The effects of electron correlation and spin-orbit coupling in the isovalent Pd-doped superconductor SrPt$_3$P

Kangkang Hu, Bo Gao, Qiucheng Ji, Yonghui Ma, Wei Li, Xuguang Xu, Hui Zhang, Gang Mu, Fuqiang Huang, Chuanbing Cai, Xiaoming Xie, and Mianheng Jiang

1State Key Laboratory of Functional Materials for Informatics and Shanghai Center for Superconductivity, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai 200050, China
2Shanghai Key Laboratory of High Temperature Superconductors, Shanghai University, Shanghai 200444, China
3School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China
4CAS-Shanghai Science Research Center, Shanghai 201203, China
5CAS Key Laboratory of Materials for Energy Conversion, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China

Dated: January 13, 2016

We present a systematical study on the roles of electron correlation and spin-orbit coupling in the isovalent Pd-doped superconductor SrPt$_3$P. By using solid state reaction method, we fabricated the strong spin-orbit coupling superconductors Sr(Pt$_{1-x}$Pd$_x$)$_3$P with strong electron correlated Pd dopant of the 4d orbital. As increasing the isovalent Pd concentrations without introducing any extra electron/hole carriers, the superconducting transition temperature $T_c$ decreases monotonously, which suggests the existence of competition between spin-orbit coupling and electron correlation in the superconducting state. In addition, the electronic band structure calculations demonstrate that the strength of electron susceptibility is suppressed gradually by the Pd dopant suggesting the incompatible relation between spin-orbit coupling and electron correlation, which is also consistent with experimental measurements. Our results provide significant insights in the natures of the interplay between the spin-orbit coupling and the electron correlation in superconductivity, and may pave a way for understanding the mechanism of superconductivity in this 5d-metal-based compound.

PACS numbers: 74.70.Wz, 75.47.-m, 71.70.Di, 74.25.Jb

I. INTRODUCTION

The study of strong interplay among charge, spin, orbital, and lattice degrees of freedom in transition metal compounds has triggered enormous research interests in the communities of condensed matter physics and material physics. One of the most prominent example is the unconventional high-transition temperature (high-$T_c$) superconductivity induced by the strong electron correlation in the copper oxide and iron-based superconductors [1] [2]. In those materials, apparently, the spin degree of freedom plays a vital role and the orbital degree of freedom is decoupled from that of spin. However, in strong spin-orbit coupling superconductors, such as the recent discovered platinum-based superconductors APt$_3$P (A = Ca, Sr and La) [3] [10], the systems display weak electron correlation effect. The relation between strong electron correlation and spin-orbit coupling still remains unclear. To clarify the nature of the interplay between spin-orbit coupling and electron correlation in superconductors is a crucial issue not only in condensed matter physics, but also in material science. Motivated by this issue, we focus our great attentions on the isovalent Pd doped platinum-based superconductors SrPt$_3$P, where the strength of the spin-orbit coupling and electron correlation can be tuned by the Pd concentration without introducing any extra electron or hole carriers into the system. This physics is quite different from the case that of the Lanthanum-based superconductor LaPt$_3$P, where the extra electron is injected into the system as strontium is replaced by Lanthanum leading to the decrease of the total density of states (DOS) at the Fermi level, which results in the suppression of superconducting transition temperature $T_c$ [7].

In this paper, the Pd dopant with strong electron correlation of 4d orbital was successfully substituted to the site of Pt in strong spin-orbit coupling superconductor SrPt$_3$P, which was confirmed by the x-ray diffraction measurements. The crystal lattice was found to shrink along the c-axis and expand along the a-axis monotonously as increasing the Pd concentrations. Importantly, we find that the superconducting transition temperature $T_c$ decreases with Pd doping, which could not be attributed to the physics of changes of the DOS at the Fermi level and the impurity scattering. Thus, it suggests that the system exhibits a competition between electron correlation and spin-orbit coupling in our system. Such a competing relation is also consistent with the first-principles calculation, which show that the strength of electron susceptibility is suppressed gradually as increasing Pd dopants.

liwei@mail.sim.ac.cn
mugang@mail.sim.ac.cn
II. EXPERIMENTS

The samples in this work were prepared via solid state reaction from the pure elements. [11] Firstly, we put stoichiometric amounts of platinum powder (purity 99.97%, Alfa Aesar), red phosphorus powder (purity 99.9%, Aladdin), and strontium pieces (purity 98%+, Alfa Aesar) together and ground them in a mortar. After that, the mixture was pressed into a small pellet and then sealed in a clean vacuum quartz tube. All the weighing and mixing procedures were carried out in a glove box with a protective argon atmosphere. The tube was heated up to 400 °C and held for 10 hours to prevent red phosphorus from volatilizing so quickly, and calcined at 900 °C for 2 days. The sintered pellet was reground and further annealed at 900 °C within an argon-filled quartz tubes for 3 days. The doped samples Sr(Pt_{1−x}Pd_x)P were prepared with adding corresponding amount of palladium powder (purity 99.95%, Alfa Aesar) using the same method as mentioned above.

The structure of the obtained samples were checked using a DX-2700 type powder x-ray diffractometer. The magnetic susceptibility measurements were carried out on the magnetic property measurement system (Quantum Design, MPMS 3). The electrical resistance was measured using a four-probe technique on the physical property measurement system (Quantum Design, PPMS).

III. RESULTS AND DISCUSSIONS

A. Crystal Structure

The crystal structure of this system has been reported by T. Takayama et al. previously [3]. Here we concentrate to the influences on the crystal lattice by the Pd substitution. For this reason, we measured the powder X-ray diffraction (XRD) on this series of materials and the diffraction patterns are shown in Fig. 1 (a). It is found that the main diffraction peaks can be indexed to the tetragonal structure with the space group P4/nmm as shown in Fig. 1(c). The black line represents the parent compound SrPt₃P. The asterisks refer to some unknown impurities which was also observed by T. Takayama et al. [3] With the increase of the amount of Pd (x), there is no obvious increase of the impurity phases. However, the positions of diffraction peaks start to move apparently when x changes from 0 to 0.4, which points to the variation of the size of the crystal lattice. This tendency can be seen clearly in Fig. 1(b), where we enlarge the region near the (220) diffraction peak as an example.

To investigate the influences on the crystal lattice by the Pd substitution quantitatively, we obtained the lattice parameters by fitting the XRD data using the software Powder-X. [12] The results are shown in Fig. 1(d). As is shown in the graph, the crystal lattice shows a shrinkage along the c-axis, while it expands along the a-axis with the increase of doping. This tendency is very similar to that observed in 4d- and 5d-metal-doped iron arsenides SrFe_{2−x}M_xAs_2 (M=Rh, Ir, Pd), [13] which proves that Pd atoms take the place of Pt atoms leading to the alteration of cell parameters. In the high doping region above 0.4, the variation of the lattice parameters becomes gentle, indicating the limit of the chemical substitution. We note that this is a common phenomenon in some chemical doped materials and such a saturated features has been reported elsewhere. [14]

B. Superconducting Properties

In order to study the effect of Pd-doping on the superconducting properties, we performed the temperature dependent magnetization and resistivity measurements on all the samples we synthesized. The temperature dependence of dc magnetic susceptibility is shown in Fig. 2(a), where we can see a sharp decline to the negative sides of the data for each sample with different doping. The clear diamagnetic signal indicates the occurrence of the superconducting transition and the onset transition point defines the critical transition temperature Tc. With the increase of amount of Pd, the value of Tc reduces apparently. This tendency is confirmed by the resistivity data, which is shown in Fig. 2(b). Clear superconducting transitions to zero resistance were observed on all the samples with different doping levels. The onset transition temperatures determined from this figure, along

FIG. 1: (color online) (a) X-ray diffraction patterns for the Sr(Pt_{1−x}Pd_x)P samples with 0 ≤ x ≤ 0.4. Small amount of impurity phases are indexed by the blue asterisks. (b) An enlarged view of the (220) peak. It is clear that the peak shifts monotonously to the left direction with doping. (c) Crystal structure of SrPt₃P. Pd element was substituted into the site of Pt in this work. (d) Doping dependence of the lattice constants along a-axis and c-axis.
with that determined from the $M - T$ curves, are displayed in Fig. 2(c). The blue symbols were obtained from the magnetization measurements while the purple ones were defined by the resistivity measurements. It can be seen that the two sets of $T_c$ values evolve parallelly and decrease linearly with doping.

Generally speaking, the suppression of superconducting transition temperature $T_c$ is usually related to the changes of DOS at Fermi level, as has been reported in the Lanthanum replaced superconductor LaPt$_3$P by comparing with SrPt$_3$P. However, the calculated DOS by means of density functional theory demonstrated that the DOS around the Fermi level remains almost the same for different concentrations of Pd dopants [see Fig. 3(d)], which will be discussed in the next section in detail. This result is reasonable since the Palladium is isovalent to Platinum making the carriers of the system remain unchanged. Thus, it rules out the possibility of the effect from the changes of DOS on superconductivity in our system.

Another issue is the possible impurity scattering effect, which comes from the Palladium substitution for Platinum. This possibility can also be ruled out since SrPt$_3$P was reported to be an s-wave superconductor. According to the Anderson’s theorem, the non-magnetic impurity does not lead to an apparent pair-breaking effect in a conventional s-wave superconductor, and thus does not suppress the transition temperature $T_c$ apparently, which is in sharp contrast to that in a d-wave superconductor, where the gap function has a nodal line and the zero energy excitation spectra can be modified significantly by non-magnetic impurities leading to the suppression of $T_c$.

Since the experimental observation of the suppression of the $T_c$ does not originate from the changes of DOS at the Fermi level and the impurity scattering effect, the $T_c$ suppression is likely to be related to the interplay between the strong spin-orbit coupling and the electron correlation. As we have known, the spin-orbit coupling strength is proportional to $Z^4$ (where $Z$ is the atomic number; $Z_{Pt} = 78$ for Pt and $Z_{Pd} = 46$ for Pd), the ratio $\gamma = (Z_{Pd}^4/Z_{Pt}^4) = 8.3$ and consequently the spin-orbit coupling strength will be decreased dramatically when the Platinum is substituted by Palladium. In addition, the bandwidth of Pd 4$d$ orbitals is narrower than that of Pt 5$d$ orbitals making the electron correlation in Pd 4$d$ orbital electrons is stronger than that in Pt 5$d$ orbital electrons. Therefore, when the enhancement of the strength of electron correlation by Palladium dopants is comparable to that of spin-orbit coupling, the interplay between electron correlation and the spin-orbit coupling will play a crucial rule in superconductivity and affect the superconducting transition temperature $T_c$.

C. First-Principles Calculations

In order to clarify the interplay between electron correlation and spin-orbit coupling and the origins for the suppression of $T_c$ by Pd doping in superconductor Sr(Pt$_{1-x}$Pd$_x$)$_3$P theoretically, we carried out the first-principles band structure calculations on the Pd dopant dependent samples with $x = 0$, $x = 0.17$, and $x = 0.33$. The calculations were performed by using the pseudopotential-based code VASP within the Perdew-Burke-Ernzerhof generalized gradient approximation. Throughout the theoretical calculations, a 500 eV cutoff in the plane wave expansion and a $12 \times 12 \times 12$ Monkhorst $\vec{k}$ grid were chosen to ensure the calculation with an accuracy of $10^{-5}$ eV. The atomic coordinates were obtained by the relaxation based on the lattice parameters from experiments. Additionally, the spin-orbit coupling had been included throughout the calculations.

In Fig. 3, we show the energy band structures and their corresponding DOS. By comparing the energy band structures and DOS with different Pd dopants, the low energy features of electronic structures remain almost the same, except for lifting the degenerate bands and changing their dispersion at some high symmetric momentum points around the Fermi level. This originates from the nature of dopant Pd. When the atom Pt in SrPt$_3$P is partially substituted by Pd, the high symmetry of point group of system was lowered leading to the lifting of some degenerate energy bands. In addition, since the Pd atom with 4$d$ orbital has a stronger electron correlation than that of Pt with 5$d$ orbital, the strong electron-electron interaction changes the low energy dispersion and makes it more flat with a large effective mass.

To quantitatively find the relation between electron
correlation and spin-orbit coupling in the present isovalent Pd doped system, we further carried out the electron susceptibility calculations. The bare electron susceptibility, χ₀(q), is given by:

\[
χ₀(q) = \frac{1}{N_k} \sum_{μνk} \frac{|\langle k + q, μ | k, ν \rangle|^2}{E_{μ,k+q} - E_{ν,k} + i0^+ [f(E_{ν,k}) - f(E_{μ,k+q})]},
\]

where \(E_{μ,k}\) represents the band energy measured at Fermi level \(E_F\), and \(f(E_{μ,k})\) is the Fermi-Dirac distribution function for an eigenstate, \(|k, μ\rangle\). In addition, \(N_k\) denotes the number of \(k\) points used for the irreducible Brillouin zone integration. The calculated real part of electron susceptibility is shown in Fig. 4, which demonstrates that the peak of electron susceptibility is suppressed as increase the Pd dopant concentrations. This result along with our experimental facts suggest the electron susceptibility of system originating from the itinerant electrons with strong spin-orbit coupling, which is responsible for superconductivity, is weakened by introducing the electron correlation, and thus suggesting this system displays a competition between the electron correlation and spin-orbit coupling, which seems to be unfavorable for superconductivity.

IV. CONCLUSION

In conclusion, we have successfully substituted Pd elements into the position of Pt in the strong spin-orbit cou-
pling superconductor SrPt$_3$P, and found that the doping of Pd not only leads to the change of lattice parameters, but also suppresses the superconducting transition temperature $T_c$. In addition, the band structure calculations reveal that the calculated strength of electron susceptibility is suppressed as increase the Pd dopant concentrations. These results suggest that the competition between spin-orbit coupling and electron correlation plays a vital role in superconductivity of the present 5$d$ electron system.

Acknowledgments

This work is supported by the Natural Science Foundation of China (No. 11204338, 11227902, and 11404359), the “Strategic Priority Research Program (B)” of the Chinese Academy of Sciences (No. XDB04040300), and the Youth Innovation Promotion Association of the Chinese Academy of Sciences (No. 2015187). This work is partly sponsored by the Science and Technology Commission of Shanghai Municipality (No. 14DZ2260700 and 14521102800).

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