# Superconductivity in Ru-doped CuIr<sub>2</sub>Te<sub>4</sub> telluride chalcogenide

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Here we report the effect of structural and superconductivity properties on Ru-doped CuIr<sub>2</sub>Te<sub>4</sub> telluride chalcogenide. X-ray diffraction results suggest that CuIr<sub>2-x</sub>Ru<sub>x</sub>Te<sub>4</sub> maintains the disordered trigonal structure with space group  $P\bar{3}m1$  (no. 164) for  $x \leq 0.3$ . The lattice constants, a and c, both decrease with increasing Ru content. Temperature-dependent resistivity, magnetic susceptibility, and specific heat measurements are performed to characterize the superconducting properties systematically. Our results suggest that the optimal doping level for superconductivity in  $\text{CuIr}_{2-x}\text{Ru}_x\text{Te}_4$  is x = 0.05, where  $T_c$  is 2.79 K with the Sommerfeld constant  $\gamma$  of 11.52 mJ mol<sup>-1</sup> K<sup>-2</sup>, and the specific heat anomaly at the superconducting transition,  $\Delta C/\gamma T_c$ , is approximately 1.51, which is slightly higher than the Bardeen-Cooper-Schrieffer value of 1.43 and demonstrates bulk superconductivity in our CuIr<sub>1.95</sub>Ru<sub>0.05</sub>Te<sub>4</sub> compound. The values of the lower { $H_{c1}(0)$ } and upper { $H_{c2}(0)$ } critical field calculated from isothermal magnetization {M(H)} and magnetotransport { $\rho(T, H)$ } measurements are 0.98 and 2.47 kOe, respectively, signifying that the compound is clearly a type-II superconductor. Finally, a "domelike" shape superconducting transition temperature ( $T_c$ ) vs x content phase diagram has been established. A low substitution (x = 0.03) of Ru for Ir leads to the disappearance of the charge density wave transition, while  $T_c$  rises and reaches a maximum value of 2.79 K at x = 0.05, followed by a decrease of  $T_c$  as x increases. This feature of the competition between the charge density wave we have established and the superconductivity could be caused by tuning the Fermi surface and density of states with Ru chemical doping.

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## I. INTRODUCTION

The group of  $AB_2X_4$  materials, with metallic A and B elements and X a chalcogen (O, S, Se, Te), has attracted much attention since it offers a versatile range of relevant physical properties. Generally speaking, the oxyspinels ( $AB_2O_4$ ) are semiconductors with antiferromagnetic interactions, whereas the sulfospinels exhibit a much richer physical property, such as metallic conduction, ferromagnetic, superconductivity, and semiconductivity as well as antiferromagnetic interactions and so on [1–8]. Especially, the copper chalcogenide (Cu $B_2X_4$ ) spinels have attracted remarkable attention due to their peculiar superconductivity and magnetism.

Copper chalcogenide, CuIr<sub>2</sub>S<sub>4</sub>, for example, exhibits a temperature-induced metal-insulator (M-I) transition at 226 K, which is highly possibly attributed to the dimerization between Ir ions and the Jahn-Teller effect [9–13]. However, the isostructural CuIr<sub>2</sub>Se<sub>4</sub> spinel remains metallic at ambient pressure, while above 4 GPa it exhibits semiconductive behavior in the temperature range of 7–300 K [9,14]. On the other hand, CuRh<sub>2</sub>S<sub>4</sub> and CuRh<sub>2</sub>Se<sub>4</sub> spinel are well known as superconductors with  $T_c = 4.35$  K and  $T_c = 3.50$  K, respectively [15–19]. Strikingly, copper chalcogenide spinel CuV<sub>2</sub>S<sub>4</sub> superconducts at 4.45–3.20 K and shows three charge density wave (CDW) states ( $T_{CDW1} = 55$  K,  $T_{CDW2} = 75$  K,  $T_{CDW3} = 90$  K) [20,21].

It is well known that chemical doping can efficiently tune the crystal and electronic structures of copper chalcogenide spinels, leading to the formation of novel physical properties. For example, the M-I transition was decreased with the increase of Se substitution for S at the X site of CuIr<sub>2</sub>S<sub>4</sub> or Rh substitution for Ir at the B site of CuIr<sub>2</sub>S<sub>4</sub> [22,23]. Besides, on Zn substitution for Cu in the Cu<sub>1-x</sub>Zn<sub>x</sub>Ir<sub>2</sub>S<sub>4</sub> solid solution, the M-I transition can be suppressed and superconductivity appears, with a maximum  $T_c$  of 3.4 K near x = 0.3[24]. Moreover, the superconductivity can be observed for Cu(Ir<sub>1-x</sub>Pt<sub>x</sub>)<sub>2</sub>Se<sub>4</sub> (0.1  $\leq x \leq 0.35$ ) with a maximum  $T_c =$ 1.76 K near x = 0.2 with Pt substitution for Ir in the CuIr<sub>2</sub>Se<sub>4</sub> solid solution [25].

Unlike  $CuB_2X_4$  sulfo or seleno compounds with cubic spinel structure,  $CuB_2X_4$  copper chalcogenide telluro compounds tend to possess lower-dimensional structure. Recently, some reports suggested that low dimensionality leads to special electronic structures and allows relatively strong fluctuations, which may enhance superconductivity, even though the charge density wave (CDW) sometime competes, especially in the quasi-one-dimensional case [26]. Intrigued by this issue, we recently have systematically studied the properties of CuIr<sub>2</sub>Te<sub>4</sub>, which adopts a disordered trigonal structure with

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space group  $P\bar{3}m1$  [27], and found the coexistence of the superconducting  $(T_c = 2.5 \text{ K})$  and CDW  $(T_{CDW} = 250 \text{ K})$  in the copper telluride chalcogenide CuIr<sub>2</sub>Te<sub>4</sub> [28]. According to our previous calculation study, we find both orbital projected band structure and density of state; the bands near the Fermi energy  $E_{\rm F}$  mainly come from Te p and Ir d orbitals, similar to that of  $CuIr_2S_4$  in spinel structure [28]. Therefore, it is reasonable to tune superconductivity properties by tuning the Fermi energy  $E_F$  of CuIr<sub>2</sub>Te<sub>4</sub> telluride chalcogenide with chemical doping. In this article we report the synthesis and physical properties of the B-site substitution solid solution  $\text{CuIr}_{2-x}\text{Ru}_x\text{Te}_4$  (0.0  $\leq x \leq 0.3$ ). The structural properties of the telluro compounds  $\text{CuIr}_{2-x}\text{Ru}_x\text{Te}_4$  (0.0  $\leq x \leq 0.3$ ) were characterized via x-ray diffraction (XRD). We characterize the effect of Ru substitution on the superconducting transition through temperature-dependent resistivity, magnetic susceptibility, and specific heat measurements. All measurements consistently confirm that the optimal doping level for superconductivity in  $CuIr_{2-x}Ru_xTe_4$  is x = 0.05. The specific heat anomaly at the superconducting transition,  $\Delta C/\gamma T_c$ , is approximately 1.51, which is slightly higher than the Bardeen-Cooper-Schrieffer BCS value of 1.43 and demonstrates bulk superconductivity in our CuIr<sub>1.95</sub>Ru<sub>0.05</sub>Te<sub>4</sub> compound. A "domelike" shape electronic phase diagram between charge density wave (CDW) and superconducting transition temperature  $T_c$  vs Ru doping content x has been established experimentally for this system. The CDW was immediately suppressed even with a small amount of Ru doping at x =0.03, while the superconducting transition temperature ( $T_c$ ) increases and reaches a maximum value of 2.79 K at x = 0.05, followed by a decrease of  $T_c$  as x increases. With discovery of this doping superconductor of CuIr<sub>2</sub>Te<sub>4</sub>, we found the effective method to improve the  $T_c$  and it also provides guidance for us to study other doping systems. This feature of the competition between CDW and the superconductivity could be induced by tuning the Fermi surface and density of states with Ru chemical doping.

#### **II. EXPERIMENTAL SECTION**

Polycrystalline samples of  $\text{CuIr}_{2-x}\text{Ru}_x\text{Te}_4(0.0 \le x \le 0.30)$  were synthesized in two steps by a solid-state reaction method. First, the mixture of high-purity powders of Cu (99.9%), Ir (99.9%), Ru (99.999%), and Te (99.999%) in the appropriate stoichiometric ratios was heated in sealed evacuated silica glass tubes at a rate of 1 °C/min to 850 °C and



FIG. 1. Structural and chemical characterizations of  $\text{CuI}_{r_2-x}\text{Ru}_x\text{Te}_4$ . (a) The powder XRD pattern with Rietveld refinement for  $\text{CuI}_{r_{1.95}}\text{Ru}_{0.05}\text{Te}_4$ . (b) The evolution of lattice parameters *a* and *c* of  $\text{CuI}_{r_{2-x}}\text{Ru}_x\text{Te}_4$  (0.0  $\leq x \leq 0.30$ ). (c) Powder XRD patterns (Cu K $\alpha$ ) for the  $\text{CuI}_{r_{2-x}}\text{Ru}_x\text{Te}_4$  samples studied (0.0  $\leq x \leq 0.30$ ). Inset shows the enlargement of peak (001).

TABLE I. Rietveld refinement structural parameters of CuIr<sub>1.95</sub>Ru<sub>0.05</sub>Te<sub>4</sub>. Space group  $P\bar{3}m1$  (no. 164), a = b = 3.9360(1) Å and c = 5.3917(2) Å,  $R_p = 6.29\%$ , and  $R_{wp} = 9.90\%$ ,  $R_{exp} = 3.71\%$ .

Label	x	У	Z	Site	Occupancy	
Ir	0.00000	0.00000	0.00000	1 <i>a</i>	0.945(2)	
Ru	0.00000	0.00000	0.00000	1 <i>a</i>	0.045(2)	
Те	0.33330	0.66670	0.2494(3)	2d	1.000	
Cu	0.00000	0.00000	0.50000	1b	0.500	

held there for 96 h. Subsequently, the as-prepared powders were reground, repelletized, and sintered again, by heating at a rate of 3 °C/min to 850 °C and holding there for 72 h. The identity and phase purity of the samples were determined by powder x-ray diffraction (PXRD) using a Bruker D8 Advance ECO with Cu  $K\alpha$  radiation and a LYNXEYE-XE detector. To determine the unit cell parameters, profile fits were performed on the powder diffraction data in the FULLPROF diffraction suite using Thompson-Cox-Hastings pseudo-Voigt peak shapes [29]. Measurements of the temperature-dependent electrical resistivity (four-point method), specific heat, and magnetic susceptibility of the materials were performed in a DynaCool Quantum Design Physical Property Measurement System (PPMS). There was no indication of air sensitivity of the materials during the study.  $T_c$  determined from susceptibility data were estimated conservatively:  $T_c$  was taken as the intersection of the extrapolations of the steepest slope of the susceptibility in the superconducting transition region and the normal state susceptibility; for resistivities, the midpoint of the resistivity  $\rho(T)$  transitions was taken, and, for the specific heat data, the critical temperatures obtained from the equal area construction method were employed.

## **III. RESULTS AND DISCUSSION**

Figure 1 shows the powder x-ray diffraction patterns at room temperature and fitting unit cell parameters for  $\text{CuIr}_{2-x}\text{Ru}_x\text{Te}_4$  (0.0  $\leq x \leq$  0.30). X-ray diffraction (XRD) results indicate that the solubility limit for Ru substitution in CuIr<sub>2</sub>Te<sub>4</sub> is x = 0.30. With higher Ru contents, the cubic RuTe<sub>2</sub> phase is obviously found as an impurity. Figure 1(a) and Table I show the detailed refinement results of the representative CuIr<sub>1.95</sub>Ru<sub>0.05</sub>Te<sub>4</sub> sample. Most of the reflections can be indexed in the  $P\bar{3}m1$  space group and the tiny impurity is attributed to the unreacted Ir. We also confirmed that the molar percentages of impurity (Ir) for  $\text{CuIr}_{2-x}\text{Ru}_x\text{Te}_4$  (0.03  $\leq x \leq 0.30$ ) via the Rietveld refinement of powder x-ray diffraction patterns were 1.46, 1.82, 2.5, 2.6, 2.6, and 2.8%, respectively. Due to the obtained Ir impurity present being  $< 3 \mod \%$ , we ensure that the real x value in  $\text{CuIr}_{2-x}\text{Ru}_x\text{Te}_4$  (0.03  $\leq x \leq 0.30$ ) is very close to the assumed one. The lattice parameters are obtained to be a = 3.9360(3) Å and c = 5.3917(5) Å for the



FIG. 2. Transport characterization of the normal states and superconducting transitions for  $\text{CuIr}_{2-x}\text{Ru}_x\text{Te}_4$ . (a) The temperature dependence of the resistivity ratio  $(\rho/\rho_{300 \text{ K}})$  for polycrystalline  $\text{CuIr}_{2-x}\text{Ru}_x\text{Te}_4$  ( $0.0 \le x \le 0.30$ ). (b) The temperature dependence of the resistivity ratio  $(\rho/\rho_{300 \text{ K}})$  for polycrystalline  $\text{CuIr}_{2-x}\text{Ru}_x\text{Te}_4$  at low temperature. (c) Magnetic susceptibilities for  $\text{CuIr}_{2-x}\text{Ru}_x\text{Te}_4$  ( $0.0 \le x \le 0.30$ ) at the superconducting transitions; applied dc fields are 20 Oe. (d) Magnetic susceptibility of  $\text{CuIr}_{1.97}\text{Ru}_{0.03}\text{Te}_4$  as a function of temperature at applied field of 1 T.

CuIr<sub>1.95</sub>Ru<sub>0.05</sub>Te<sub>4</sub> sample (Table I). The inset pattern shows that the CuIr<sub>1.95</sub>Ru<sub>0.05</sub>Te<sub>4</sub> sample adopts a disordered trigonal structure, which embodies two-dimensional (2D) IrTe<sub>2</sub> layers and is intercalated by Cu between the layers, with Ir partially replaced by Ru. We further determined the unit cell parameters of the CuIr<sub>2-x</sub>Ru<sub>x</sub>Te<sub>4</sub> (0.03  $\leq x \leq 0.30$ ) by fitting the powder x-ray diffraction patterns, which are shown in Fig. 1(b). With the increasing Ru doping contents, the lattice parameters a and c decrease linearly by following the Vegard's law. For example, the lattice parameter a decreased from 3.9397(5) Å (x = 0) to 3.9238 (2) Å (x = 0.30); meanwhile, the lattice parameter c decreased from 5.3965 (3) Å (x = 0) to 5.3776 (6) Å (x = 0.30). The enlargement of the (001) peak in Fig. 1(c) shows obvious right shift with the increasing contents of Ru substitution for Ir. This phenomenon was also according with the decline of fitting lattice parameter c in Fig. 1(b) by the means of the crystal plane spacing formula.

We next perform the temperature dependence of the electrical resistivity  $\rho(T)$  and magnetic susceptibility M(T) measurements for CuIr<sub>2-x</sub>Ru<sub>x</sub>Te<sub>4</sub> ( $0.0 \le x \le 0.30$ ). Figure 2(a) shows the temperature dependence of the normalized electrical resistivities  $(\rho/\rho_{300K})$  for the polycrystalline samples of  $\text{CuIr}_{2-x}\text{Ru}_x\text{Te}_4$  (0.0  $\leq x \leq 0.30$ ). At low temperatures [see Fig. 2(b)], a clear, sharp drop of  $\rho(T)$  is observed in the CuIr<sub>2-x</sub>Ru<sub>x</sub>Te<sub>4</sub> samples ( $0.0 \le x \le 0.20$ ) except for the highest doping content sample CuIr<sub>1.7</sub>Ru<sub>0.3</sub>Te<sub>4</sub>, signifying the onset of superconductivity at low temperatures. The transition temperature  $(T_c)$  slightly increases and reaches a maximum value of 2.79 K at x = 0.05, followed by a decrease of  $T_c$ as x increases. This trend is also clearly seen in the susceptibility data [Fig. 2(c)]—the onset of the negative magnetic susceptibility signaling the systematical superconducting state for  $CuIr_{2-x}Ru_xTe_4$ . The superconducting volume fraction can be estimated approximately to be 96%, which reveals the high purity of the CuIr<sub>2-x</sub>Ru<sub>x</sub>Te<sub>4</sub> ( $0.0 \le x \le 0.20$ ) samples. In addition, it is obviously seen that there are no CDW humps for the Ru-doped compounds CuIr<sub>2-x</sub>Ru<sub>x</sub>Te<sub>4</sub>  $(0.03 \leq x \leq 0.30)$  in the temperature-dependent resistivity results, indicating that the CDW state can be suppressed even by small-amount substitution of Ru for Ir in the host compound  $CuIr_2Te_4$ , as shown in Fig. 2(a). To further prove it, we adopt the measurement of the magnetic susceptibility at applied field of 1 T for the smallest doping content compound  $CuIr_{1.97}Ru_{0.03}Te_4$ . As shown in Fig. 2(d), unlike the pristine sample CuIr<sub>2</sub>Te<sub>4</sub>, the susceptibility exhibits no change around 250 K, which consistently indicates the CDW transition has been suppressed completely with small-amount Ru doping at x = 0.03. This significant feature of the interplay between CDW and the superconductivity could be attributed to modifying the Fermi surface and density of states with Ru chemical doping.

Temperature-dependent measurements of the magnetization under incremental magnetic field M(H) were applied to determine the low critical field  $\mu_0 H_{c1}(0)$ . Figure 3 show the temperature dependence of the lower critical field ( $\mu_0 H_{c1}$ ) for the selected CuIr<sub>2-x</sub>Ru<sub>x</sub>Te<sub>4</sub> (x = 0.05, 0.10, 0.15) compounds. The bottom left corner insets display the magnetic susceptibilities at low applied magnetic fields at various temperatures for CuIr<sub>2-x</sub>Ru<sub>x</sub>Te<sub>4</sub> (x = 0.05, 0.10, 0.15)



FIG. 3. Temperature dependence of the lower critical fields  $(\mu_0 H_{c1})$  for CuIr<sub>2-x</sub>Ru<sub>x</sub>Te<sub>4</sub> (x = 0.05, 0.10, 0.15). Bottom left corner inset shows magnetic susceptibility at low applied magnetics fields at various temperatures for CuIr<sub>2-x</sub>Ru<sub>x</sub>Te<sub>4</sub> (x = 0.05, 0.10, 0.15). Top right inset shows  $M-M_{fit}$  vs H.

samples. The top right insets show  $M - M_{\rm fit}$  vs H plots. For example, Fig. 3(a) shows how the  $\mu_0 H_{c1}(0)$  for the optimal CuIr<sub>1.95</sub>Ru<sub>0.05</sub>Te<sub>4</sub> compound was determined. First, applied field magnetization measurements M(H) were performed at 1.8, 2.0, 2.2, and 2.4 K to calculate the demagnetization factor (*N*). With the hypothesis that the beginning linear response to

Material	CuIr <sub>1.95</sub> Ru <sub>0.05</sub> Te <sub>4</sub>	CuIr <sub>1.9</sub> Ru <sub>0.1</sub> Te <sub>4</sub>	CuIr <sub>1.85</sub> Ru <sub>0.15</sub> Te <sub>4</sub>	CuIr <sub>1.8</sub> Ru <sub>0.2</sub> Te <sub>4</sub>	CuIr <sub>2</sub> Te <sub>4</sub>	$CuRh_2S_4$	CuRh <sub>2</sub> Se <sub>4</sub>	$Cu_{0.7}Zn_{0.3}Ir_2S_4$	CuIr <sub>1.6</sub> Pt <sub>0.4</sub> Se <sub>4</sub>
$\overline{T_c(\mathbf{K})}$	2.79	2.75	2.70	2.39	2.50	4.7	3.5	3.4	1.76
$\gamma$ (mJ mol <sup>-1</sup> K <sup>-2</sup> )	12.26				12.05	26.9	21.4		16.5
$\beta$ (mJ mol <sup>-1</sup> K <sup>-4</sup> )	1.87				1.97				1.41
$\Theta_D(\mathbf{K})$	193.6(2)				190.3 (1)	258	218		212
$\Delta C / \gamma T_c$	1.51				1.50	1.89	1.68		1.58
$\lambda_{ep}$	0.65				0.63	0.66	0.63		0.57
$N(E_{\rm F})({\rm states/eVf.u.})$	3.15				3.10				4.45
$-dH_{c2}/dT(T/K)$	0.125	0.112	0.100	0.095	0.066	0.614	0.181		2.62
$\mu_0 H_{c2}(0)(T)$	0.247	0.216	0.189	0.158	0.12	2.0	0.44		3.2
$\mu_0 H^{\mathrm{P}}(T)(T)$	5.24	5.12	5.02	4.45	4.65	8.74	6.51	6.32	3.27
$\mu_0 H_{c1}(0)(T)$	0.098	0.095	0.091		0.028				
$\xi_{GL}(0)(nm)$	36.3	39.1	41.7	45.5	52.8				0.96

TABLE II. Comparison of superconducting parameters in  $AB_2X_4$  superconductors.

the magnetic field is perfectly diamagnetic  $(dM/dH = -\frac{1}{4}\pi)$ for this bulk superconductor, we obtained the values of demagnetization factor N, of 0.55 – 0.75 (from  $N = \frac{1}{4}\pi \chi_V + 1$ ), where  $\chi_V = dM/dH$  is the value of the linearly fitted slope for the bottom left corner inset of Fig. 3(a). The experimental data can be fitted with the formula  $M_{\text{fit}} = a + bH$  at low magnetic fields, where a is an intercept and b is a slope from fitting the low magnetic field magnetization measurements data. The top right corner inset of Fig. 3(a) shows the  $M(H)-M_{\rm fit}$  data vs the magnetic field (*H*).  $\mu_0 H_{c1}^*$  was determined at the field when *M* deviates by  $\sim 1\%$  above the fitted data ( $M_{\rm fit}$ ), as is the common practice [30]. We can calculate the lower critical field  $\mu_0 H_{c1}(T)$  in the consideration of the demagnetization factor (N), via using the relation  $\mu_0 H_{c1}(T) = \mu_0 H_{c1}^*(T)/(1-N)$ [31–33]. The main panel of Fig. 3(a) reveals  $\mu_0 H_{c1}(T)$  as the function of temperature for CuIr<sub>1.95</sub>Ru<sub>0.05</sub>Te<sub>4</sub>. We estimated  $\mu_0 H_{c1}(0)$  by fitting the  $\mu_0 H_{c1}(T)$  data via the formula  $\mu_0 H_{c1}(T) = \mu_0 H_{c1}(0) [1 - (T/T_c)^2]$ , which is shown by the black solid lines. The obtained zero-temperature lower critical field  $\mu_0 H_{c1}(0)$ 's for CuIr<sub>1.95</sub>Ru<sub>0.05</sub>Te<sub>4</sub>, CuIr<sub>1.9</sub>Ru<sub>0.1</sub>Te<sub>4</sub>, and CuIr<sub>1.85</sub>Ru<sub>0.15</sub>Te<sub>4</sub> are 0.098, 0.095, and 0.091 T, respectively (Table II), which are higher than that of the pristine compound CuIr<sub>2</sub>Te<sub>4</sub>.

With the purpose of estimating the critical field  $\mu_0 H_{c2}(0)$ , we examined the temperature-dependent electrical resistivity at various applied fields  $\rho(T, H)$  for CuIr<sub>1-x</sub>Ru<sub>x</sub>Te<sub>4</sub> (x = 0.05, 0.10, 0.15, and 0.2) samples. Figure 4 exhibits the  $\rho(T,$ H) measurement data for  $\text{CuIr}_{1-x}\text{Ru}_x\text{Te}_4$  (x = 0.05, 0.10, 0.15, and 0.2). Inset of Fig. 4 shows upper critical field values  $\mu_0 H_{c2}$  plotted vs temperature (T) with  $T_c$  obtained from resistivity at different applied fields. The  $\mu_0 H_{c2}$  vs T curve near  $T_c$  of  $\text{CuIr}_{1-x}\text{Ru}_x\text{Te}_4$  (x = 0.05, 0.10, 0.15 and 0.2) samples show the good linear fitting, which is represented by the solid line. The values of the fitting data slopes  $(dH_{c2}/dT)$  of CuIr<sub>1-x</sub>Ru<sub>x</sub>Te<sub>4</sub> (x = 0.05, 0.10, 0.15) and 0.2) samples are shown in Table II. We can estimate the zero-temperature upper critical fields  $[\mu_0 H_{c2}(0)]$  of 0.247, 0.216, 0.189, and 0.158 T for  $CuIr_{1-x}Ru_{x}Te_{4}$  (x = 0.05, 0.10, 0.15, and 0.2) from the data, respectively, using the Werthamer-Helfand-Hohenberg (WHH) expression formula  $\mu_0 H_{c2}(T) = -0.693 T_c (dH_{c2}/dT_c)$  for the dirty limit superconductivity [33–37]. The obtained  $\mu_0 H_{c2}(0)$  values for  $CuIr_{1-x}Ru_{x}Te_{4}$  (x = 0.05, 0.10, 0.15, and 0.2) are all higher than that of the pristine compound CuIr<sub>2</sub>Te<sub>4</sub>. Especially, the CuIr<sub>1.95</sub>Ru<sub>0.05</sub>Te<sub>4</sub> with the highest  $T_c$  is two times higher as compared to the pristine CuIr<sub>2</sub>Te<sub>4</sub>, as summarized in Table II. In addition, the Pauli limiting field  $[\mu_0 H^P(T)]$  of CuIr<sub>1-x</sub>Ru<sub>x</sub>Te<sub>4</sub> (x = 0.05, 0.10, 0.15, and 0.2) can be calculated from  $\mu_0 H^P(T) = 1.86T_c$ . The calculated values of  $\mu_0 H^P(T)$  were also larger than that of the host compound CuIr<sub>2</sub>Te<sub>4</sub>. Then, with this formula  $\mu_0 H_{c2}(T) = \frac{0}{2\pi\xi_{GL}^2}$ , where  $\phi_0$  is the flux quantum, the Ginzburg-Laudau coherence length [ $\xi_{GL}(0)$ ] was calculated ~36.3 nm for CuIr<sub>1.95</sub>Ru<sub>0.05</sub>Te<sub>4</sub> (Table II).

Temperature-dependent specific heat measurements were performed with the exception of magnetic susceptibility and resistivity measurements to confirm that superconductivity is an intrinsic property of CuIr<sub>1.95</sub>Ru<sub>0.05</sub>Te<sub>4</sub>. The inset of Fig. 5 shows  $C_p/T$  vs  $T^2$ , where the data were fitted above the critical temperature to  $C_p = \gamma T + \beta T^3$ , where  $\beta T^3$  is the phonon contribution  $(C_{ph.})$  and  $\gamma T$  is the electronic contribution  $(C_{el})$  to the specific heat. By fitting the data, we obtain the value of  $\beta$  and  $\gamma$  as  $1.87 \text{ mJ mol}^{-1} \text{ K}^{-4}$ and  $12.26 \text{ mJ mol}^{-1} \text{ K}^{-2}$ , respectively. Figure 5 (main panel) shows the electronic specific heat divided by temperature  $(C_{el.}/T)$  vs T for CuIr<sub>1.95</sub>Ru<sub>0.05</sub>Te<sub>4</sub> from 2.0 to 3.8 K under zero magnetic field, in which a large peak can be seen in the specific heat.  $C_{el}$ . is obtained by subtracting the phonon contribution to the specific heat:  $C_{el.} = C_p - \beta T^3$ . The  $T_c$ is estimated to be 2.72 K for these data using an equalarea entropy construction (red solid lines), which is close to the critical temperature from the resistivity and magnetic susceptibility measurements. The normalized specific heat jump value  $\Delta C/\gamma T_c$  obtained from the data (inset of Fig. 5) was 1.51 for CuIr<sub>1.95</sub>Ru<sub>0.05</sub>Te<sub>4</sub>, which is higher than the Bardeen-Cooper-Schrieffer (BCS) weak-coupling limit value (1.43), confirming bulk superconductivity. Then we obtain the Debye temperature by the formula  $\Theta_D = (12\pi^4 nR/5\beta)^{1/3}$ using the fitted value of  $\beta$ , where *n* is the number of atoms per formula unit and R is the gas constant. Thus, we can estimate the electron-phonon coupling constant  $(\lambda_{ep})$  by using the Debye temperature  $(\Theta_D)$  and critical temperature  $T_c$  from the inverted McMillan formula:  $\lambda_{ep} = \frac{1.04 + \mu^* \ln(\frac{\Theta_D}{1.4ST_c})}{(1 - 1.62\mu^*)\ln(\frac{\Theta_D}{1.4ST_c}) - 1.04}$ [33]. This resultant  $\lambda_{ep}$  is calculated to be 0.65. The electron density of states at the Fermi level  $[N(E_F)]$  can be calculated



FIG. 4. Low temperature resistivity at various applied fields for  $\text{CuIr}_{1.95}\text{Ru}_{0.05}\text{Te}_4$  (a),  $\text{CuIr}_{1.9}\text{Ru}_{0.1}\text{Te}_4$  (b),  $\text{CuIr}_{1.35}\text{Ru}_{0.15}\text{Te}_4$  (c), and  $\text{CuIr}_{1.8}\text{Ru}_{0.2}\text{Te}_4$  (d). Inset shows  $\mu_0 H(T)$  at different  $T_c$ , red solid line shows linear fitting to the data to estimate  $\mu_0 H_{c2}$ .



FIG. 5. Heat capacity characterization of CuIr<sub>1.95</sub>Ru<sub>0.05</sub>Te<sub>4</sub>. Electronic heat capacity divided by temperature  $(C_{el.}/T)$  vs *T* measured from 2.0 to 3.8 K under zero applied magnetic field. Inset:  $C_p/T$  vs  $T^2$  shown for the low-temperature region and fitted to a line.

from  $N(E_{\rm F}) = \frac{3}{\pi^2 k_B^2 (1+\lambda_{ep})} \gamma$  with the  $\gamma$  and  $\lambda_{ep}$ . We got the values  $N(E_{\rm F}) = 3.15$  states/eV f.u. for CuIr<sub>1.95</sub>Ru<sub>0.05</sub>Te<sub>4</sub> and  $N(E_{\rm F}) = 3.10$  states/eV f.u. for CuIr<sub>2</sub>Te<sub>4</sub> (Table II). This result indicates that the higher density of electronic states at the Fermi energy matched the higher transition temperature due to the Ru doping into CuIr<sub>2</sub>Te<sub>4</sub>.

To further understand the effect of doping on superconducting transition temperature, we have established the electronic phase diagram plotted  $T_c$  vs x doping content for  $\text{CuIr}_{2-x}\text{Ru}_x\text{Te}_4$  (0.0  $\leq x \leq 0.30$ ), as shown in Fig. 6. All the  $T_c$  were obtained from the temperature dependence of the normalized  $(\rho/\rho_{300 \text{ K}})$  resistivities and magnetic susceptibility data. From the phase diagram we can easily find that the  $T_c$  vs x contents present a "domelike" shape. Using Ru chemical doping as finely controlled tuning parameters, the CDW state has been immediately suppressed; meanwhile superconducting transition temperature  $(T_c)$  rises to the first peak (x = 0.05) and then decreases until it reaches its minimum value at x = 0.3. On the basis of these results, we can conclude that this feature of the competition between CDW and the superconductivity could be induced by tuning the Fermi surface and density of states with Ru chemical doping. Nevertheless, the reason why the CDW state can be suppressed by Ru doping so



FIG. 6. The electronic phase diagram for  $\text{CuIr}_{2-x}\text{Ru}_x\text{Te}_4$ ( $0.0 \le x \le 0.30$ ). Inset shows an enlarged phase diagram for  $T_c$ .

quickly has not yet been studied. Extensive theoretical study to understand the present experimental results is required.

## **IV. CONCLUSION**

Here the solid solutions  $\text{CuIr}_{2-x}\text{Ru}_x\text{Te}_4$  ( $0.0 \le x \le 0.3$ ) have been successfully synthesized via solid-state reaction to study the effect of the *B*-site substitution on the superconductivity. The structural and superconductivity properties for this system were evaluated systematically by means of powder x-ray diffraction (PXRD), magnetization, resistivity, and specific heat measurements. PXRD analysis reveals that  $\text{CuIr}_{2-x}\text{Ru}_x\text{Te}_4$  ( $0.0 \le x \le 0.3$ ) crystallized a disordered trigonal structure with space group  $P\bar{3}m1$  (no. 164). Spe-

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cific heat, isothermal magnetization  $\{M(H)\}$ , and magnetotransport  $\{\rho(T, H)\}$  measurement results signify that the optimal doping content compound CuIr<sub>1.95</sub>Ru<sub>0.05</sub>Te<sub>4</sub> is a type-II superconductor with  $T_c \approx 2.79(1)$  K, a lower critical field  $H_{c1}(0) = 980$  Oe, and an upper critical field,  $H_{c2}(0) =$ 2470 Oe. Finally, we established a "domelike" electronic phase diagram, in which the CDW-superconducting transition temperatures are plotted as a function of Ru doping content x. We can easily find that the CDW has been suppressed immediately at x = 0.03 and the superconducting transition temperature ( $T_c$ ) rises to the peak (x = 0.05) and then decreases until it reaches its minimum value at x = 0.3, which displays a good material platform for further study of the competition between CDW and superconductivity.

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*Correction:* The second and third affiliations were given in the wrong order and have now been fixed.