Superconductivity with the enhanced upper critical field in the Pt-doped CuRh$_2$Se$_4$ spinel

Yiyi He,$^{1,*}$ Yi-Xin You,$^{2,*}$ Lingyong Zeng,$^1$ Shu Guo,$^{3,4}$ Huawei Zhou,$^1$ Kuan Li$^1$, Yanhao Huang,$^1$ Peifeng Yu,$^1$
Chao Zhang,$^1$ Chao Cao,$^{2,5}$ and Huixia Luo$^{1,†}$

$^1$School of Materials Science and Engineering, State Key Laboratory of Optoelectronic Materials and Technologies, Key Lab of Polymer Composite & Functional Materials, Guangzhou Key Laboratory of Flexible Electronic Materials and Wearable Devices, Sun Yat-Sen University, No. 135, Xingang Xi Road, Guangzhou 510275, People’s Republic of China
$^2$School of Physics and Hangzhou Key Laboratory of Quantum Matters, Hangzhou Normal University, Hangzhou 311121, People’s Republic of China
$^3$Shenzhen Institute for Quantum Science and Engineering, Southern University of Science and Technology, Shenzhen 518055, China
$^4$International Quantum Academy, Shenzhen 518048, China
$^5$Department of Physics and Center for Correlated Matter, Zhejiang University, Hangzhou 310013, People’s Republic of China

(Received 27 November 2021; revised 29 January 2022; accepted 7 February 2022; published 22 February 2022)

We report the effect of Pt doping on the superconductivity in CuRh$_2$Se$_4$ spinel using a combined experimental and theoretical study. Our x-ray diffraction results reveal that the Cu(Rh$_{1-x}$Pt$_x$)$_2$Se$_4$ (0 ≤ x ≤ 0.35) crystallizes in the structure with a space group of Fd$ar{3}$m (No. 227), and the lattice parameter a increases with Pt doping. The resistivity and magnetic susceptibility measurement results verify that the superconducting transition temperature ($T_c$) forms a domelike shape with a maximum value of 3.84 K at x = 0.06. It is also observed that the Pt doping slightly reduces the lower critical magnetic field from 220 Oe in CuRh$_2$Se$_4$ to 168 Oe in Cu(Rh$_{0.94}$Pt$_{0.06}$)$_2$Se$_4$, while it significantly enhances the upper critical magnetic field, reaching the maximum of 4.93 T in the Cu(Rh$_{0.94}$Pt$_{0.06}$)$_2$Se$_4$ sample. The heat capacity result indicates that the sample Cu(Rh$_{0.91}$Pt$_{0.09}$)$_2$Se$_4$ is a bulk superconductor. First-principles calculations suggest that the Pt doping leads to a redshift of a density of state near the Fermi level, consistent with the domelike $T_c$ observed experimentally.

DOI: 10.1103/PhysRevB.105.054513

I. INTRODUCTION

As a family of well-studied materials, spinel structural compounds are well-known for their excellent electrical, magnetic, thermal, and unique properties such as colossal magnetostriiction, gigantic Kerr rotation, and multiferroic [1–6]. The chemical composition of spinel could be described by $A_{2}B_{4}X_4$, where metal ions occupy $A$ and $B$ sites, and $X$ sites are filled with elements such as oxygen, sulfur, selenium, tellurium. Even though thousands of spinels have been discovered, only a few spinels exhibit superconductivity (SC). So far, Li$_{1+}$Ti$_{2-}\delta$O$_{4-}\delta$ is the only bulk superconducting oxide spinel and hosts the highest superconducting critical transition temperature ($T_c$) of 13.7 K among the spinel compound family [7]. Recently, SC has been observed in MgTi$_2$O$_4$ oxide spinel film grown on the MgAl$_2$O$_4$ substrate, which can be achieved by engineering a superlattice of MgTi$_2$O$_4$ and SrTiO$_3$ [8]. The other spinel superconductors that have been reported so far are undoped ternary sulfo- and selenospinels CuRh$_2$S$_4$, CuRh$_2$Se$_4$, and CuCo$_2$S$_4$, as well as electron-doped CuIr$_2$S$_4$ and CuIr$_2$Se$_4$ [9–18].

Significantly, the heavy metal chalcogenide spinel CuIr$_2$S$_4$ has attracted considerable interest due to the metal-insulator (M-I) transition ($T_{MI}$) at T ≈ 230 K, accompanied by an intricate structural transition that simultaneously engenders both charge ordering and metal-metal pairing [19,20]. Besides, the peculiar $T_{MI}$ in CuIr$_2$S$_4$ increases with pressure and disappears gradually at higher pressure [21], whereas the $T_{MI}$ is suppressed by Zn substitution for Cu in the Cu$_{1-x}$Zn$_x$Ir$_2$S$_4$ series, and SC is induced with a maximum $T_c$ of 3.4 K near $x = 0.3$ [16]. It is reminiscent of the emergence of SC in the doped chalcogenide series [17] and the high-temperature (HT) superconductors (e.g., cuprates and iron-based pnictides) [22,23], where the charge density wave or the magnetism was suppressed by different dopants as a result of doping-induced destabilization of the charge-ordered or spin-paired state.

In contrast, such M-I transition is absent in the isostructural selenospinell CuRh$_2$Se$_4$, in which $T_c$ is around 3.5 K [24]. In addition, $T_c$ in CuRh$_2$Se$_4$ can be enhanced to 4.9 K at 6.5 GPa and possible superconductor-insulator transition emerges upon further compression with a key characteristic of broad peak in resistivity [25], which implies that CuRh$_2$Se$_4$ may be in close proximity to some kind of instabilities owing to an external disturbance despite the absence of charge-ordering or metal-metal pairing in CuRh$_2$Se$_4$. However, there are rare reports on the effect of chemical doping on the physical properties of CuRh$_2$Se$_4$ so far. Thus, this situation inspires us to explore the chemical doping effect on the physical properties of CuRh$_2$Se$_4$. In addition, compared with CuRh$_2$S$_4$, the Rh-4d and Cu-3d orbitals in CuRh$_2$Se$_4$ contribute more to the electronic states near the Fermi level, as proposed by previous first-principles calculations [26]. Besides, as far as we know, the 3d, 4d, and 5d transition metal dopants (e.g.,
Co, Ni, Ru, Ir) play an essential role in tuning SC in the iron-based superconductors [27–31]. Therein, Pt substitution for Fe in BaFe2As2 is reported to cause a significant increment on the $T_c$ and the upper critical magnetic field ($\mu_0H_c^\text{2}$) [32]. Therefore, it will be interesting to study the properties of CuRh2Se4 using the maximally projected Wannier function method [36] and symmetrized using full crystal symmetry [37]. The Hamiltonians for doped compounds were then interpolated in the spirit of virtual crystal approximation (VCA).

III. RESULTS AND DISCUSSION

Figure 1 shows the PXRD patterns of CuRh2Se4 (0 ≤ x ≤ 0.35) and the relative analyses. The XRD Rietveld refinement for the representative sample CuRh2Se4 at room temperature is shown in Fig. 1(a), which can be well indexed by spinel CuRh2Se4 (PDF card number: 04-005-8682), while some samples contain a small amount of RhSe2 impurity (less than 5%, see Table. S2 in the Supplemental Material [49]). The refined data of other compositions in the system is presented in Fig. S1 and Table S1. Further, EDXS is employed to confirm the atomic ratio (see Fig. S2), implying the obtained compositions are very close to the target compositions. Also, the EDXS mappings are shown in Fig. S3, suggesting homogeneity in polycrystalline samples. When the doping amount of Pt is beyond $x = 0.35$, a large amount of PtSe2 phases appears. As shown in the right side of Fig. 1(b), the peaks at around 35° are enlarged. A clear left shift for peaks can be perceived when the doping amount of Pt gradually increases. Based on Bragg's Law $2d \sin \theta = n\lambda$, it is not difficult to draw out the explanation that the interplanar distance increases with the doping amount of Pt increasing gradually since the ionic radius of Pt is greater than that of Rh. Subsequently, we perform quantitative analysis on the XRD data by fitting with FULLPROF suite using Thompson-Cox-Hastings pseudo-Voigt peak shapes to obtain the lattice parameters. The lattice parameter increases from 10.2645(4) Å for CuRh2Se4 to 10.3297(4) Å for CuRh0.65Pt0.35Se4. Figure 1(c) shows the lattice parameters as a function of the Pt doping content with a good linearity.

The R-T and M-T measurements are carried out to survey the SC. Figure 2(a) displays the normalized resistivity ($\rho/\rho_\text{0K}$) vs temperature. For $0 \leq x \leq 0.35$, resistivity decreases as the temperature going down from 300 K to the onset of the zero-drop (around 4 K), implying they are metallic. Figure 2(b) shows the resistivity trend at low temperatures, ranging from 1.8 to 4.2 K. The superconducting transition width is defined as the temperature difference between 90% and 10% resistance. Resistivity for CuRh0.65Pt0.35Se4 (0 ≤ x ≤ 0.12) samples reveals a dramatic decrement that the width is less than 0.3 K. Besides, the $T_c$ of each sample, which is defined from the average value of the temperature when resistivity becomes 1%, is followed by a rapid decline as $x$ increases. Once the doping percentage reaches 15%, no zero resistivity can be observed down to 1.8 K. In the light of 5% RhSe2 impurity observed in part of our studied CuRh0.65Pt0.35Se4 (0 ≤ x ≤ 0.35) samples, we should examine whether the $T_c$ may originate from the RhSe2 compounds or not. Based on the previous reports, we find out there is no accurate $T_c$ for the undoped RhSe2 compound. Besides, the $T_c$ of RhSe2 varies irregularly from 1 to 6 K depending on the Se content [38]. The $T_c$ of the most similar compound Rh0.94Se2 was around 5 K [39]. These facets can rule out that the $T_c$s in CuRh0.65Pt0.35Se4...
FIG. 1. Structural characterizations of Cu(Rh\(_{1-x}\)Pt\(_x\))\(_2\)Se\(_4\) (0 \(\leq\) x \(\leq\) 0.35). (a) The XRD results after Rietveld refinement for Cu(Rh\(_{0.95}\)Pt\(_{0.05}\))\(_2\)Se\(_4\); (b) XRD patterns for Cu(Rh\(_{1-x}\)Pt\(_x\))\(_2\)Se\(_4\) (0 \(\leq\) x \(\leq\) 0.35). The peak representing the lattice plane (400) was enlarged in the inset. (c) The trend of lattice parameter as the change of the Pt doping amount. (0 \(\leq\) x \(\leq\) 0.35) are from RhSe\(_2\) impurity, combining with the following magnetic and specific heat measurements. The \(T_c\) change in Cu(Rh\(_{1-x}\)Pt\(_x\))\(_2\)Se\(_4\) (0 \(\leq\) x \(\leq\) 0.12) can be considered related to the shift of the Fermi level and scattering effect based on the following first-principles calculations and RRR values. When 0 \(\leq\) x \(\leq\) 0.06, \(T_c\) increases with the increasing x due to the enhancement of density of states (DOS); while x \(>\) 0.06, \(T_c\) decreases with the increment of x, which may be the disorder effect become more remarkably. Moreover, the residual resistivity ratio (RRR) for each sample is exhibited in Fig. 2(c). The parent sample exhibits a high RRR value of 37 and a sharp transition to the superconducting state at 3.45 K, denoting that the undoped sample is highly homogeneous [40]. Also, the subsequent reduction of RRR points out a reinforced effect in electron scattering, which might be related to the rising trend of the upper critical field. Furthermore, SC of Cu(Rh\(_{1-x}\)Pt\(_x\))\(_2\)Se\(_4\) (0 \(\leq\) x \(\leq\) 0.12) is also investigated by magnetic measurements. Zero-field-cooling (ZFC) measurements under 30 Oe magnetic field were applied to detect the diamagnetism of superconducting Cu(Rh\(_{1-x}\)Pt\(_x\))\(_2\)Se\(_4\) (0 \(\leq\) x \(\leq\) 0.12) samples. As shown in Fig. 2(d), strong diamagnetic shields and clear superconducting transitions are observed. The tendency of \(T_c\) shows great agreement with the R-T result at slightly lower level due to the suppression from the applied magnetic field. However, the superconducting transition does not appear as steep as it is expected to be. We suggest that this phenomenon is originated from the decay of the Meissner screen current, which happens commonly in polycrystalline samples [32]. Besides, we employed cylindrical powder samples with an applied magnetic field parallel to the axis of the cylinder for ZFC measurements [41]. Therefore, the demagnetization effect caused the \(4\pi\chi\) values to be less than \(-1\). We then used the formula \(H_i = \frac{H_a}{1-n}\) to modify the value of \(4\pi\chi\), where \(H_i\) is the strength of the magnetic field inside the sample and \(H_a\) is the applied magnetic field. The values of the demagnetization factor \(n\) calculated from geometric elements vary from 0.5924 to 0.6268.

Subsequently, to determine the lower critical transition magnetic field \(\mu_0H_{c1}(0)\), we measured the M-H curves at different temperatures. For comparison, the parent sample CuRh\(_2\)Se\(_4\) and the representative sample Cu(Rh\(_{0.95}\)Pt\(_{0.05}\))\(_2\)Se\(_4\) are chosen for the test. The test details of \(\mu_0H_{c1}(0)\) are...
FIG. 2. The measurements of R-T and M-T for Cu(Rh$_{1-x}$Pt$_x$)$_2$Se$_4$ (0 \(\leq x \leq 0.35\)). (a) The overview of the normalized resistivity ($\rho/\rho_{300\,K}$) in the range of 1.8 to 300 K; (b) The temperature dependence of normalized resistivity ($\rho/\rho_{300\,K}$) in the range of 1.8 to 4.5 K; (c) The RRR value vs Pt content; (d) The ZFC M-T curves for Cu(Rh$_{1-x}$Pt$_x$)$_2$Se$_4$ (0 \(\leq x \leq 0.12\)) in the range of 1.8 to 4.2 K.

The upper right insets of Figs. 3(a) and 3(b) display the M-H curves at various temperatures. When the external magnetic field is weak, the magnetization intensity $M$ performs as a linear relation of the external magnetic field $H$: $M = e + f H$, where $e$ is the intercept and $f$ is the slope of the line [42]. The lower left insets of Figs. 3(a) and 3(b) exhibit the $M-M_{\text{fit}}$ vs $H$ curves. Commonly, the value of $\mu_0 H^*_1$ is extracted when the difference between $M$ and $M_{\text{fit}}$ over 1% $M_{\text{max}}$. The obtained points shown in the main panel of Figs. 3(a) and 3(b) are comply well with the formula $\mu_0 H^*_1(0) = \mu_0 H^*_1(0)[1-(T/T_c)^2]$. The estimated value $\mu_0 H^*_1(0)$ of CuRh$_2$Se$_4$ and Cu(Rh$_{0.94}$Pt$_{0.06}$)$_2$Se$_4$ are identified as 100 Oe, 84 Oe, respectively. Due to demagnetization, the modified lower critical field $\mu_0 H^*_1(0)$ should be modified using the formula $\mu_0 H^*_1(0) = \mu_0 H^*_1(0) / n$, where the demagnetization factor $n$ of CuRh$_2$Se$_4$ and Cu(Rh$_{0.94}$Pt$_{0.06}$)$_2$Se$_4$ is 0.5461 and 0.5, respectively. This result suggests that Pt substitution can slightly affect the $\mu_0 H^*_1(0)$.

The upper critical fields are studied by the R-T measurement under diverse applied fields systematically. Figures 4(a)–4(f) show the measurement process of Cu(Rh$_{1-x}$Pt$_x$)$_2$Se$_4$ (x = 0, 0.05, 0.06). It can be seen in Figs. 4(b), 4(d), and 4(f) that $T_c$ puts up a continuous declination with the increase of the applied magnetic field intensity. Data plots of the upper critical field $\mu_0 H^*_2$, which are determined by the 50% criterion of normal-state resistivity values, are used to estimate $\mu_0 H^*_2(0)$ following the Werthamer-Helfand-Hohenberg (WHH) and Ginzberg-Landau (G-L) theories, respectively. $dH^*_2/dT_c$, which refers to the slope of plots near $T_c$, is used in the simplified WHH formula: $\mu_0 H^*_2(0) = -0.693T_c(dH^*_2/dT_c)$. As a dirty limit from the WHH model, the calculated values of CuRh$_2$Se$_4$, Cu(Rh$_{0.95}$Pt$_{0.05}$)$_2$Se$_4$, and Cu(Rh$_{0.94}$Pt$_{0.06}$)$_2$Se$_4$ are 0.81(2) T, 3.22(2) T, 3.75(8) T, respectively. It is worth mentioning that the calculated upper critical field from WHH model must be less than the Pauling limiting field $H^p = 1.86T_c$, which is a precondition derived from the Pauling-limiting effect [43]. In this case, $H^p$'s of
CuRh$_2$Se$_4$, Cu(Rh$_{0.95}$Pt$_{0.05}$)$_2$Se$_4$, and Cu(Rh$_{0.94}$Pt$_{0.06}$)$_2$Se$_4$ are 6.311(2) T, 7.072(2) T, and 7.176(4) T, respectively. $\mu_0H^*_{c2}$ also follows the function distribution based on G-L theory: $\mu_0H^*_{c2}(T) = \mu_0H_{c2}(0) \cdot (1 - T/T_c)^\beta$, which in the upper-right corner showed the variation of magnetization intensity with the increment of the applied magnetic field. The inset located in the low left quarter showed the intersection point of $M-M_{\text{in}}$ and $1\%M_{\text{max}}$. The curves in the insets of the figure are taken by applying the field after zero-field cooling.

CuRh$_2$Se$_4$, Cu(Rh$_{0.95}$Pt$_{0.05}$)$_2$Se$_4$, and Cu(Rh$_{0.94}$Pt$_{0.06}$)$_2$Se$_4$ are 6.311(2) T, 7.072(2) T, and 7.176(4) T, respectively. $\mu_0H^*_{c2}$ also follows the function distribution based on G-L theory: $\mu_0H^*_{c2}(T) = \mu_0H_{c2}(0) \cdot (1 - T/T_c)^\beta$, which in the upper-right corner showed the variation of magnetization intensity with the increment of the applied magnetic field. The inset located in the low left quarter showed the intersection point of $M-M_{\text{in}}$ and $1\%M_{\text{max}}$. The curves in the insets of the figure are taken by applying the field after zero-field cooling.

$$\begin{align*}
\text{FIG. 3.} & \quad \text{The temperature dependence measurement of lower critical } (\mu_0H_{c1}) \text{ field for CuRh}_2\text{Se}_4 \text{ and Cu(Rh}_{0.94}\text{Pt}_{0.06})_2\text{Se}_4. \text{ The inset located in the upper-right corner showed the variation of magnetization intensity with the increment of the applied magnetic field. The inset located in the low left quarter showed the intersection point of } M-M_{\text{in}} \text{ and } 1\%M_{\text{max}}. \text{ The curves in the insets of the figure are taken by applying the field after zero-field cooling.}
\end{align*}$$

$$\begin{align*}
\text{FIG. 3.} & \quad \text{The temperature dependence measurement of lower critical } (\mu_0H_{c1}) \text{ field for CuRh}_2\text{Se}_4 \text{ and Cu(Rh}_{0.94}\text{Pt}_{0.06})_2\text{Se}_4. \text{ The inset located in the upper-right corner showed the variation of magnetization intensity with the increment of the applied magnetic field. The inset located in the low left quarter showed the intersection point of } M-M_{\text{in}} \text{ and } 1\%M_{\text{max}}. \text{ The curves in the insets of the figure are taken by applying the field after zero-field cooling.}
\end{align*}$$

$$\begin{align*}
\text{FIG. 3.} & \quad \text{The temperature dependence measurement of lower critical } (\mu_0H_{c1}) \text{ field for CuRh}_2\text{Se}_4 \text{ and Cu(Rh}_{0.94}\text{Pt}_{0.06})_2\text{Se}_4. \text{ The inset located in the upper-right corner showed the variation of magnetization intensity with the increment of the applied magnetic field. The inset located in the low left quarter showed the intersection point of } M-M_{\text{in}} \text{ and } 1\%M_{\text{max}}. \text{ The curves in the insets of the figure are taken by applying the field after zero-field cooling.}
\end{align*}$$

$\text{FIG. 3.}$ The temperature dependence measurement of lower critical $(\mu_0H_{c1})$ field for CuRh$_2$Se$_4$ and Cu(Rh$_{0.94}$Pt$_{0.06}$)$_2$Se$_4$. The inset located in the upper-right corner showed the variation of magnetization intensity with the increment of the applied magnetic field. The inset located in the low left quarter showed the intersection point of $M-M_{\text{in}}$ and $1\%M_{\text{max}}$. The curves in the insets of the figure are taken by applying the field after zero-field cooling.

$\text{FIG. 3.}$ The temperature dependence measurement of lower critical $(\mu_0H_{c1})$ field for CuRh$_2$Se$_4$ and Cu(Rh$_{0.94}$Pt$_{0.06}$)$_2$Se$_4$. The inset located in the upper-right corner showed the variation of magnetization intensity with the increment of the applied magnetic field. The inset located in the low left quarter showed the intersection point of $M-M_{\text{in}}$ and $1\%M_{\text{max}}$. The curves in the insets of the figure are taken by applying the field after zero-field cooling.
FIG. 4. The temperature dependence measurement of the upper critical ($\mu_0H_{c2}$) fields for Cu(Rh$_{1-x}$Pt$_x$)$_2$Se$_4$ ($x = 0, 0.05, 0.06$); (a), (c), and (e) show the refinements of Cu(Rh$_{1-x}$Pt$_x$)$_2$Se$_4$ ($x = 0, 0.05, 0.06$), respectively. The red curve exhibits the refinement by G-L theory, while the blue curve displays the refinement by WHH model; (b), (d), and (f) show the detailed process for determining $\mu_0H_{c2}$.

FIG. 5. The temperature-dependent specific heat for Cu(Rh$_{0.95}$Pt$_{0.05}$)$_2$Se$_4$. (a) Specific heat divided by temperature $C_p/T$ vs squared temperature $T^2$ under diverse applied magnetic fields. (b) Electronic contribution to the heat capacity divided by temperature ($C_{el}/T$) vs temperature $T$ in the range of 2.0 to 3.8 K without an applied magnetic field.
TABLE I. The comparison of superconducting characteristic parameters for spinel compounds. $\mu_0H^p$ is the Pauling limited field. $\xi_{\text{GL}}$ is the Ginzburg-Laudau coherence length at 0 K. $\gamma$ is the constant of electronic specific heat and $\beta$ is the phonon contribution terms. $\Theta_D$ is the Debye temperature. $\Delta C/\gamma T_c$ is the normalized specific heat jump value. $\lambda_{ep}$ is the electron-phonon coupling constant. $N(E_F)$ is the DOS located at the Fermi level.

| Compound          | CuRh$_2$Se$_4$   | Cu(Rh$_{0.95}$Pt$_{0.05}$)$_2$Se$_4$ | Cu(Rh$_{0.94}$Pt$_{0.06}$)$_2$Se$_4$ | Cu(Rh$_{0.91}$Pt$_{0.09}$)$_2$Se$_4$ | Cu(Ir$_{0.8}$Pt$_{0.2}$)$_2$Se$_4$ | CuRh$_2$S$_4$ |
|-------------------|------------------|-------------------------------------|-------------------------------------|-------------------------------------|----------------------------------|---------------|
| $T_c$ (K)         | 3.38(1)          | 3.80(1)                             | 3.84(2)                             | 3.47(3)                             | 1.76                             | 3.5           |
| $\mu_0H^p$(Oe)    | 220(6)           | -                                   | 168(12)                             | -                                   | -                                | -             |
| $\mu_0H^p$(T) ($\rho^{505}_N$ G-L theory) | 1.00(1)          | 4.03(1)                             | 4.93(1)                             | -                                   | -                                | -             |
| $-dH_c^2/dT_c$ (T/K) | 0.352(8)        | 1.233(8)                            | 1.418(31)                           | -                                   | 2.6                              | 0.614         |
| $\mu_0H^p$(T) ($\rho^{505}_N$ WHH theory) | 0.81(2)          | 3.22(2)                             | 3.75(8)                             | -                                   | 3.2                              | 2.0           |
| $\mu_0H^p$(T) ($\rho^{505}_N$ WHH theory) | 6.311(2)         | 7.072(2)                            | 7.176(4)                            | -                                   | 3.2                              | 8.74          |
| $\xi_{\text{GL}}$ ($\rho^{505}_N$ WHH theory) | 20.1             | 10.1                                | 9.36                                | -                                   | 101                             | -             |
| $\gamma$ (mJ·mol$^{-1}$·K$^{-2}$) | 21.4             | -                                   | -                                   | -                                   | 22.57(20)                       | 16.5          |
| $\beta$ (mJ·mol$^{-1}$·K$^{-4}$) | -                | -                                   | -                                   | 1.65(1)                             | 1.41                             | -             |
| $\Theta_D$ (K)    | 218              | -                                   | -                                   | 202.0                               | 212                              | 258           |
| $\Delta C/\gamma T_c$ | 1.68             | -                                   | -                                   | 1.52                                | 1.58                             | 1.89          |
| $\lambda_{ep}$    | 0.63             | -                                   | -                                   | 0.63                                | 0.57                             | 0.66          |
| $N(E_F)$ (states/eV·f.u.) | -                | -                                   | -                                   | 5.87                                | 4.45                             | -             |
| $\xi$ (nm)        | 18.2             | 8.89                                | 8.16                                | -                                   | 10.1                             | -             |

The electronic phase diagram for Cu(Rh$_{1-x}$Pt$_x$)$_2$Se$_4$ ($0 \leq x \leq 0.12$) is performed to summarize our characterizations. The acquired $T_c$ from the experiment result of R-T and M-T is summed up as a curve related to the Pt doping concentration. From Fig. 6, we can find that with the increment of Pt substitution, $T_c$ shows an upward trend and reaches the maximum value of 3.85 K for Cu(Rh$_{0.6}$Pt$_{0.12}$)$_2$Se$_4$. Subsequently, $T_c$ drops down at the higher Pt doping region. It can be taken as evidence that Pt chemical doping can be used to tune the SC for the spinel CuRh$_2$Se$_4$.

In order to understand the above experimental results, we have also performed first-principles calculations. Figure 7(a) shows the electronic band structure of pristine CuRh$_2$Se$_4$ and CuPt$_2$Se$_4$. For CuRh$_2$Se$_4$ [Fig. 7(a), left panel], two doubly degenerate bands (band No. 89 – 92) cross the Fermi level once SOC interaction is considered, creating three doubly degenerate bands (band No. 89 – 92) cross the Fermi level, resulting in a peak of $N(E_F)$. Increasing Pt doping to $x = 0.1$ the DOS peak shifts very close to the Fermi level, resulting in a peak of $N(E_F)$ [inset of Fig. 7(d)]. Increasing Pt doping to $x > 0.1$, the DOS peak moves away from the Fermi level, and $N(E_F)$ decreases monotonically [inset of Fig. 7(d)]. In addition, it is apparent that the van Hove singularity close to the band edge (located approximately 0.2 eV above the Fermi level) for pristine CuRh$_2$Se$_4$ is quickly suppressed upon Pt doping. This can be understood since the Pt-5$d$ orbital radius is much larger than the Rh-4$d$ orbital radius. Therefore, the enhanced hoppings effectively enhance the three dimensionality. According to the BCS theory $T_c \propto \exp(- \frac{1}{N(E_F)^2})$, where $V$ is the attractive potential, the $N(E_F)$ change with respect to doping content as well as a pair of starlike pockets around $\Gamma$ point [Fig. 7(b)]. Interestingly, these two doubly degenerate bands are well separated from all other band states, and are dominated by the Se-4$p$ and Rh-4$d$ orbitals, as also evident from the DOS calculation [Fig. 7(c)]. In general, the CuPt$_2$Se$_4$ band structure [Fig. 7(a), right panel] resembles a heavily electron-doped CuRh$_2$Se$_4$, since the top of band 91/92 is now ~0.6 eV below the Fermi level. However, there are several important differences, which invalidate the commonly adopted rigid-band shifting method. Firstly, bands 89–92 are now entangled with the bands below them. Secondly, bands 89–92 became more dispersive than they were in CuRh$_2$Se$_4$, possibly due to the larger hopping terms between Pt-5$d$ orbitals and Se-4$p$ orbitals than those between Rh-4$d$ and Se-4$p$, as a result of the larger atomic radius of 5$d$ wave functions. As a result, although a direct gap is always present between bands 91/92 and 93/94, the indirect gap between them is decreased from 247 meV to ~30 meV.

With the electronic structure of both pristine compound explained, we now address the electronic structure of Cu(Rh$_{1-x}$Pt$_x$)$_2$Se$_4$ under the spirit of VCA. The doping-dependent DOS is shown in Fig. 7(d). The elemental substitution causes a significant red-shift of the DOS peak around 0.1 eV above the Fermi level, corresponding to the electron doping effect. At $x = 0.1$, the DOS peak shifts very close to the Fermi level, resulting in a peak of $N(E_F)$ [inset of Fig. 7(d)]. Increasing Pt doping to $x > 0.1$, the DOS peak moves away from the Fermi level, and $N(E_F)$ decreases monotonically [inset of Fig. 7(d)]. In addition, it is apparent that the van Hove singularity close to the band edge (located approximately 0.2 eV above the Fermi level) for pristine CuRh$_2$Se$_4$ is quickly suppressed upon Pt doping. This can be understood since the Pt-5$d$ orbital radius is much larger than the Rh-4$d$ orbital radius. Therefore, the enhanced hoppings effectively enhance the three dimensionality. According to the BCS theory $T_c \propto \exp(- \frac{1}{N(E_F)^2})$, where $V$ is the attractive potential, the $N(E_F)$ change with respect to doping content.

FIG. 6. The electronic phase diagram for Cu(Rh$_{1-x}$Pt$_x$)$_2$Se$_4$ ($0 \leq x \leq 0.12$) vs Pt content.
x is roughly consistent with the experimental observation. However, the existence of RhSe₂ plays the role of hole dopant. Based on the monovalence assumption of copper, the absence of copper in the impurity produces 0.5 hole/f.u., causing an additional blueshift depending on the concentration of the RhSe₂ impurity. As a result, the measured peak was discovered at a lower doping level than the calculated one.

IV. CONCLUSION

In summary, we have succeeded in synthesizing a series of Cu(Rh₁₋ₓPtₓ)₂Se₄ (0 ≤ x ≤ 0.35) spinels via a conventional solid-state reaction. Combining the experimental and theoretical studies, we find that Pt substitution plays a positive role in Tc enhancement, reaching a maximum Tc of 3.85 K in the optimal doping composition Cu(Rh₀.94Pt₀.06)₂Se₄. Meanwhile, it can vastly raise the upper critical magnetic field μ₀Hc₂(0) by the disorder. This finding sheds light on the discovery of new spinel SC materials and provide a material platform to study the mechanism of spinel superconductors.

ACKNOWLEDGMENTS

This work is supported by the National Natural Science Foundation of China (Grants No. 11922415 and No. 11874137), Guangdong Basic and Applied Basic Research Foundation (2019A1515011718), Key Research & Development Program of Guangdong Province, China (2019B110209003), and the Pearl River Scholarship Program of Guangdong Province Universities and Colleges (20191001). The calculations were performed on the High Performance Computing Center at School of Physics, Hangzhou Normal University.

[1] J. Hemberger, H.-A. rugvon Nidda, V. Tsurkan, and A. Loidl, Phys. Rev. Lett. 98, 147203 (2007).
[2] A. P. Ramirez, R. J. Cava, and J. Krajewski, Nature (London) 386, 156 (1997).
[3] Z. Yang, S. Tan, Z. Chen, and Y. Zhang, Phys. Rev. B 62, 13872 (2000).
[4] S. Weber, P. Lunkenheimer, R. Fichtl, J. Hemberger, V. Tsurkan, and A. Loidl, Phys. Rev. Lett. 96, 157202 (2006).
[5] K. Ohgushi, T. Ogasawara, Y. Okimoto, S. Miyasaka, and Y. Tokura, Phys. Rev. B 72, 155114 (2005).
[6] J. Hemberger, P. Lunkenheimer, R. Fichtl, H. A. Krug von Nidda, V. Tsurkan, and A. Loidl, Nature (London) 434, 364 (2005).
[7] D. C. Johnson, J. Low Temp. Phys. 25, 145 (1976).
[8] W. Hu, Z. Feng, B.-C. Gong, G. He, D. Li, M. Qin, Y. Shi, Q. Li, Q. Zhang, J. Yuan, B. Zhu, K. Liu, T. Xiang, L. Gu, F. Zhou,
X. Dong, Z. Zhao, and K. Jin, Phys. Rev. B 101, 220510(R) (2020).

[9] T. Bitoh, T. Hagino, Y. Seki, S. Chikazawa, and S. Nagata, J. Phys. Soc. Jpn. 61, 3011 (1992).

[10] M. Ito, J. Hori, H. Kurisaka, H. Okada, A. J. Perez Kuroki, N. Ogita, M. Udagawa, H. Fujii, F. Nakamura, T. Fujita, and T. Suzuki, Phys. Rev. Lett. 91, 077001 (2003).

[11] M. Ito, A. Taira, and K. Sonoda, Acta Phys. Pol. A 131, 1450 (2017).

[12] T. Shirane, T. Hagino, Y. Seki, T. Bitoh, S. Chikazawa, and S. Nagata, J. Phys. Soc. Jpn. 62, 374 (1993).

[13] R. N. Shelton, D. C. Johnston, and H. Adrian, Solid State Commun. 20, 1077 (1976).

[14] T. Hagino, Y. Seki, N. Wada, S. Tsuji, T. Shirane, K.-I. Kumagai, and S. Nagata, Phys. Rev. B 51, 12673 (1995).

[15] H. Suzuki, T. Furubayashi, G. Cao, H. Kitazawa, A. Kamimura, K. Hirata, and T. Matsumoto, J. Phys. Soc. Jpn. 68, 2495 (1999).

[16] G. Cao, H. Kitazawa, H. Suzuki, T. Furubayashi, K. Hirata, and T. Matsumoto, Physica C 341–348, 735 (2000).

[17] H. Luo, T. Klimczuk, L. Müchler, L. Schoop, D. Hirai, M. K. Fuccillo, C. Felser, and R. J. Cava, Phys. Rev. B 87, 214510 (2013).

[18] Y. Y. Jin, S. H. Sun, Y. W. Cui, Q. Q. Zhu, L. W. Ji, Z. Ren, and G. H. Cao, Phys. Rev. Mater. 5, 074804 (2021).

[19] T. Furubayashi, T. Matsumoto, T. Hagino, and S. Nagata, J. Phys. Soc. Jpn. 63, 3333 (1994).

[20] S. Nagata, Chinese J. Phys. 43, 722 (2005).

[21] G. Oomi, T. Kagayama, I. Yoshida, T. Hagino, and S. Nagata, J. Magn. Magn. Mater. 140–144, 157 (1995).

[22] M. Boubeche, J. Yu, C. Li, H. Wang, L. Zeng, Y. He, X. Wang, W. Su, M. Wang, D. Yao, Z. Wang, and H. Luo, Chin. Phys. Lett. 38, 037401 (2021).

[23] Y. Qi, Z. Gao, L. Wang, D. Wang, X. Zhang, C. Yao, C. Wang, C. Wang, and Y. Ma, EPL 97, 17008 (2012).

[24] M. Robbins, R. H. Willens, and R. C. Miller, Solid State Commun. 5, 933 (1967).

[25] M. Ito, K. Ishii, F. Nakamura, and T. Suzuki, Physica B 359–361, 1198 (2005).

[26] M. I. Kholil and M. T. H. Bhuiyan, Results Phys. 12, 73 (2019).

[27] N. Ni, M. E. Tillman, J. Q. Yan, A. Kracher, S. T. Hannahs, S. L. Bud’ko, and P. C. Canfield, Phys. Rev. B 78, 214515 (2008).

[28] C. Wang, Y. K. Li, Z. W. Zhu, S. Jiang, X. Lin, Y. K. Luo, S. Chi, L. J. Li, Z. Ren, M. He, H. Chen, Y. T. Wang, Q. Tao, G. H. Cao, Z. A. Xu, Phys. Rev. B 79, 054521 (2009).

[29] L. Li, Y. Luo, Q. Wang, H. Chen, Z. Ren, Q. Tao, Y. Li, X. Lin, M. He, Z. Zhu, G. Cao, and Z. Xu, New J. Phys. 11, 025008 (2009).

[30] F. Han, X. Zhu, P. Cheng, G. Mu, Y. Jia, L. Fang, Y. Wang, H. Luo, B. Zeng, B. Shen, L. Shan, C. Ren, and H.-H. Wen, Phys. Rev. B 80, 024506 (2009).

[31] S. Sharma, A. Bharathi, S. Chandra, V. R. Reddy, S. Paulraj, A. T. Satya, V. S. Sastry, A. Gupta, and C. S. Sundar, Phys. Rev. B 81, 174512 (2010).

[32] X. Zhu, F. Han, G. Mu, P. Cheng, J. Tang, J. Ju, K. Tanigaki, and H.-H. Wen, Phys. Rev. B 81, 104525 (2010).

[33] G. Kresse, J. Non-Cryst. Solids 192–193, 222 (1995).

[34] G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).

[35] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).

[36] N. Marzari and D. Vanderbilt, Phys. Rev. B 56, 12847 (1997).

[37] G. Zhi, C. Xu, S. Wu, F. Ning, and C. Cao, Comp. Phys. Commun. 271, 108196 (2022).

[38] B. T. Matthias, E. Corenzwit, and C. E. Miller, Phys. Rev. 93, 1415 (1954).

[39] J. Guo, Y. Qi, S. Matsuishi, and H. Hosono, J. Am. Chem. Soc. 134, 20001 (2012).

[40] J. D. Splett, D. F. Vecchia, and L. F. Goodrich, U.S. Department of Commerce, J. Res. Natl. Inst. Stan. 116, 489 (2011).

[41] R. Prozorov and V. G. Kogan, Phys. Rev. Appl. 10, 014030 (2018).

[42] H. Luo, W. Xie, J. Tao, I. Pletikosic, T. Valla, G. S. Sahasrabudhe, G. Osterhoudt, E. Sutton, K. S. Burch, E. M. Seibel, J. W. Krizan, Y. Zhu, and R. J. Cava, Chem. Mater. 28, 1927 (2016).

[43] A. M. Clogston, Phys. Rev. Lett. 9, 266 (1962).

[44] X. L. Wang, S. X. Dou, M. Hossain, Z. X. Cheng, and T. Silver, Phys. Rev. B 81, 224514 (2010).

[45] K. S. B. De Silva, X. Xu, X. L. Wang, D. Wexler, D. Attard, F. Xiang, and S. X. Dou,Scr. Mater. 67, 802 (2012).

[46] H. T. Wang, L. J. Li, D. S. Ye, X. H. Cheng, and Z. A. Xu, Chin. Phys. B 16, 2471 (2007).

[47] M. X. Liu and Z. Z. Gan, Chin. Phys. B 16, 826 (2007).

[48] W. L. McMillan, Phys. Rev. 167, 331 (1968).

[49] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.105.054513 for details on the Rietveld refinements and EDXS data.