ core levels exhibit a signature of two nonequivalent Ba sites with respect to the Madelung potential at the Ba sites in the crystal structure at room temperature.

II. THEORETICAL METHODS

The electronic band structure calculations were carried out using full potential linearized augmented plane wave (FP-LAPW) method (WIEN2K software¹¹) within the local spin density approximations (LSDA). The crystal structure considered for these calculations has $B2/m$ space group with the c axis as the unique axis. The lattice parameters ($a = 10.005$ Å, $b = 15.174$ Å, $c = 5.571$ Å, $\alpha = \beta = 90^\circ$, and $\gamma = 103.27^\circ$) and the atomic positions used for all the calculations correspond to the room temperature structure reported for well characterized polycrystalline and single crystalline samples in Refs. 1 and 3. It is noted here that most of these studies for the crystal structure analysis report the space group as $C2/m$ with the b axis as the unique axis, which has been transformed to the $B2/m$ space group by coordinate transformations ($a'b'c' \leftrightarrow acb$) in order to satisfy the requirement of the WIEN2K software. The muffin-tin radii (R_{MT}) for Ba, Ir, and O were set to 1.217 Å, 1.111 Å, and 0.847 Å, respectively. The convergence for different calculations were achieved considering 512 k points within the Brillouin zone. The error bar for the energy convergence was set to < 1 meV.

III. RESULTS AND DISCUSSIONS

In Fig. 2, we show the density of states calculated for the nonmagnetic ground state using the lattice parameters corre-

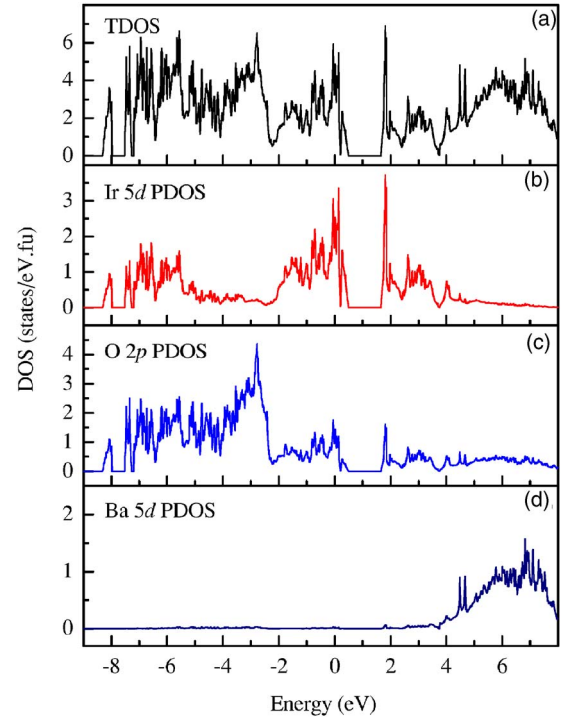


FIG. 2. (Color online) Calculated (a) TDOS, (b) Ir $5d$ PDOS, (c) O $2p$ PDOS, and (d) Ba $5d$ PDOS for the nonmagnetic ground state. The large intensity at the Fermi level suggests a metallic ground state in contrast to the experimental observations. The states at the Fermi level have primarily Ir $5d$ character with O $2p$ states appearing below -2.3 eV.

sponding to room temperature structure as mentioned in the previous section. The total density of states (TDOS), Ir $5d$ partial density of states (PDOS), O $2p$ PDOS, and Ba $5d$ PDOS are plotted in Figs. 2(a)–2(d), respectively. Ba $5d$ electronic states contribute in the energy range 4 eV above the Fermi level as shown in Fig. 2(d) with almost no contribution at lower energies. O $2p$ contribution in the Ba $5d$ dominated energy region is very little, which is expected for the $5d$ energy level in this heavy alkaline earth atom compared to the cases observed for lighter alkaline earth atoms such as Sr in Sr-compounds or Ca in Ca-compounds having unoccupied $4d$ and $3d$ levels, respectively.¹² This suggests that the role of Ba–O covalency in the electronic/crystal structure is not significant in this system.

There are three groups of features observed in TDOS in the occupied part of the electronic structure shown below ϵ_F ($=0$ eV). The energy range between -5.5 eV to -2.3 eV is primarily dominated by the O $2p$ PDOS with negligible contributions from Ir $5d$ PDOS. This suggests that the electronic states in this energy range are not bonded with the Ir $5d$ states and are known as nonbonding O $2p$ states. In the energies below -5.5 eV (-5.5 eV $> \epsilon > -8.5$ eV), O $2p$ states have the largest intensity with finite contributions from Ir $5d$ electronic states. Thus, these features can be assigned as bonding bands having primarily O $2p$ character. The antibonding bands having t_{2g} symmetry appears in the energy range -2.5 eV to $+0.5$ eV (total width ~ 3 eV). The e_g band appears above the Fermi level with a minimum excitation

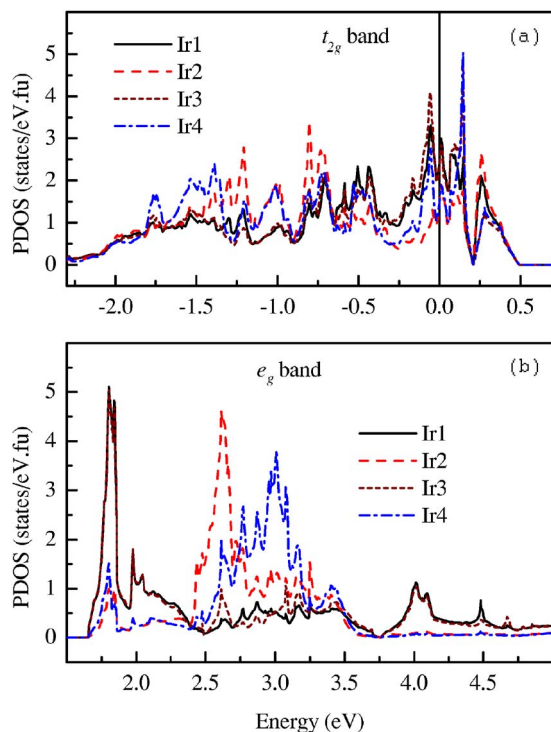


FIG. 3. (Color online) Ir 5*d* band with (a) t_{2g} symmetry and (b) e_g symmetry for all four nonequivalent Ir atoms in the structure. The assignment of Ir atoms are made as shown in Fig. 1.

gap of about 1.2 eV from the upper edge of t_{2g} band. The DOS in these regions are essentially contributed by the Ir 5*d* electronic states with minimal contributions from O 2*p* states. Thus, the electronic states at and around ϵ_F have primarily Ir 5*d* character, which naturally determines the transport and thermodynamic properties. Interestingly, DOS at ϵ_F is found to be significantly large as also observed before⁶ suggesting highly metallic behavior of the system in contrast to the insulating transport, small specific heat coefficient observed¹ and the high-resolution photoemission results recently published.⁵

In order to investigate the contribution from various non-equivalent Ir sites separately, we plot the t_{2g} and e_g band in Figs. 3(a) and 3(b), respectively. The total t_{2g} bandwidth for each of the Ir atoms is found to be close to 3 eV spanning the same energy region. The PDOS corresponding to Ir2 and Ir4 are almost uniformly distributed over the whole energy range. However, Ir1 and Ir3 exhibit largest intensity close to the Fermi level suggesting largest contribution to the conduction electrons. Such a scenario is expected since inter Ir₃O₁₂ trimer connectivity is established via (Ir1)-O-(Ir3) superexchange interaction as shown in Fig. 1 and has largest extended character. Ir2 and Ir4 provide intratrimer connectivity via *d-d* interactions with Ir1 and Ir3, respectively. Thus, there is a relative shift between the center of gravity of Ir1, Ir3 contributions and Ir2, Ir4 contributions. The features in the energy range $\epsilon < -0.75$ eV has largest contribution from Ir2 and Ir4 sites and for $\epsilon > -0.75$ eV, the intensity arises primarily from Ir1 and Ir3 contributions.

The effective width of the e_g bands is significantly narrower in this system as shown in Fig. 3(b). While Ir2 and Ir4

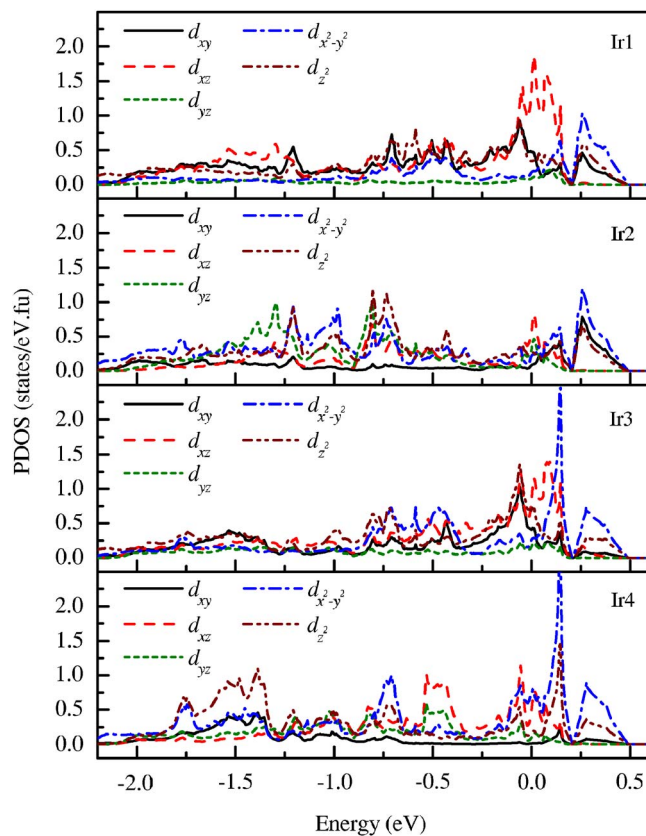


FIG. 4. (Color online) PDOS for the t_{2g} band in the nonmagnetic ground state having d_{xy} character (solid line), d_{xz} character (dashed line), d_{yz} character (short dashed line), $d_{x^2-y^2}$ character (dotted-dashed line), and d_{z^2} character (dotted-dotted-dashed line) are shown separately for four non equivalent Ir atoms.

are primarily contributing in the energies 2.5–3.5 eV above ϵ_F , the Ir1 and Ir3 contributions appear below 2.5 eV. Interestingly, Ir1 and Ir3 are found to be very similar in both the energy regions, and Ir2 and Ir4 have similar DOS distributions.

Since the axis of any of the IrO₆ octahedra are not aligned along any of the crystal axis as shown in Fig. 1, the t_{2g} bands will have contributions from all the *d*-orbital states (d_{xy} , d_{yz} , d_{xz} , $d_{x^2-y^2}$, and d_{z^2}) defined in the axis system shown in Fig. 1. The projected partial density of states corresponding to these orbital are shown separately for each of the Ir sites in Fig. 4. Interestingly, the primary contribution ($\sim 35.77\%$) at ϵ_F comes from d_{xz} electronic states located at Ir1 and Ir3 sites. d_{xy} and d_{z^2} at Ir1 and Ir3 sites also exhibit large contributions (14.3% and 16.6%, respectively) at ϵ_F . The largest contributions from Ir2 and Ir4, however, arise from d_{xz} (8.4%) and $d_{x^2-y^2}$ (7.6%) electronic states. These numbers clearly manifest that the electronic states containing the quasi-one-dimensional axis of the crystal structure (*x* axis) have the largest contribution at ϵ_F and hence clearly manifests the signature of large anisotropy observed in various bulk properties.¹

We now turn to the understanding of the magnetic behavior of BaIrO₃. We carried out the spin-polarized calculations using the same crystal structure as in the case of nonmagnetic calculations and use local spin density approximations.

The magnetic moment has been defined by the difference in occupancy of the majority (up) and minority (down) spin states. Spin-orbit interaction was not considered in these calculations. Interestingly, the calculations for various magnetic configurations reveal that the ferromagnetic ground state is 3.25 meV lower than (error bar used for convergence is <1 meV) the total energy found for the nonmagnetic ground state. This energy difference is about 20% of $k_B T_C$ ($T_C = 185$ K). This calculation, thus, once again establish that LSDA approximations are quite accurate in capturing the magnetic ground state of various transition metal oxides as has also been observed in $3d$ transition metal oxides¹³ despite the fact that the electron correlation effects are underestimated in these calculations. The total spin magnetic moment is found to be about $1.34 \times 10^{-3} \mu_B$. This is significantly small compared to that expected for t_{2g}^5 electronic configuration for Ir^{4+} . Such a small value of the spin moment appears presumably due to the highly extended nature of the $5d$ orbitals leading to large kinetic energy of the associated electrons. The calculated spin moment is consistent with the experimental observation of small saturation magnetic moment ($\sim 0.03 \mu_B$) in the magnetic measurements of single crystalline BaIrO_3 ; this moment could be measured only after applying a magnetization field as high as 20 T.¹ No magnetic contribution is found from the Ba-related bands, as all these bands are either completely occupied and appear much below ϵ_F or completely unoccupied appearing far above ϵ_F . The contribution from O $2p$ states is of the order of $10^{-4} \mu_B$. The primary contribution to the total magnetic moment arises from the spin polarization of Ir $5d$ partial density of states. Interestingly, all the Ir atoms are found to order ferromagnetically and the magnetic moment at the central Ir site of the Ir_3O_{12} trimer is almost the half of that observed at the other Ir sites.

In Fig. 5, we show the spin-polarized Ir $5d$ partial density of states for the ferromagnetic ground state, where Figs. 5(a)–5(d) show the results corresponding to Ir1, Ir2, Ir3, and Ir4, respectively. The down-spin contributions are shown by inverting the y axis in the same figure with same energy scale for up-spin contributions shown along the x axis. No signature of exchange splitting is observed at any of the Ir sites. The up- and down-spin DOS reveal almost identical structures in all the cases. In order to investigate the origin of the spin moment, we show the total Ir $5d$ PDOS for both up- and down-spin states in Fig. 6(a) and the difference between up- and down-spin contributions in Fig. 6(b). It is clear that the observed magnetic moment appears due to small asymmetry of the up- and down-spin density of states as a function of energy. Thus, the occupancy of the up- and down-spin contributions is different leading to a small spin-moment.

Now, we compare the calculated results with the experimental photoemission spectra published recently for BaIrO_3 .⁵ In Fig. 7(a), we show the Ir $5d$ band obtained from He II spectra⁵ and overlap with the calculated t_{2g} band of Ir $5d$ PDOS. While the calculated results exhibit large intensity at the Fermi level suggesting highly metallic behavior of the system, the experimental Ir $5d$ feature at room temperature exhibit only very small intensity. The total width of the occupied part in the calculated PDOS is also substantially smaller compared to the Ir $5d$ signal in the experimental

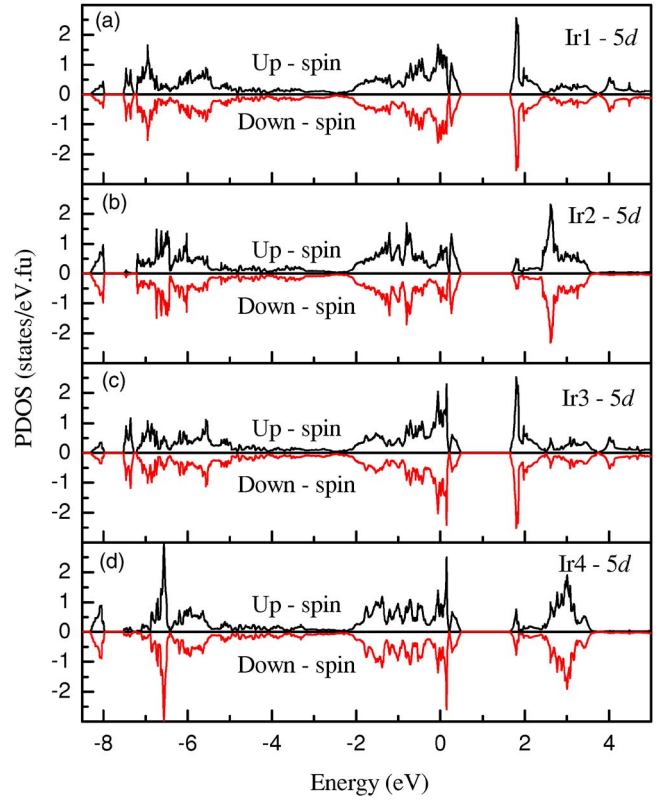


FIG. 5. (Color online) Ir $5d$ PDOS corresponding to ferromagnetic ground state. Up and down spin contributions are shown by positive and negative y axis, respectively. None of the cases show a signature of exchange splitting.

spectra. Such observations of significant reduction of spectral weight at the Fermi level and the population of the higher binding energy region often attributed to the underestimation of electron-electron Coulomb repulsion effect in the *ab initio* approaches. However, such a strong correlation effect in these highly extended $5d$ electrons is unexpected.

It is noted here that the difference between experimental bulk spectral functions and the *ab initio* results could well be explained in the $4d$ transition metal oxides¹⁴ using the perturbative approach to introduce the correlation effect in the self-energy of the system. The effective correlation strength, U/W (U =electron-electron Coulomb repulsion strength, W =bandwidth) was found to be small ($U/W \sim 0.2$) in these systems. We thus calculate the spectral function for BaIrO_3 in the same way, using the second order perturbation method employed by Treglia *et al.*¹⁵ In this method, the spectral function can be expressed as,

$$f(\epsilon) = -\frac{1}{\pi} \text{Im} \sum_k G_k(\epsilon),$$

where, $G_k(\epsilon)$ is the retarded Green's function representing the many electron system and is given by

$$G_k(\epsilon) = \frac{1}{(\epsilon - \Sigma_k(\epsilon) - \epsilon_k)},$$

where $\Sigma_k(\epsilon)$ is the self-energy of the system. For small U , $\Sigma_k(\epsilon)$ can be calculated using perturbation approach up to the

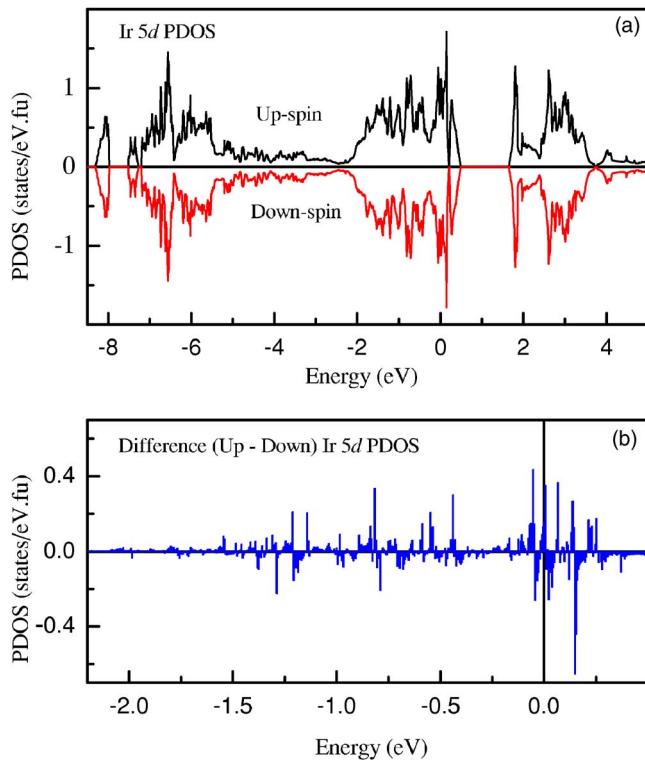


FIG. 6. (Color online) Total Ir 5d PDOS corresponding to the ferromagnetic ground state. The difference between up and down spin PDOS are shown in (b). The spin moment appears due to unequal occupancy of the up and down spin bands as shown in the figure.

second order term^{15,16} within the local approximations. We have used Ir t_{2g} PDOS shown in Fig. 7(a) as the band DOS for these calculations. The calculated spectral functions for different U/W are shown in Fig. 7(b) and the calculated self energy is shown in the inset of the same figure. The increase in U/W leads to a significant spectral weight transfer to higher energies. The new features appearing at higher binding energies due to such spectral weight transfer is known as incoherent feature and represent the electronic states essentially localized due to such correlation effect. The feature at the Fermi level represent the delocalized states and is known as coherent feature. The total weight of the coherent feature diminishes gradually with the increase in U/W . However, the intensity at the Fermi level remains almost the same for U/W as large as 1.0. The spectral function obtained in this process could not generate the spectral lineshape observed in the experimental spectrum for any value of U/W . This suggests that this procedure may not be adequate to determine the experimental results.

Interestingly, a rigid shift of the calculated t_{2g} band by 0.5 eV towards higher binding energies provide a significantly good description of the experimental spectrum. The width and spectral distribution in the shifted spectral function shown in Fig. 7(a) is remarkably similar to that observed in the Ir 5d band in the He II spectrum. In order to investigate this further we compare the O 2p PDOS with the experimental spectra as it is well known that the *ab initio* calculations are quite successful in providing a good description of the O

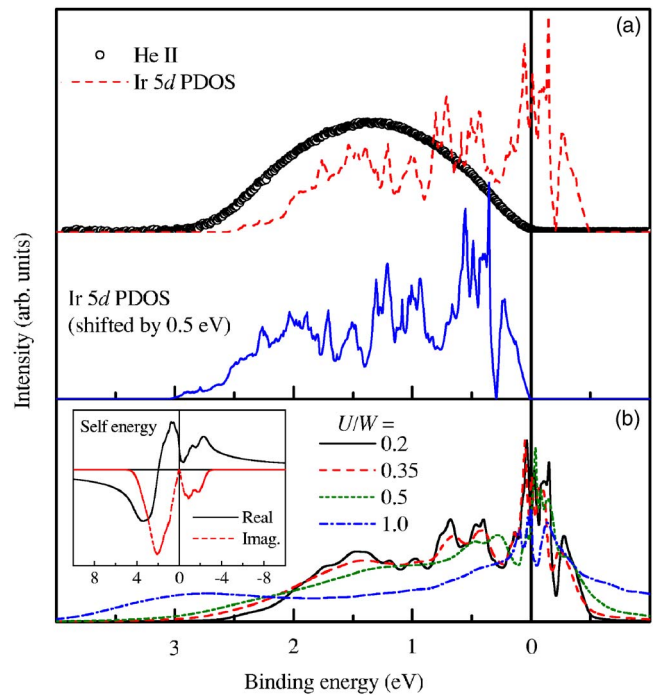


FIG. 7. (Color online) (a) The t_{2g} band (dashed line) obtained from *ab initio* calculations is compared with the experimental Ir 5d band (circles) delineated from the He II spectrum. The experimental results are adopted from Ref. 5. The calculated DOS is significantly different from the experimental ones. The calculated DOS shifted by 0.5 eV towards higher binding energies (solid line) reveal a better description of the experimental spectrum. (b) Spectral functions obtained by introducing electron correlation effects into the self-energy by second order perturbative approach using *ab initio* results. The change in U/W leads to a spectral weight transfer toward higher binding energies. The inset shows the real (solid line) and imaginary (dashed line) part of the self-energy.

2p band even in 3d transition metal oxides.¹³ We show the experimental Al $K\alpha$ and He I spectra in Fig. 8 adopted from Ref. 5. The changes in these experimental spectra in the energy range between 3 and 9 eV binding energies concomitant

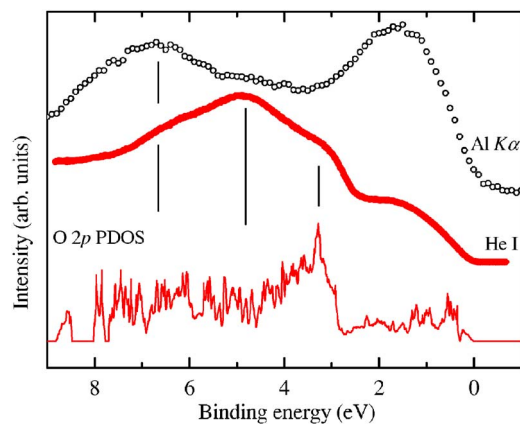


FIG. 8. (Color online) Experimental He I (solid circles) and Al $K\alpha$ spectra (open circles) adopted from Ref. 5 are compared with the calculated O 2p PDOS (solid line) shifted by 0.5 eV towards higher binding energies.

to the change in relative photoemission cross section¹⁷ of the O $2p$ and Ir $5d$ electronic states suggest that the features in 3–6 eV binding energies appear primarily due to the excitations of O $2p$ nonbonding states and the intensity at higher binding energies are due to the bonding electronic states having large O $2p$ character. Interestingly, the calculated O $2p$ PDOS shows the intense nonbonding O $2p$ features around 2.3–5.5 eV binding energies with the peak at 2.8 eV binding energy (see Fig. 2), where the dip appears in the He I spectrum. This clearly suggests that it is necessary to shift the O $2p$ PDOS by at least 0.5 eV towards higher binding energies to compare it with the experimental spectra. The shifted O $2p$ PDOS shown by a solid line in Fig. 8 provides a good description of the experimental results.

Thus, the results in Figs. 7 and 8 suggest that the Fermi level is shifted to the upper edge of the t_{2g} band presumably due to the electron doping into the system. Such a shift would stabilize the system due to the closeness to the fully filled electronic configuration resulting to lowering in energy. Interestingly, various experimental results indeed indicate that the oxygen content is often found to be less than 3.0,^{3,7} which effectively leads to electron doping into the Ir $5d$ band. In addition, the transport measurements always exhibit insulating temperature dependence.¹ Such a behavior is not unusual since it is natural that the small intensity at the upper edge of the t_{2g} band will be localized due to the disorder and/or crystallographic distortions^{9,10} in this quasi-one-dimensional structure leading to an insulating nature. All these observations, thus, clearly indicate that the electron correlation may not be the primary origin for the differences between experimental and theoretical results. The electron doping due to the oxygen nonstoichiometry intrinsic to BaIrO₃ possibly plays the key role in determining the electronic structure and subsequently various physical properties in this system. While a direct verification of this effect is difficult due to the limitations of the computing power to handle a large supercell corresponding to a composition having small oxygen nonstoichiometry, further photoemission studies on samples having different oxygen nonstoichiometry may ensure such an effect experimentally.

We now turn to the question of multiple Ba core level signals in the experimental spectra.⁵ We show the DOS corresponding to Ba $5p$ core levels in Fig. 9. There are three nonequivalent Ba sites in the structure with respect to the Ba-O bond length and the symmetries. It is clear that the DOS corresponding to Ba1 and Ba2 appear in the same energy range. While the width of the DOS corresponding to Ba2 $5p$ states is similar to those corresponding to Ba1 and Ba3, the peak position appears at higher binding energies. The energy difference between these spectral features is about 0.25 eV. This observation clearly suggests that the Madelung potential at all the Ba sites are not same and is

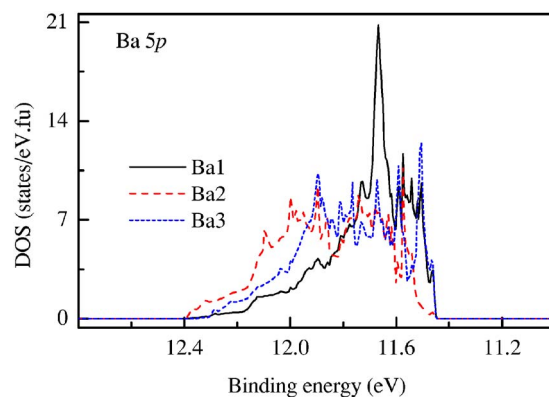


FIG. 9. (Color online) Calculated Ba $5p$ DOS corresponding to three nonequivalent Ba atoms present in the monoclinic structure. The results show that Ba2 contributions appear at higher binding energies compared to that in other Ba atoms.

consistent with the experimental observation of two nonequivalent features corresponding to each Ba core level photoemissions. Such relative shift of the DOS corresponding to different nonequivalent Ir atoms is not observed in these calculations (e.g., see Fig. 3 for the t_{2g} bands corresponding to four nonequivalent Ir sites).

IV. CONCLUSIONS

In summary, we investigate the detailed electronic structure of BaIrO₃ in this study using full potential linearized augmented plane wave method within the local spin density approximations. The calculations for various magnetic configurations reveal lowest energy for the ferromagnetic ground state and is consistent with the experimental observations. The ferromagnetic ground state energy calculated using room temperature crystal structure is found to be 3.25 meV lower than the nonmagnetic ground state. No exchange splitting is observed in any of the electronic states involved in forming the valence band. The small magnetic moment appears due to unequal population of the different Ir $5d$ spin density of states.

Comparison with the photoemission spectra suggests that electron-electron Coulomb repulsion may not be the key factor in determining the electronic structure as expected for the highly extended nature of the $5d$ electronic states. The discrepancy between the experimental spectra and the calculated results appears to arise primarily from the intrinsic nonstoichiometry of BaIrO₃ leading to electron doping into the t_{2g} band. The calculations for Ba $5p$ core levels exhibit the signature of multiple nonequivalent Ba sites in the room temperature structure as observed experimentally. Thus, these results provide a significant advance towards understanding the electronic properties of the exotic compound, BaIrO₃.

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