Contrasted Sn Substitution effects on Dirac line node semimetals SrIrO$_3$ and CaIrO$_3$

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Perovskite-type iridates SrIrO$_3$ and CaIrO$_3$ are a Dirac line node semimetal protected by crystalline symmetry, providing an interesting playground to investigate electron correlation effects on topological semimetals. The effect of Sn doping was examined by growing SrIr$_{1-x}$Sn$_x$O$_3$ and CaIr$_{1-x}$Sn$_x$O$_3$ thin films epitaxially on SrTiO$_3$(001) substrate using pulsed laser deposition. Upon doping, the semimetallic ground state switches into an insulator. As temperature is lowered, the resistivity, $\rho(T)$, of SrIr$_{1-x}$Sn$_x$O$_3$ above a critical doping level ($x_e \sim 0.1$) shows a well-defined transition from the semimetal to a weakly ferromagnetic insulator at $T = T_c$. In contrast, the $\rho(T)$ of CaIr$_{1-x}$Sn$_x$O$_3$ with increasing $x$ shows a rapid increase of magnitude but does not show clear signature of metal-insulator transition in the temperature dependence. We argue that the contrasted behavior of the two closely related iridates reflects the interplay between the effects of electron correlation and disorder enhanced by Sn doping.

Recently 5$d$ iridium oxides with perovskite-related structures have been explored extensively as a mine for exotic quantum phases, partly because of an interplay of strong spin-orbit interaction and electron correlation of the 5$d$ electrons$^4$. The strong spin-orbit coupling of $\sim 0.4$ eV for 5$d$ electrons, which is larger than the typical crystal field splitting of $\lesssim 0.1$ eV within $t_2g$ bands with five $d$ electrons into upper half-filled $J_{\text{eff}} = 1/2$ band and lower completely filled $J_{\text{eff}} = 3/2$ bands. In the two-dimensional layered perovskite Sr$_2$IrO$_4$, a modest on-site Coulomb $U$ of $\sim 2$ eV$^2$ brings the system to a spin-orbital Mott state with the $J_{\text{eff}} = 1/2$ moments$^{15}$. Such a spin-orbital Mott state has been identified in many two-dimensional layered iridium oxides, where exotic magnetism of $J_{\text{eff}} = 1/2$, particularly the Kitaev spin liquid state, has been explored$^{15}$. In the three-dimensional perovskites SrIrO$_3$ and CaIrO$_3$, in contrast, the $J_{\text{eff}} = 1/2$ band remains metallic marginally due to the increased band width$^3$ and forms a "correlated" topological semimetal.

SrIrO$_3$ and CaIrO$_3$ have a GdFeO$_3$-type distorted perovskite structure where the rotation and the buckling of IrO$_6$ octahedra give rise to a unit cell with the size of $\sqrt{2}a_c \times \sqrt{2}a_c \times 2a_c$ ($a_c$ is the lattice constant of the original cubic lattice) as shown in Fig. 1(a)$^{15}$. The results of band calculations indicate that SrIrO$_3$ and CaIrO$_3$ have Dirac electron bands with a line of nodes and heavy hole bands at the Fermi level$^1$. The line nodes of Dirac bands are protected by the time-reversal symmetry and the gliding symmetry of the GdFeO$_3$-type perovskite structure$^{10}$. The existence of Dirac electrons has been supported by experiments, for example, by ARPES$^{11,12}$ and transport measurements$^{13,14}$. Their proximity to the spin-orbital Mott state and moderately strong electron correlations are evident, for example, from the observation of a transition from a Dirac semimetal to a magnetic insulator by decreasing the number of SrIrO$_3$ layers in (SrIrO$_3$)$_{10}$(SrTiO$_3$)$_1$ superlattice structures$^{15}$. The presence of an apparent correlation effect is a prominent feature of the two Ir perovskites when compared with many other topological semimetals which are only weakly correlated, and makes them an interesting arena to explore the effect of electron correlation in topological semimetals. As the ionic radius of Ca$^{2+}$ (1.34 Å) is smaller than that of Sr$^{2+}$ (1.44 Å$^{16}$, the lattice is more distorted in CaIrO$_3$ than in SrIrO$_3$, which reduces the band width of CaIrO$_3$ appreciably as compared with that of SrIrO$_3$. The effect of electron correlation should be larger in CaIrO$_3$ than SrIrO$_3$. Recently, it was shown that the strong electron correlation modifies the semimetallic band structures appreciably in the two three-dimensional iridium perovskites. The stronger electron correlation effects of CaIrO$_3$ bring its Fermi level closer to the Dirac node and therefore further reduces its density of electrons and holes when compared to SrIrO$_3$.$^{14}$

A transition from the Dirac semimetal to a magnetic insulator was also discovered in bulk polycrystalline SrIrO$_3$ by substituting Ir with Sn$^{12}$. As Sn ions are tetravalent like Ir ions in SrIrO$_3$, Sn doping does not change the valence of Ir ions and therefore reduces the hopping path of the Ir 5$d$ electrons in real space, and hence the effective width of $J_{\text{eff}} = 1/2$ band, as in the case of the superlattice structure. We note here that Sn doping should modify not only the effective band width, but also the degree of disorder. With this unique opportunity of controlling the electron correlations and disorder in mind, we synthesized epitaxial thin films of SrIr$_{1-x}$Sn$_x$O$_3$ and CaIr$_{1-x}$Sn$_x$O$_3$ and measured their resistivity to probe the effects of Sn doping. A transition from a semimetal to a (magnetic) insulator is observed in both SrIr$_{1-x}$Sn$_x$O$_3$ and

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Table I. The bulk lattice parameters of SrIrO$_3$ and CaIrO$_3$ and their matching to the cubic lattice parameter of SrTiO$_3$ ($a_{\text{STO}}$ = 3.905 Å).

| Material   | $a$ (Å)  | $b$ (Å)  | $c$ (Å)  | $a_{\text{pc}}$ (Å) | $c_{\text{pc}}$ (Å) |
|------------|---------|---------|---------|---------------------|---------------------|
| SrIrO$_3$  | 0.597(1) | 0.581(1) | 0.752(2) | +1.2 %              | -0.7 %              |
| CaIrO$_3$  | 0.535(5) | 0.613(4) | 0.762(4) | -0.6 %              | -1.6 %              |

The results of 2θ-θ scans of XRD indicate that all the grown SrIr$_{1-x}$Sn$_x$O$_3$ and CaIr$_{1-x}$Sn$_x$O$_3$ films crystallize in the perovskite structure without any trace of impurity phase within the given resolution (Fig. 1b). The full width at half maximum of the rocking curve is typically as narrow as 0.1° at the pseudo-cubic (001) peak and the Laue oscillations around the Bragg peaks are clearly observed. Reciprocal space mapping (RSM) measurements reveal that the in-plane lattice of the films is locked to that of the SrTiO$_3$ substrate (Figs. 1d, d). Those observations clearly demonstrate the epitaxial growth and high crystallinity of the grown films. The out-of-plane lattice constant of the CaIr$_{1-x}$Sn$_x$O$_3$ films as a function of Sn content $x$, as an average, increases almost 0.7 % from $x = 0$ to $x = 0.2$ which should reflect the larger ionic radius of Sn$^{4+}$. (0.690 Å) than that of Ir$^{4+}$ (0.625 Å)24 (Fig. 1b).

The film orientation was identified by RSM measurements of XRD and transition electron microscopy (Figs. 1c–c). We will describe the lattice orientation of films by the pseudocubic unit cell in this paper using lattice parameters $a_{\text{pc}} = \sqrt{a^2 + b^2 + c^2}$ and $c_{\text{pc}} = c/2$, where $a$, $b$, and $c$ denote the orthorhombic unit cell parameters of the distorted GdFeO$_3$ structure25. In case of SrIr$_{1-x}$Sn$_x$O$_3$, the $c_{\text{pc}}$ axis (|| orthorhombic $c$) lies within the substrate plane independent of Sn doping (Fig. 1c). This is natural because $c_{\text{pc}}$ is closer to that of SrTiO$_3$ substrate than $a_{\text{pc}}$ (See Table I). In contrast, $a_{\text{pc}}$ is closer to that of SrTiO$_3$ in CaIrO$_3$. The $c_{\text{pc}}$ axis (|| orthorhombic $c$) therefore aligns perpendicular to the substrate plane in the CaIrO$_3$ case (Fig. 1c). The inclusion of minority domains with the $c_{\text{pc}}$ axis lying within the substrate plane as in SrIr$_{1-x}$Sn$_x$O$_3$ are observed for the high Sn content films ($x \geq 0.1$) (Fig. 1g), which very likely reflects the expansion of $c_{\text{pc}}$ due to Sn doping and the resultant proximity to the lattice constant of SrTiO$_3$. As $a_{\text{pc}}$ is larger than $c_{\text{pc}}$, the orientation of $c_{\text{pc}}$ within the substrate plane can be controlled by introducing additional epitaxial strain using step edges of vicinal substrate26,27. We used a vicinal SrTiO$_3$(001) substrate with the substrate plane 0.4° rotated from (001) towards the [100] direction for the growth of SrIr$_{1-x}$Sn$_x$O$_3$. Because of the epitaxial strain from the side (100) plane at the step edges, the $c_{\text{pc}}$ (|| orthorhombic $c$) axis prefers to align along the edge, namely [010]$_{\text{STO}}$ direction (Fig. 1b). The RSM measurements clearly indicate that more than 95 % of domains have $c_{\text{pc}}$ axis parallel to the substrate [010] direction for the films on the vicinal substrates. Consistent with the in-plane preferred orientation, a
clear anisotropy of magnetization within the substrate plane was observed for \( x = 0.2 \) sample on the vicinal substrate as we describe below. Pronounced anisotropy in the magnetization was not observed in the resistivity \( \rho(T) \).

The resistivity \( \rho(T) \) measurements on the SrIr\(_{1-x}\)Sn\(_x\)O\(_3\) films indicate the presence of a metal-insulator transition accompanied by a weak ferromagnetism as in the bulk. The SrIrO\(_3\) \((x = 0)\) film shows only weakly temperature-dependent behavior of \( \rho(T) \), where a gradual increase followed by the temperature-independent behavior is observed with decreasing temperature (Fig. 3a). This agrees well with previous reports on SrIrO\(_3\) thin films\(^{15,23}\) and can be understood as a typical behavior of semimetals with extra conductivity at high temperature from thermally excited electrons and holes. With Sn doping (Fig. 3b), we do not observe an appreciable change of the \( \rho(T) \) up to the critical concentration \( x_c = 0.1 \). Above \( x_c = 0.1 \), however, the resistivity shows a transition from the semimetal to a weak insulator at a transition temperature \( T_c \) where we observe a kink in \( \rho(T) \) and a well-defined peak of the second derivative \( d^2\rho(T)/dT^2 \) (Fig. 3c). \( T_c \) increases rapidly with increasing \( x \). The metal-insulator transition below \( T_c \) is accompanied by a weak ferromagnetism with the easy axis parallel to the pseudo-cubic \( c_{pc} \) axis (\( l \) orthorhombic \( c \)), as seen in Fig. 3b. This behavior, the emergence of the magnetic insulator out of the Dirac node semimetal with Sn doping, can be summarized as a Sn content \( x-T \) phase diagram on top of contour map of the magnitude of \( \rho(T) \) (Fig. 3d). The stabilization of the magnetic insulator phase at low temperatures above \( x_c = 0.1 \) highly likely originates from the increase of the effective electron correlation. We argue that this is because of the reduced hopping of \( J_{eff} = 1/2 \) electrons by the introduction of Sn\(^{4+}\) without conduction electrons.

We find contrasting behavior in the Sn doping effect on \( \rho(T) \) in CaIr\(_{1-x}\)Sn\(_x\)O\(_3\) compared to SrIr\(_{1-x}\)Sn\(_x\)O\(_3\). For CaIrO\(_3\) \((x = 0)\) films (Fig. 3e), the overall behavior of \( \rho(T) \) is similar to that observed in SrIrO\(_3\). The magnitude of resistivity is, however, appreciably larger than that of SrIrO\(_3\). A weak increase of \( \rho(T) \), reminiscent of a weak localization and not observed in SrIrO\(_3\), is seen below 20 K, which is suggestive of the presence of appreciable disorder effect. It was discussed in the recent transport study on single crystal CaIrO\(_3\) that the Fermi level is much closer to the Dirac nodes and hence the electron and the hole densities are lower in CaIrO\(_3\) than SrIrO\(_3\) due to the enhanced correlation effect originating from the narrow band in CaIrO\(_3\). The effect of disorder should be enhanced in CaIrO\(_3\) because of the reduced carrier density, which may account for the larger resistivity and the weakly localized behavior.

With Sn substitution, \( \rho(T) \) gradually increases and shows a poorly insulating behavior with a power-law divergence (Figs. 3f, 3g). We do not see a well-defined semimetal-insulator transition as a function of \( T \) and \( x \) in contrast to the case for SrIrO\(_3\). We argue that the gradual transition from the Dirac node semimetal to a weak insulator is driven by the disorder and perhaps the inhomogeneity, and that the nature of semimetal-insulator transition is distinct from that of SrIrO\(_3\). It is natural that the effect of disorder associated with Sn-doping is much more profound in CaIrO\(_3\) than in SrIrO\(_3\) because of the lower carrier density and Fermi energy of CaIrO\(_3\). For CaIr\(_{0.8}\)Sn\(_{0.2}\)O\(_3\), a very weak ferromagnetic moment appears to emerge below \( T_{mag} \sim 100 \) K with \( B \) perpendicular to the film plane, smaller in magnitude and lower in temperature...
defined Dirac node semimetal to a magnetic insulator transition. While a well-aligned and perpendicular to the substrate plane respectively. In the case of SrIr$_1$-$x$Sn$_x$O$_3$, the $c$ axis can be aligned within the substrate plane using a vicinal substrate. While a well-defined Dirac node semimetal to a magnetic insulator transition. We argue that the contrast between SrIr$_1$-$x$Sn$_x$O$_3$ and CaIr$_1$-$x$Sn$_x$O$_3$ is a consequence of the interplay between the enhanced effective electron correlation and the disorder effect by Sn doping. While the correlation effect dominates in the case of SrIr$_1$-$x$Sn$_x$O$_3$, the disorder effect and the carrier localization dominate in the CaIr$_1$-$x$Sn$_x$O$_3$ due to the proximity of the Fermi level to the Dirac nodes and the resultant low carrier concentration. These results clearly indicate that Sn-doped iridium perovskite oxides are an interesting playground to study the effect of electron correlations and disorders in a topological semimetal.

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Strictly speaking, in both SrIrO$_3$ and CaIrO$_3$, cells of film layers on SrTiO$_3$(001) slightly deform from orthorhombic to monoclinic due to epitaxial strain.

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