Important Roles of Te 5p and Ir 5d Spin-orbit Interactions on the Multi-band Electronic Structure of Triangular Lattice Superconductor Ir\textsubscript{1-x}Pt\textsubscript{x}Te\textsubscript{2}

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We report an angle-resolved photoemission spectroscopy (ARPES) study on a triangular lattice superconductor Ir\textsubscript{1-x}Pt\textsubscript{x}Te\textsubscript{2} in which the Ir-Ir or Te-Te bond formation, the band Jahn-Teller effect, and the spin-orbit interaction are cooperating and competing with one another. The Fermi surfaces of the substituted system are qualitatively similar to the band structure calculations for the undistorted IrTe\textsubscript{2} with an upward chemical potential shift due to electron doping. A combination of the ARPES and the band structure calculations indicates that the Te 5p spin-orbit interaction removes the $p_x/p_y$ orbital degeneracy and induces $p_x \pm ip_y$ type spin-orbit coupling near the A point. The inner and outer Fermi surfaces are entangled by the Te 5p and Ir 5d spin-orbit interactions which may provide exotic superconductivity with singlet-triplet mixing.
KEYWORDS: spin-orbit coupling, Ir$_{1-x}$Pt$_x$Te$_2$, orbital degeneracy, angle-resolved photoemission spectroscopy, ...

4$d$ and 5$d$ transition-metal compounds with $t_{2g}$ orbital degeneracy exhibit rich and interesting physical properties due to the competition and/or the collaboration between the spin-orbit interaction and the (band) Jahn-Teller effect. For example, in perovskite-type Ca$_2$RuO$_4$, the Jahn-Teller splitting between the Ru 4$d$ $t_{2g}$ $yz/zx$ and $xy$ orbitals collaborates with the 4$d$ $t_{2g}$ spin-orbit coupling to stabilize the $yz + ixy$ or $zx + ixy$ orbital to give the magnetic anisotropy.\textsuperscript{1,2) In other perovskite-type Sr$_2$IrO$_4$, the strong spin-orbit interaction of the Ir 5$d$ $t_{2g}$ orbitals is dominating and provides the unique $j_{1/2}$ state.\textsuperscript{3,4)} On the other hand, in spinel-type CuIr$_2$S$_4$, the band Jahn-Teller effect and the Ir-Ir bond dimerization play essential roles in the charge-orbital ordering with the Ir 5$d$ $t_{2g}$ spin-orbit interaction being apparently inactive.\textsuperscript{5–7) The difference between the perovskite-type and spinel-type systems can be attributed to that between the corner sharing and edge-sharing Ir$_6$ octahedra. Yet, in Na$_3$IrO$_3$ with the edge-sharing of Ir$_6$ octahedra, whereas the $j_{1/2}$ state is suggested,\textsuperscript{8,9) based on the ab-initio calculation, it has recently been proposed that the $j_{1/2}$ and $j_{3/2}$ states are mixed due to formation of Ir 5$d$ molecular orbitals.\textsuperscript{10) In this context, it is highly desirable to study the Ir 5$d$ $t_{2g}$ electronic states in various Ir compounds in a systematic way.

The discovery of superconductivity in doped or intercalated IrTe$_2$ by Pyon \textit{et al.}\textsuperscript{11) and by Yang \textit{et al.}\textsuperscript{12) have added a new family of Ir chalcogenides to the list of fascinating 4$d$ and 5$d$ electron systems. IrTe$_2$ undergoes a structural phase transition at $\sim 270$ K from the trigonal (P-3m1) to the monoclinic (C2/m) structure.\textsuperscript{13) IrTe$_2$ and its derivatives show an interesting interplay between lattice instabilities and superconductivity in the triangular lattice. Since the Ir 5$d$-to-Te 5$p$ charge-transfer energy is found to be small,\textsuperscript{14) the Te 5$p$ orbitals can play significant roles as proposed by Fang \textit{et al.} and Oh \textit{et al.}\textsuperscript{15,16) Also the multi-band electronic structure of the Ir 5$d$ and Te 5$p$ orbitals in IrTe$_2$ can induce the (band) Jahn-Teller instability and the Peierls instability.\textsuperscript{17)} In the case of Ir$_{1-x}$Pt$_x$Te$_2$, the Ir-Ir bond,\textsuperscript{11,18) the Ir-Te bond, and/or the Te-Te bond\textsuperscript{15) can be affected by the Pt doing. In addition, the large Ir 5$d$ spin-orbit interaction can entangle the spin and orbital degrees of freedom in IrTe$_2$ and may induce nontrivial topological states.\textsuperscript{12) In order to reveal possible roles of the Ir 5$d$ and Te 5$p$ spin-orbit interactions in the Ir$_{1-x}$Pt$_x$Te$_2$, we have performed angle-resolved photoemission spectroscopy (ARPES) of Ir$_{0.95}$Pt$_{0.05}$Te$_2$ and compared the ARPES results with theoretical calculations with and without the Ir 5$d$ and Te 5$p$ spin-orbit interactions.

Single crystal samples of Ir$_{1-x}$Pt$_x$Te$_2$ were prepared using a self-flux method.\textsuperscript{15,19) The
photoemission measurements were performed at beamline 9A, Hiroshima Synchrotron Radiation Center using a SCIENTA R4000 analyzer with circularly polarized light. The total energy resolutions were set to 18 meV, 22 meV, and 29 meV for excitation energies of $h\nu = 23$ eV, 26 eV, and 29 eV, respectively. The angular resolution was set to $\sim 0.3^\circ$ that gives the momentum resolutions of $\sim 0.015$ Å$^{-1}$, 0.016 Å$^{-1}$, and 0.017 Å$^{-1}$ for $h\nu = 23$ eV, 26 eV, and 29 eV, respectively. The incident beam is 50$^\circ$ off the sample surface. The base pressure of the spectrometer was in the $10^{-9}$ Pa range. The samples were cleaved at 20 K under the ultrahigh vacuum. The samples were oriented by ex situ Laue measurements. The spectra were acquired within 8 hours after the cleavage. Binding energies were calibrated using the Fermi edge of gold reference samples. For the band structure calculations, we employ the code WIEN2k\cite{20} based on the full-potential linearized augmented-plane-wave method and present the calculated results obtained in the generalized gradient approximation (GGA) for electron correlations, where we use the exchange-correlation potential of Ref.\textsuperscript{21}.\cite{21} The spin-orbit interaction is taken into account for both Ir and Te ions when necessary. We use the crystal structure and atomic positions measured for IrTe\textsubscript{2} at room temperature.\cite{22} In the self-consistent calculations, we use 264 $k$-points in the irreducible part of the Brillouin zone with an anisotropic sampling to achieve better convergence. Muffin-tin radii ($R_{MT}$) of 2.50 (Ir) and 2.42 (Te) Bohr are used and we assume the plane-wave cutoff of $K_{\text{max}} = 7.0/R_{MT}$.

In Fig. 1, the ARPES spectra along the A-H direction of Ir\textsubscript{0.95}Pt\textsubscript{0.05}Te\textsubscript{2} are compared with those of IrTe\textsubscript{2} above the structural transition temperature. The ARPES spectra are compared with the band dispersions obtained for undistorted IrTe\textsubscript{2} using the GGA calculation with the Ir 5$d$ and Te 5$p$ spin-orbit interactions. As for Ir\textsubscript{0.95}Pt\textsubscript{0.05}Te\textsubscript{2}, it is assumed that the Pt doping introduces 0.05 electron per Ir and that the chemical potential is shifted upwards in the band structure for undistorted IrTe\textsubscript{2}. The experimental and theoretical band dispersions are in qualitative agreement for IrTe\textsubscript{2} above the transition temperature as well for Ir\textsubscript{0.95}Pt\textsubscript{0.05}Te\textsubscript{2}. Near the Fermi level, as predicted by the calculation, the inner band forms the small hole pockets around the A point (the inner Fermi surfaces) while the outer band forms the large Fermi surface (the outer Fermi surface). If the Pt doping supplies electrons to the Ir 5$d$ and Te 5$p$ bands, the entire band should be shifted downwards in going from IrTe\textsubscript{2} to Ir\textsubscript{0.95}Pt\textsubscript{0.05}Te\textsubscript{2}. Indeed, the calculation for Ir\textsubscript{0.95}Pt\textsubscript{0.05}Te\textsubscript{2} is shifted downwards assuming the rigid band model and agrees very well with the experimental result. The energy shift between IrTe\textsubscript{2} and Ir\textsubscript{0.95}Pt\textsubscript{0.05}Te\textsubscript{2} is consistent with the rigid band shift of the calculated results, indicating that the Pt doping provides electrons to the Ir 5$d$ and Te 5$p$ bands.

Figure 2(a) and (b) show the Fermi surface maps for Ir\textsubscript{0.95}Pt\textsubscript{0.05}Te\textsubscript{2} taken at 23 eV with
right-handed and left-handed circularly polarized light, respectively. The six hole pockets around the A point (the inner Fermi surfaces) and the large Fermi surface (the outer Fermi surface) are partly observed as predicted by the band structure calculation. As for the inner Fermi surfaces, the upper three hole pockets tend to be emphasized with the right-handed circularly polarized light, while the lower three hole pockets gain their intensity with the left-handed circularly polarized light. The asymmetric intensity due to the transition-matrix element effect is partially removed by summing the Fermi surface maps, and the six fold symmetry of the six hole pockets are more clearly seen as displayed in Fig. 2(c). Here, the transition-matrix element effect still remains since the incident light is 50° off the sample surface.

Figures 3(a), (b) and (c) show the evolution of the Fermi surfaces by changing the photon energy. The momentum perpendicular to the surface \( k_z \) is \( \sim \pi/c, 9\pi/10c, \) and \( 8\pi/10c \) for 23 eV, 26 eV, and 29 eV, respectively. The Fermi surface maps extracted from the ARPES data are compared with the theoretical Fermi surfaces which are obtained by the rigid band shift of the GGA calculation with and without the spin-orbit interactions for undistorted IrTe\(_2\) for \( k_z = \pi/c, 9\pi/10c, \) and \( 8\pi/10c, \) respectively. The calculations with and without the spin-orbit interactions indicates that the effect of the spin-orbit interaction is more significant for the inner Fermi surfaces than the outer one. At 23 eV, the area of the inner Fermi surfaces is well reproduced by the calculation with the spin-orbit interactions as shown in Fig. 3(a). The effect of the spin-orbit interaction is more pronounced at 29 eV. Without the spin-orbit interactions, even the geometry of the calculated Fermi surfaces is different from the ARPES results. On the other hand, the Fermi surfaces calculated with the spin-orbit interaction are consistent with the ARPES results.

In Fig. 3(d), the Fermi surface map is compared with the calculation with (without) the Te 5\( p \) (Ir 5\( d \)) spin-orbit interaction and that with (without) the Ir 5\( d \) (Te 5\( p \)) spin-orbit interaction. The calculation with the Ir 5\( d \) spin-orbit interaction agrees with the ARPES results than the calculation with the Te 5\( p \) spin-orbit interaction, indicating that the Ir 5\( d \) spin-orbit interaction is more important than the Te 5\( p \) spin-orbit interaction for the area of the inner Fermi surfaces.

The band dispersions along the A-H and A-L directions are compared with the calculated results with and without the spin-orbit interactions in Figs. 4(a) and (b). The spin-orbit band splitting at -0.5 eV between the inner bands around the A point and that at -0.25 eV between the inner and outer bands in the A-H cut are clearly observed in the APRES results (indicated by the arrows), as predicted by the GGA calculation with the spin-orbit interactions. The GGA calculation predicts that, around the A point, the inner bands near the Fermi level are
mainly derived from the Te 5px and 5py orbitals. Therefore, the band splitting at -0.5 eV around the A point can be attributed to the px ± ipy type spin-orbit coupling. In going from the A point to the H point, the inner bands dominated by the Te 5px and 5py orbitals tend to have some contribution of the Ir 5d e_g orbitals. On the other hand, the outer Fermi surface is mainly constructed from the Te 5pz orbitals with some contribution of the Ir 5d a_1g orbitals. The band splitting at -0.25 eV between the inner and outer bands in the A-H cut would be due to the pz ± ipx type or pz ± ipy type Te 5p spin-orbit coupling with some contribution of the Ir 5d spin-orbit coupling. In order to clarify the different roles of the Ir 5d and Te 5p spin-orbit interactions, the band dispersions along the A-H and A-L directions are compared with the calculation with (without) the Te 5p (Ir 5d) spin-orbit interaction and that with (without) the Ir 5d (Te 5p) spin-orbit interaction in Figs. 4(c) and (d). Although the intensity of the outer band is very small in Figs. 4(a) and (c), the dispersion of the outer band can be seen in the enlarged plot of Fig. 4(e). The band splitting at -0.5 eV around the A point is dominated by the Te 5p spin-orbit interaction which provides the px ± ipy type spin-orbit coupling as discussed above. On the other hand, although the band splitting at -0.25 eV between the inner and outer bands in the A-H cut is induced by the Te 5p spin-orbit interaction, the magnitude of the splitting is much more enhanced by the inclusion of the Ir 5d spin-orbit coupling. Therefore, as for the spin-orbit coupling between the inner and outer bands, the coupling between the Ir 5d a_1g and Ir 5d e_g orbitals has a substantial contribution although the inner and outer bands are dominated by the Te 5p character.

In Ir1−xPtxTe2, the inner and outer bands are very close to each other near the Fermi level along the A-H direction, and the Te 5p and Ir 5d spin-orbit interactions introduce the strong entanglement between the spin and orbital parts of the electrons. The recent ARPES study on Sr2RuO4 revealed that the strong spin-orbital entanglement provides mixing of spin-singlet and spin-triplet Cooper pairs and may cause an exotic superconducting state. Since the magnitude of the spin-orbit interaction in Ir0.95Pt0.05Te2 is much stronger than that in Sr2RuO4, one can expect stronger mixing between spin-singlet and spin-triplet Cooper pairing in the Ir0.95Pt0.05Te2.

In conclusion, we have studied the multi-band electronic structure of triangular lattice superconductor Ir1−xPtxTe2 using ARPES. The Pt doping introduces the electrons to the Ir 5d and Te 5p bands and the simple rigid band model is consistent with the observed band dispersions and the Fermi surfaces. The inner and outer Fermi surfaces with the strong Te 5p character are very close to each other along the A-H direction, and the strong Te 5p and Ir 5d spin-orbit interaction in this particular momentum region results in the mixing between the
Fig. 1. (color online) (a) ARPES spectra of IrTe₂ along the A-H direction taken at 300 K above the structural transition temperature. The solid curves indicate the band dispersions obtained for undistorted IrTe₂ using the GGA calculation with the Te 5p and Ir 5d spin-orbit interactions. (b) ARPES spectra of Ir₀.₉₅Pt₀.₀₅Te₂ along the A-H direction taken at 20 K. The solid curves indicate the calculation shifted by the electron doping by Pt. (c) Schematic drawings for the crystal structure visualized using the software VESTA³³ and the first Brillouin zone of Ir₀.₉₅Pt₀.₀₅Te₂.

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Fig. 2. (color online) (a) Fermi surface map for Ir\(_{0.95}\)Pt\(_{0.05}\)Te\(_2\) with right-handed circularly polarized light. (b) Fermi surface map for Ir\(_{0.95}\)Pt\(_{0.05}\)Te\(_2\) with left-handed circularly polarized light. (c) Sum of the Fermi surface maps.

Fig. 3. (color online) (a) Fermi surface map for Ir\(_{0.95}\)Pt\(_{0.05}\)Te\(_2\) at 23 eV compared with the GGA calculations with and without the spin-orbit interactions. (b) Fermi surface map for Ir\(_{0.95}\)Pt\(_{0.05}\)Te\(_2\) at 26 eV compared with the GGA calculations with and without the spin-orbit interactions. (c) Fermi surface map for Ir\(_{0.95}\)Pt\(_{0.05}\)Te\(_2\) at 29 eV compared with the GGA calculations with and without the spin-orbit interactions. (d) The GGA calculation with (without) the Te 5\(p\) (Ir 5\(d\)) spin-orbit interaction and that with (without) the Ir 5\(d\) (Te 5\(p\)) compared with the Fermi surface map at 23 eV.
Fig. 4. (color online) ARPES spectra of Ir$_{0.95}$Pt$_{0.05}$Te$_2$ along the A-H direction (a) and along the A-L direction (b) compared with the GGA calculations with and without the spin-orbit interactions. The red dots and light blue curves indicate the band dispersions calculated with and without the spin-orbit interaction, respectively. The arrows indicate spin-orbit splitting. ARPES spectra of Ir$_{0.95}$Pt$_{0.05}$Te$_2$ along the A-H direction (c) and along the A-L direction (d) compared with the GGA calculation with (without) the Te 5$p$ (Ir 5$d$) spin-orbit interaction and that without (with) the Te 5$p$ (Ir 5$d$). The red closed circles and the blue open circles indicate the band dispersions calculated with the Ir 5$d$ and Te 5$p$ spin-orbit interactions, respectively. The arrows indicate spin-orbit splitting. (e) Second derivative plot of momentum distribution curves(MDC) for the region indicated by the box in panel (a). The open circles indicate the peak position obtained from MDC.
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