The Ir$^{4+}$ substitution dependence of electric polarization as a probe of magnetic phase stability in multiferroic MnWO$_4$

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ABSTRACT

Hubnerite MnWO$_4$ is a highly frustrated magnetic compound that has been known for its multiferroic properties. The intrinsic connection of ferroelectric polarization and magnetically frustrated structure allows an opportunity to probe the stability of magnetic structures against perturbations by means of measuring ferroelectric polarization. In this work, we investigate the ferroelectric polarization of Mn$_{1-x}$Ir$_x$WO$_4$ to probe the stability of the low-temperature ($T$) collinear antiferromagnetic (AF1) phase against the Ir substitution, considering the strong spin-orbital coupling of Ir$^{4+}$ that would enhance the single-ion anisotropy, on the one hand, and would favor the noncollinear spin alignment, on the other hand. Different from Mn$_{1-x}$Ru$_x$WO$_4$, it is suggested that the AF1 phase is only partially suppressed by the Ir substitution, allowing the emergence of the noncollinear antiferromagnetic (AF2) phase in coexistence with the collinear AF1 phase. Proper Ir substitution may promote both the magnetocrystalline anisotropy and the Dzyaloshinskii-Moriya interaction, thus making the modulation of the magnetic structure more complicated.

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I. INTRODUCTION

Magnetic frustration represents a phenomenon in condensed matter where magnetic moments can be aligned in more than one configuration due to geometrical reasons or multifold competing interactions. Consequently, multiple degenerate ground states would be allowed. This also implies the absence of high-temperature ($T$) magnetic ordering and the appearance of emergent phenomena nonavailable in those well-ordered magnetic systems. Examples include spin liquids, glass states, and multiferroicity among many others. Frustrated magnetism has been a long-standing subject in condensed matter physics.

For the latter case, a ferroelectric (FE) polarization ($P$) may be generated in a multiferroic with proper spin spiral structure, while spin spiral as one of the noncollinear spin structures is certainly a typical frustrated configuration, noting that magnetism-induced ferroelectricity in type-II multiferroics has been a hot topic in recent years. It is understood that frustrated structures raise challenges to direct experimental probing by means of neutron scattering or other techniques and, in particular, for those noncollinear spin structures whose deconvolution is not easy. Since a noncollinear spin structure can be ferroelectric in many cases, an electrical probing of the magnetic structure and its transition in multiferroics can be a good complementary to those standard methods, e.g., neutron scattering.

A noncollinear spin structure (e.g., spin spiral here) usually accompanies the existence of nonzero spin-orbit (SO) coupling. It is known that the SO coupling provides a relativistic modification to the exchanges via the Dzyaloshinskii-Moriya (DM) interaction, which is proportional to the cross-product term ($S_i \times S_j$), where $S_i$ and $S_j$ are the neighboring spin-pair. This implies that SO coupling is associated with the noncollinear spin structure. On
the other hand, the consequence of SO coupling is multifaceted, and it is also known that SO coupling is responsible for the single-ion anisotropy or magnetocrystalline anisotropy. This anisotropy, which is usually twofold degenerate, favors the collinear spin structure for most lattice symmetries such as tetragonal, orthorhombic, and monoclinic lattices. Briefly, the SO coupling may benefit simultaneously to the formation of collinear and noncollinear structures. Here, the key point is that such a weak SO coupling may play a core role in frustrated systems.

In proceeding, one may take the hubnerite compound MnWO$_4$ (MWO) as an example, based on two aspects of consideration. On one aspect, MWO is a multiferroic with magnetism-induced ferroelectricity.$^{15,16}$ On the other hand, MWO is a frustrated magnet,$^{17}$ and earlier work suggested that more than 12-fold exchanges, none of which is negligible, drive a complicated sequence of phase transitions from a collinear antiferromagnetic (AFM) order to noncollinear one, and then to another collinear one, in a narrow $T$-window of $\sim$6 K.$^{18}$ This implies that an electrical probing can be advantageous. In fact, the magnetic structure can be easily modulated by intrinsic or extrinsic perturbations that have been extensively investigated.$^{19-30}$

An electric field driven magnetic variation in MWO was demonstrated experimentally.$^{31}$ A modulation via tuning the SO coupling was also tested by means of substitution of Mn ions by 4d Ru ions.$^{30}$ MWO has a relatively simple lattice structure,$^{15}$ with two basic units, the distorted octahedral MnO$_6$ and WO$_6$, which stack into infinite zigzag chains along the $c$-axis, as shown in Fig. 1(a). Consequently, the two zigzag chains constitute the monoclinic structure with the $P2_1/c$ space group. The proper size-match between Mn$^{2+}$ and W$^{6+}$ ions makes the comparable nearest-neighbor interaction ($J_1$), the next-nearest-neighbor one ($J_2$), and more up to the 12th-order neighbor interaction ($J_{12}$), accounting for the strong frustration in MWO.$^{15,19}$

Summarizing the data from the literature, one can see that MWO remains paramagnetic above $T_{N3} \sim 13.5$ K and transits into the AF3 phase at $T_{N3}$. This AF3 phase, collinear and sinusoidal and thus nonferroelectric, survives only in a window of 1.0 K and is replaced by the AF2 phase at $T_{N2} \sim 12.5$ K. This AF2 phase, noncollinear and ferroelectric (FE) due to the SO coupling, survives only down $T_{N1} \sim 7.5$ K, below which another collinear and non-FE AF1 phase takes over. For an illustration, plots in Figs. 1(b) and 1(c) of

![Figure 1](https://example.com/figure1.png)
the magnetic structures of the AF1 and AF2 phases are guide for eyes. The AF3 and AF1 phases, both in collinear alignment, are different. The AF1 phase has its spins alternating along the a-axis. The AF2 phase has its spiral wave-vector $q_2 \sim (-0.214, 0.5, 0.457)$, as shown in Figs. 1(c) and 1(d), allowing a generation of FE polarization $P$ associated with the SO coupling.32 The spatial geometry of the spins, polarization, and zigzag MnO$_6$ chain is drawn in Fig. 1(e).

Although the ground state is indeed the collinear AF1 phase (below $T_{N1}$), these phases are actually similar in energy due to the high-degree frustration. The energy difference between the AF1 and AF2 phases should be on the order of magnitude of $\sim 1.0$ meV, as estimated from the values of $T_{N1}$, and the energy gap between AF2 and AF3 phases is similar. Such a small gap can be easily covered by thermal fluctuations of $\sim 10$ K or applying small electric/magnetic fields.19–30 One can immediately see that the stability of the AF2 phase can be enhanced over the AF1 phase by slightly increasing the SO coupling and thus increasing the DM interaction term. An inclusion of this term certainly favors the spin noncollinearity. This idea was proposed in our earlier work on the Ru$^{4+}$ substitution of Mn$^{2+}$ in MWO, considering that the SO coupling in 4d oxides is somehow $\sim 1.0$ meV.30 Experimental data confirmed that the Ru substitution does favor the AF2 phase in replacement of the AF1 phase below $T_{N2}$ and it seems that the low-$T$ region below $T_{N1}$ is fully occupied by the AF2 phase in (Mn$_{0.8}$Ru$_{0.2}$)WO$_4$.

Nevertheless, the SO coupling can also promote magnetocrystalline anisotropy via the orbital-lattice field coupling.32 If the anisotropy is strong, the spin structure would favor the collinear alignment. Therefore, the strong SO coupling may not necessarily stabilize the noncollinear structure, hinting that for MWO, the low-$T$ AF1 phase may not necessarily be replaced by the noncollinear AF2 phase even if the SO coupling can be enhanced. Along this line, one easily thinks of the 5d Ir substitution of Mn in MWO, because 5d ions are expected to have stronger SO coupling than 4d ions. One would observe a different consequence if magnetocrystalline anisotropy can be remarkably enhanced by the Ir substitution.

In this work, our major motivation is to check this scenario, which is yet to be performed.31–33 We shall investigate the multiferroic evolution of MWO by partially substituting 3d Mn$^{2+}$ by 5d Ir$^{4+}$ at low levels, addressing electric polarization as an indirect probe of the magnetic phases while the structural and magnetic behaviors will be characterized too. Due to the stronger SO coupling of 5d Ir$^{4+}$ than 4d Ru$^{4+}$, it is expected that the replacement of the collinear AF1 ground state by noncollinear AF2 phase should appear at a substitution level lower than that would be favored. Nevertheless, our results reveal that, contrary to this prediction, the Ir$^{4+}$ substitution of Mn$^{2+}$ up to the level $x=0.10$ does favor the AF2 phase but cannot suppress completely the AF1 phase. Instead, a coexistence of the AF2 and AF1 phases is observed, noting that the substitution of Mn$^{2+}$ by Ru$^{4+}$ at level $x=0.10$ is sufficient to remove the whole AF1 phase although Ru$^{4+}$ and Ir$^{4+}$ have almost the same ionic radius.30 It seems that the Ir$^{4+}$ substitution may induce stronger magnetocrystalline anisotropy than the Ru$^{4+}$ substitution, although the DM interaction may be enhanced too. Such a competition should be responsible for the less variations of the AF1 phase stability against the AF2 phase.

II. EXPERIMENTAL DETAILS

MWO accommodates both Mn$^{2+}$ and W$^{6+}$ ions. The ionic radius values for Mn$^{2+}$, W$^{6+}$, and Ir$^{4+}$ are $\sim 0.80$, 0.62, and 0.077 nm, respectively, noting that Ru$^{4+}$ has its ionic radius of 0.076 nm. The one-to-one substitution of Mn by Ir would induce no serious lattice distortion since Mn$^{2+}$ and Ir$^{4+}$ have similar ionic radius, but the charge neutrality cannot be maintained. Since we focus on the low-level substitution, the charge neutrality would be of first priority. Our samples are a set of Mn$_{1-x}$Ir$_x$WO$_4$ (MWO) where one Ir$^{4+}$ ion would occupy one Mn$^{2+}$ site but also leave one Mn$^{2+}$ site empty. This composition also allows us to compare our results with those of Mn$_{1-x}$Ir$_x$WO$_4$ (MRWO).30 The existence of empty Mn sites implies that the substitution level cannot be high.

The polycrystalline MIRO samples were prepared using the conventional solid-state sintering method, and the sintering procedure was optimized by monitoring the samples’ density. The high-purity powder WO$_3$, MnO, and IrO$_2$ oxides were weighted in the stoichiometric ratios and sufficiently mixed for more than 24 h, followed by mixture grinding for 2.0 h plus annealing for 12 h at 600 °C in air. This process is cycled for several times and eventually the as-prepared powder was compressed into pellets of 20 mm in diameter for subsequent annealing for 20 h at 900 °C in air. The high-quality ceramic samples were obtained after the spontaneous cooling down to room temperature.

The crystallinity of the as-prepared pellets was measured using the θ–2θ X-ray diffraction (XRD, Bruker Co.) with Cu $K_\alpha$ radiation at the step mode of 0.01°. The θ–2θ data are used for evaluating the lattice constants, including the monoclinic lattice constants ($a$, $b$, $c$, $β$). The microstructures were imaged using the scanning electron microscopy (SEM, Quanta 200, FEI Company) with high-resolution EDEX mapping of chemical compositions. The X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe, ULVAC-PHI, Inc.) for valence states of Mn/W/Ir ions was performed, and particular attention was paid to the dependences of these valence states on $x$.

On the other hand, a set of characterizations on the specific heat, dc magnetization, dielectric constant, and ferroelectric polarization of these samples were carried out. The details of these characterizations were described in an earlier work, and only a brief presentation is given here. The specific heat $C_p$ was measured using the Physical Properties Measurement System (PPMS, Quantum Design Inc.) in the standard procedure. The $dc$ magnetization $M$ under the zero-field cooled (ZFC) and field cooled (FC) modes, starting from room temperature, was probed using the Quantum Design Superconducting Quantum Interference Device (SQUID), respectively, with the measuring field of 1000 Oe.

For electrical measurements, the samples were cut into disk-like plates with 0.5 mm thickness and 10.0 mm diameter. The Au electrodes were deposited on the top and bottom surfaces of the plate-like samples using the sputtering method. The ferroelectric polarization $P$ was evaluated from the standard pyroelectric current method, while the standard ferroelectric testers cannot be used to probe such small remnant polarization. Each sample under measurement was electrically polarized under a poling field as high as 10 kV/cm during the cooling sequence down to the lowest temperature $T_{end}=2$ K. Then, the sample was short-circuited at this temperature for 30 min...
and submitted to a slow warming process at a fixed heating rate (2, 4, or 6 K/min, respectively). During heating, the current released from the sample was collected using the Keithley 6514A electrometer connected to the PPMS, and this current should be the pyroelectric current $I_p$, as demonstrated in earlier reports.30

III. RESULTS AND DISCUSSION

A. Microstructural characterizations

We first check the microstructure of the as-prepared samples. The substitution up to $x = 0.10$ does not change the sintered microstructure, and the representative SEM image on sample $x = 0.02$ is shown in Fig. 2. It is seen that the grains are roughly uniform in size ($\sim 5.0 \mu m$) with a dense microstructure. Since Ir is not an easily volatile element, inclusion of IrO$_2$ into the sample does not change much the sintering reaction.

We pay attention to the crystallinity of these samples, and the XRD $\theta$–$2\theta$ spectra are plotted in Fig. 3(a). Here, the substitution of two Mn$^{2+}$ ions by one Ir$^{4+}$ ion is designed for the charge neutrality consideration, thus leaving a Mn vacancy, which is certainly not preferred. However, for the low-level cases, it seems that the lattice structure remains noncollapsed until $x > 0.10$, while no more substitution is possible since an identifiable impurity appears as $x > 0.08$. To check the impurity and also ensure the effective substitution of Mn by Ir, we zoom-in the range from $2\theta = 27^\circ$ to $29^\circ$ in which tiny impurities can be detected, as indicated by the arrows in Fig. 3(b), and these impurities can be properly assigned as IrO$_2$. These impurities seem irrelevant with those concerned properties, and thus we no longer discuss them.

The Ir substitution results in the shifting of reflections toward the high angle, as shown in Fig. 3(c) by taking the (002) reflection as an example. This reflection does not show peak-splitting, suggesting that the monoclinic lattice symmetry with the $P2/c$ group remains unchanged upon the Ir substitution, further confirmed by the high-reliability Rietveld refinement of the XRD data presented in Fig. 3(d) on sample $x = 0.02$ as an example. The peak shifting is understandable because the Ir$^{4+}$ ion is slightly smaller than the Mn$^{2+}$ ion, on the one hand, and each Ir substitution leaves one Mn vacancy contributing to the lattice contraction too, on the other hand. The lattice parameters ($a$, $b$, $c$, angle $\beta$, unit cell volume $V$, and ratio $a/c$) for the monoclinic $P2/c$ lattice, evaluated from the Rietveld refinement of the XRD data, are presented as functions of $x$ in Fig. 4. For a comparison, the data for MRWO samples are also inserted, as taken from Ref. 30. Here, it should be mentioned that the data on MWO are from two samples and the refined data between them are slightly different.

Several issues regarding the lattice distortion, as revealed in Fig. 4, can be highlighted. First, the substitution leads to lattice shrinking along the $a$-, $b$-, and $c$-axis simultaneously, but the shrinking is weaker than the Ru substitution, as shown in Figs. 4(a)–4(c).

FIG. 2. A scanning electron microscope image of the microstructure of MIWO ceramic sample $x = 0.02$.  

FIG. 3. The XRD $\theta$–$2\theta$ spectra for a set of MIWO samples. (a) The spectra over the broad $2\theta$ range and the arrows indicate the tiny impurity phase (IrO$_2$). A zoom-in set within $2\theta = 27^\circ$–$29^\circ$ for the impurity phase (b) and the (002) reflection (c). (d) The Rietveld refined spectrum for sample $x = 0.02$. The arrowhead in this figure indicates the tiny impurity.
Second, the $x$-dependence of monoclinic angle $\beta$ for the two types of systems shows no big difference and the $x$-dependences are also weak, as shown in Fig. 4(d), suggesting that the lattice shrinking upon the Ir and Ru substitutions are spatially isotropic. Third, the lattice unit cell volume $V$ decreases roughly in a linear way as a function of $x$ but the volume contraction in MIWO is weaker than that in MRWO, as shown in Fig. 4(e). This linear relation, consistent with Vegard’s law, illustrates that the Ir ion does take the Mn site instead of other sites.

Briefly, the Ir substitution makes the lattice slightly shrink. In comparison with MRWO, MIWO has weaker lattice shrinking due to the fact that Ru$^{4+}$ is slightly smaller than Ir$^{4+}$. The lattice distortion of MIWO, as seen from the $a/c$ ratio which is closer to one, is also weaker than that in MRWO. These weak effects likely imply that the magnetic structure of MWO may not be seriously modulated by the Ir substitution with respect to the Ru substitution, to be further checked below by other characterizations.

As a complementary, it is also critical to confirm the valence states of Mn and Ir in MIWO. The XPS spectra for Mn$^{2+}$ and Ir$^{4+}$ in these samples are plotted in Figs. 5(a) and 5(c), and the data fitting using the standard Gaussian method are shown in Figs. 5(b) and 5(d). It is revealed that all the samples show the stable Mn$^{2+}$ and Ir$^{4+}$ valence states without identifiable variation, hinting that the charge neutrality in these samples is maintained although one Mn$^{2+}$ vacancy is generated upon each Ir$^{4+}$ occupation of one Mn$^{2+}$ site.

In fact, the Ir (or Ru) substitution in MWO represents an unusual consideration due to the appearance of Mn$^{2+}$ vacancies. A high-level substitution would certainly destroy the present lattice and we thus only focus on the low-level substitution up to $x = 0.10$. It is fortunate that the lattice symmetry can be maintained in these cases, allowing us the opportunity to check the multiferroic behavior.

**B. Specific heat and magnetism**

Now, we investigate the magnetic phase transitions and the measured specific heat normalized by $T$, $C_p/T$, and $dc$ magnetizations under the ZFC and FC modes, $M_{ZFC}$ and $M_{FC}$, plotted in Figs. 6(a)–6(f), respectively. First, the $C_p/T$ data on sample $x = 0$, as shown in Fig. 6(a), present three consecutive AFM transitions at $T_{N3}$, $T_{N2}$, and $T_{N1}$, respectively, identified by the kink ($T_{N3}$), peak ($T_{N2}$), and shoulder ($T_{N1}$). Second, the $M$–$T$ curves under both the ZFC and FC modes show weak anomalies at $T_{N3}$ and $T_{N1}$ while no clear anomaly at $T_{N2}$ can be identified.

Both the $C_p/T$–$T$ and $M$–$T$ curves are $x$-dependent, as shown in Figs. 6(b)–6(f). We highlight the major features. First, the anomalies of the $C_p/T$–$T$ curves at $T_{N3}$ and $T_{N2}$ remain clear and sharp, but the anomaly at $T_{N1}$ is seriously smeared out and becomes very faint at $x > 0.06$, indicating the gradual suppression of the AF2–AF1 transition with increasing $x$. The evaluated $T_{N3}$, $T_{N2}$, and $T_{N1}$ as a function of $x$ are plotted in Fig. 6(g), where $T_{N1}(x)$ between $x = 0.06$ and 0.10 is plotted as a dashed line because it is hard to define from the data. Second, the $C_p/T$–$T$ curve downshifts gradually with increasing $x$, obviously owing to the weaker moment of Ir$^{4+}$ than that of Mn$^{2+}$ and the appearance of Mn$^{2+}$ vacancies. Third, and similarly, the ZFC and FC curves $M_{ZFC}(T)$ and $M_{FC}(T)$ all shift downward with increasing $x$, as confirmed by the maximal
$M_{\text{max}}$, from the $M$–$T$ curve [marked in Fig. 6(c)], as a function of $x$, plotted in Fig. 6(h). Fourth, the Ir substitution gradually fills in the difference between the ZFC and FC curves that is remarkable for $x = 0$, suggesting that the Ir substitution partially suppresses the magnetic frustration.

Qualitatively, the above data suggest that the Ir substitution may promote the AF2 phase stability over the AF1 phase, and thus partially suppress the AF2–AF1 transition, although it is certainly insufficient to conclude these effects only from the conventional magnetic measurements. While this tendency can be partially ascribed to the fact that the Ir substitution would enhance the SO coupling and thus favor the AF2 phase, which is noncollinear, however, whether the AF1 phase below $T_{N1}$ would be completely replaced by the AF2 phase or not remains to be an issue, and again one cannot identify this issue only from the specific heat and magnetic data. We then consult to the electric polarization data as shown below, although these data can only provide indirect evidence either.

C. Ferroelectric polarization

These MIWO samples are also submitted to pyroelectric current measurements in the standard mode, and the results on several samples are summarized in Fig. 7. An overall comparison of pyroelectric current $I_p$ and polarization $P$ data for MIWO and MRWO suggests a substantial difference between them. For MRWO, the Ru substitution up to $x = 0.1$ is sufficient to enable the whole $T$ region below $T_{N2}$ to be ferroelectric with nonzero electric polarization, evidenced with the continuously increasing polarization $P$ with decreasing $T$. It implies that the region below $T_{N2}$ may be occupied by the AF2 phase due to the Ru substitution. For MIWO, one indeed observes the appearance of nonzero electric polarization
below $T_{N1}$, but its magnitude is small, most likely suggesting that the low-$T$ non-FE AF1 phase is only partially instead fully taken over by the AF2 phase. We discuss the data in more detail.

We first check possible other sources to the measured $I_p$ besides the pyroelectric current, and the results on pure MW sample are shown in Fig. 7(a) where the $I_p$-$T$ curves at three different warming rates (2, 4, 6 K/min) are plotted. Each curve exhibits a positive peak around $\sim 12.5$ K ($T_{N2}$) and a negative peak around $\sim 7.5$ K ($T_{N1}$). These three curves have the same positive and negative peak positions, confirming that the measured current is indeed from the pyroelectric effect. It is also seen that the underpeak areas of the two peaks (denoted as $A_+$ and $A_-$, respectively) meet $A_+$ to $-A_-$, suggesting that the low-$T$ region below $T_{N1}$ is indeed occupied with the non-FE phase (i.e., collinear AF1 phase).

Second, we check the influence of Ir substitution. The measured $I_p(T)$ and $P(T)$ curves at all the warming rate of 2 K/min are shown in Figs. 7(b)–7(i). Both $A_+(x)$ and $A_-(x)$ first increase and then decrease, but their variations are different quantitatively resulting in the in-balance between $A_+$ and $A_-$ in magnitude. Consequently, the evaluated $P(T)$ data show that the polarization of the AF2 phase is enhanced first and then reduced with increasing $x$. The maximal $P$ for each $P(T)$ curve, $P_{\text{max}}$, as a function of $x$, is plotted in Fig. 7(j) where $P_{\text{max}}$ reaches $20 \mu$C/cm$^2$ at $x = 0.04$, beyond which $P_{\text{max}}(x)$ begins to fall.

Nevertheless, it is surprising to observe that the Ir substitution, supposed to induce stronger SO coupling than the Ru substitution, does not follow the routine of the Ru substitution. With increasing $x$, we do observe the enhanced polarization in the AF2 phase region, and at the same time, nonzero polarization appears below $T_{N1}$. However, this tendency does not continue. As $x > 0.06$, the polarization in the AF2 phase region seems to fall gradually, as shown in Fig. 7(j) by $P_{\text{max}}$. However, until $x = 0.1$, one does not see a rapid increase in the polarization below $T_{N1}$. This implies that the substitution cannot completely suppress the AF1 phase below $T_{N1}$, different from MRW where a gradual and eventually complete suppression of the AF1 phase below $T_{N1}$ is observed. It should be mentioned that the low-$T$ polarization, e.g., $P(T = 2$ K), as plotted in Fig. 7(j), where $P(T = 2$ K) does increase monotonously with increasing $x$ up to 0.10.

Here, it should be mentioned again that the above discussion on the transition between the AF1 and AF2 phases against the Ir substitution relies on the variation of electric polarization instead of directly probing the magnetic phases themselves. To confirm this discussion, a future neutron scattering experiment is certainly needed. Given this fact, it would be informative to compare the ferroelectric data for MW and MRW, as shown in Fig. 8 for $I_p(T)$ and $P(T)$ curves for $x = 0.10$, and $P_{\text{max}}$ and $P(2$ K) as a function of $x$. It is seen clearly from Fig. 8(a) that MW has until the positive...
and negative peaks around $T_{N2}$ and $T_{N1}$ respectively, for MRWO the current over the whole $T$-range is always positive, resulting in very big gap in polarization between MIWO and MRWO, as shown in Fig. 8(b). This big gap can be seen in Figs. 8(c) and 8(d) if one can plot the maximal value of polarization $P(T)$, $P_{\text{max}}$, and $P(T=2\text{ K})$.

D. Discussion

To this stage, all the presented results seem to suggest that the 5d Ir substitution, in comparison with the 4d Ru substitution, on the one hand, enhances the stability of the noncollinear AF2 phase over the non-FE AF1 phase. Consequently, the AF2 phase invades into the original AF1 phase region ($T < T_{N2}$). On the other hand, different from the case of MRWO, the AF1 phase is not completely suppressed by the Ir substitution, indirectly evidenced by the small polarization in that region. One observes the complete disappearance of the collinear AF1 phase in MRWO as $x=0.10$, but this does not happen for MIWO as $x=0.10$, although the Ir$^{4+}$ ions offer much stronger SO coupling than the Ru$^{4+}$ ions.

Earlier investigations on the substitution effects in MWO, including Zn, Mg, Fe, Co, Ni, Cu, and Ru, suggested that three physical ingredients should be considered:

1. The ionic size effect: A substitution using ion of different size would induce additional lattice distortion, which would change the exchanges. This effect has not yet been well clarified since the substitution of larger Zn and Mg ions and smaller Fe, Co, Ru, and Ni ions does not contribute to a clear conclusion. The reason lies in that the exchanges in MWO are 12-folded and a well-defined modulation of these exchanges becomes nearly impossible.

2. The magnetocrystalline anisotropy: This effect was claimed in Fe-substituted MWO in comparison with the Co substituted systems. A strong anisotropy certainly stabilizes the collinear AF1 phase against the noncollinear AF2 phase.

3. The DM interaction: This effect is believed to favor the noncollinearity of spin alignment, and thus the AF2 phase.

It is seen that the latter two ingredients are tightly related to the SO coupling. When the strong SO coupling promotes the DM interaction rather than the magnetocrystalline anisotropy, one will see enhanced stability of the noncollinear AF2 phase over the collinear AF1 phase. The AF1 phase would be enhanced if the magnetocrystalline anisotropy is promoted more significantly.

In the present case, it is suggested that a proper Ir substitution level promotes the DM interaction, on the one hand, thus promoting the stability of AF2 phase. On the other hand, the magnetocrystalline anisotropy becomes stronger too owing to the substitution, thus enhancing the stability of the AF1 phase. The two effects are most likely comparable, and their competition results in the coexistence of the AF1 and AF2 phases below TN1, while the ferroelectricity in the AF2 phase is enhanced. For MRWO, it seems that the Ru substitution does not make the magnetocrystalline anisotropy very different, and thus the AF1 phase is completely suppressed by the AF2 phase.

This competing scenario works only if the two phases are very close to each other in energy, which is exactly the character of MWO as a highly frustrated system. An energy modulation of $\sim 1.0\text{ meV}$ is sufficient to reverse the stability order of the AF1 and AF2 phases. It is the reason why we believe that MWO is a nice platform for studying magnetic frustration, while the ferroelectric polarization plays as a sensitive indicator of such frustration.

IV. CONCLUSION

In conclusion, we have characterized the structural, magnetic, and ferroelectric behaviors of a series of Ir-substituted MnWO4 ceramics in order to investigate the role of the spin-orbital coupling in modulating the frustrated magnetic structure by probing the electric polarization. Based on the assumption of one-to-one correspondence between the electric polarization and noncollinear AF2 phase, it is revealed that the Ir substitution in MIWO, different from the Ru-substituted MRWO, leads to the enhanced stability of the noncollinear AF2 phase to compete with the collinear AF1 phase, thus resulting in the coexistence of AF2 and AF1 phases as the ground state. It is suggested that the Ir substitution introduces the strong spin-orbital coupling, benefiting both the Dzyaloshinskii-Moriya (DM) interaction that favors the noncollinear AF2 phase and magnetocrystalline anisotropy that favors the collinear AF1 phase. Such a competing multifold effect, remarkable in the Ir-substituted MIWO, seems to be weak in MRWO where the collinear AF1 phase is completely suppressed by the noncollinear AF2 phase. It is also shown that MWO as a highly frustrated system is a good platform for investigating the sensitive modulation of the magnetic structure by intrinsic and extrinsic perturbations.

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