Effect of Pt substitution on the electronic structure of AuTe$_2$

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We report a photoemission and x-ray absorption study on a Au$_{1-x}$Pt$_x$Te$_2$ ($x = 0$ and 0.35) triangular lattice in which superconductivity is induced by Pt substitution for Au. Au 4$f$ and Te 3$d$ core-level spectra of AuTe$_2$ suggest a valence state of Au$^{1+}$(Te$_2$)$^{2-}$, which is consistent with its distorted crystal structure with Te-Te dimers and compressed AuTe$_6$ octahedra. On the other hand, valence-band photoemission spectra and preedge peaks of the Te 3$d$ absorption edge indicate that Au 5$d$ bands are almost fully occupied and that Te 5$p$ holes govern the transport properties and the lattice distortion. The two apparently conflicting pictures can be reconciled by strong Au 5$d$/Au 6$s$--Te 5$p$ hybridization. The absence of a core-level energy shift with Pt substitution is inconsistent with the simple rigid band picture for hole doping. The Au 4$f$ core-level spectrum gets slightly narrow with Pt substitution, indicating that the small Au 5$d$ charge modulation in distorted AuTe$_2$ is partially suppressed.

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I. INTRODUCTION

Layered transition-metal dichalcogenides with a triangular motif have been attracting renewed interest due to the discovery of superconductivity in chemically substituted IrTe$_2$ [1–4] and AuTe$_2$ [5] with a maximum $T_c$ of 3.1 and 4.0 K, respectively. In particular, the electronic structure of IrTe$_2$ and its derivatives has been studied intensively using various spectroscopic methods under anticipation that the strong spin-orbit interaction in the Ir 5$d$ and Te 5$p$ orbitals may provide a novel spin-momentum entangled quantum state [6–9]. Also details of the structural transition in IrTe$_2$ [10,11] have been revealed by recent studies using advanced x-ray diffraction and scattering techniques [12–16]. On the other hand, so far, electronic structure studies on AuTe$_2$ and its derivatives have been limited, although the Au 5$d$ and/or Te 5$p$ electrons with strong spin-orbit interaction can provide an interesting electronic state.

AuTe$_2$ is known as a natural mineral Calaverite with a monoclinically distortedCd$_2$-type layered structure (space group $C2/m$) [17]. Each Au-Te layer contains edge-shared AuTe$_6$ octahedra that are strongly distorted with two short (2.67 Å) and four long (2.98 Å) Au-Te bonds due to Te-Te dimer formation in the average structure [17,18]. A detailed analysis of the crystal structure has revealed incommensurate structural modulation, which may indicate charge ordering of Au 5$d$ and/or Te 5$p$ valence electrons [19]. Although Au$^+$/Au$^{3+}$ charge disproportionation has been suggested to explain the structural distortion [19], the expected Au valence modulation has not been detected by x-ray photoemission spectroscopy [20]. In addition, ab initio calculations have indicated that the Au 5$d$ subshell is almost fully occupied by electrons, and the Te-Te dimer formation due to the partially occupied Te 5$p$ subshell should be responsible for the structural distortion [21]. Very recently, Kudo et al. have found that Pt substitution for Au suppresses the lattice distortion of AuTe$_2$, and that Au$_{1-x}$Pt$_x$Te$_2$ with an undistortedCd$_2$-type ($P5_21m$) structure exhibits superconductivity with a maximum $T_c$ of 4.0 K [5]. The electronic phase diagram for Au$_{1-x}$Pt$_x$Te$_2$ is similar to Ir$_{1-x}$Pt$_x$Te$_2$, indicating an intimate relationship between the lattice distortion in AuTe$_2$ and the superconductivity in Au$_{1-x}$Pt$_x$Te$_2$. In the present work, we have studied the fundamental electronic structure of Au$_{1-x}$Pt$_x$Te$_2$ ($x = 0$ and 0.35) by means of ultraviolet photoemission spectroscopy (UPS), x-ray photoemission spectroscopy (XPS), and x-ray absorption spectroscopy (XAS). The valence-band UPS and XPS results show that the Au 5$d$ and Te 5$p$ orbitals are strongly hybridized near the Fermi level. The core-level XPS results indicate small charge distribution of the Au 5$d$ electrons, which is suppressed by the Pt substitution. The active role of the Te 5$p$ holes is indicated by the Te 3$d$ XAS measurement.

II. EXPERIMENTS

The polycrystalline samples of Au$_{1-x}$Pt$_x$Te$_2$ ($x = 0.35$, $T_c = 4.0$ K) and single crystals of AuTe$_2$ were prepared as reported in the literature [5]. Single crystals of AuTe$_2$ were cleaved for UPS and XAS at 300 K. UPS measurements were performed at UBC using a SPECS Phoibos 150 analyzer with the He I line (21.2 eV) from a monochromatized UVS300 lamp. The total energy resolution was set to 25 meV. The base pressure was in the 10$^{-11}$ mbar range. XAS measurements were performed at beamlines 11ID-1 and 10ID-2 [22], Canadian Light Source. The total-energy resolution was 100 meV. The base pressure of the XAS chamber was in the 10$^{-9}$ mbar range. The spectra were measured in the total-electron-yield (TEY) mode. XPS measurements were carried out using a JEOL JPS9200 analyzer. Mg Kα (1253.6 eV) was used as an x-ray...
of Au is +4 in Au1−xPtxTe2, the Au 4f1/2 peaks are slightly higher in binding energy than that of pure Au (84.0 eV) and located between the Au+ and Au3+ peaks of Cs2Au2Br6, suggesting that the actual average Au valence in Au1−xPtxTe2 is close to 2+. Although the Au2+ ion is expected to take the 5d0 configuration, the band-structure calculations on the average structure indicate that the Au 5d bands are almost fully occupied [21,24].

The Te 3d core-level spectra of Au1−xPtxTe2 (x = 0 and 0.35) are displayed in Fig. 2. The binding energy of the Te 3d3/2 core level is close to that of pure Te (573.0 eV) [25], suggesting that the Te 5p orbitals are not fully occupied and contribute to the electronic states at the Fermi level. The shoulder structures located at ~576 eV and ~587 eV for Te 3d5/2 and Te 3d3/2 are derived from Te oxide contaminations, which were also observed in the IrTe2 single crystals and the Ir1−xPtxTe2 polycrystalline samples [6]. The shoulder structures in the AuTe2 single crystal and the polycrystalline Au1−xPtxTe2 are much smaller than that in the polycrystalline Ir1−xPtxTe2 and are as small as that in the high-quality IrTe2 single crystal, indicating that the surface quality of AuTe2 and Au1−xPtxTe2 is reasonably good.

To clarify the effect of Pt substitution, we have subtracted the core-level spectrum of Au0.65Pt0.35Te2 from that of AuTe2 as displayed in Figs. 1 and 2. The Au 4f and Te 3d core-level peaks do not show an appreciable energy shift with the Pt substitution. The difference spectrum shows that the Au 4f core-level spectrum of AuTe2 gets slightly narrow with the Pt substitution, while it does not affect the Te 3d core level appreciably. This indicates small Au 5d charge modulation in distorted AuTe2 and partial suppression of the charge modulation by the Pt substitution. Here, one cannot fully exclude the possibility that the Au valence at the surface is different from the bulk and that the surface component is enhanced in AuTe2. However, the surface condition of the AuTe2 single crystal is expected to be better than Au0.65Pt0.35Te2, and the surface component in AuTe2 should be smaller than the polycrystalline case if it exists. On the other hand, the Au 4f peak is broader in the AuTe2 single crystal than the polycrystalline case. Therefore, it is natural to assign the extra broadening in AuTe2 to the extra charge modulation instead of the surface effect.

In Fig. 3, valence-band XPS and UPS spectra of Au1−xPtxTe2 (x = 0 and 0.35) taken at 300 K are displayed. The valence-band UPS and XPS spectra of Au1−xPtxTe2 show several structures. The broad structures ranging from 0 to 4 eV below the Fermi level can be assigned to the Te 5p orbitals (mixed with the Au 5d/6s orbitals) on the basis of the band-structure calculations on AuTe2 [21,24]. The structures from 4.0 to 6.5 eV can be assigned to the charge modulation by the Pt substitution. Here, one cannot fully exclude the possibility that the Pt substitution for Au may correspond to hole doping to the Te 5p bands mixed with the Au 5d/6s orbitals. Another possibility is that mixing of the

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**III. RESULTS AND DISCUSSION**

Figure 1 shows the Au 4f core-level spectra of Au1−xPtxTe2 (x = 0 and 0.35) taken at 300 K, which are compared with Cs2Au2Br6 with Au+ and Au3+ sites. The broad Au 4f1/2 peak of AuTe2 would be consistent with the Au valence modulation due to the lattice distortion. However, the Au 4f1/2 peak width of Au0.65Pt0.35Te2 without the distortion is also comparable to that of AuTe2. While the formal valence
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FIG. 2. (Color online) Te 3d core-level XPS spectra of AuTe₂ and Au₀.₆₅Pt₀.₃₅Te₂. The dash-dot curves indicate background due to secondary electrons. The background subtracted spectra of Au₀.₆₅Pt₀.₃₅Te₂ are overlaid with that of AuTe₂, and the difference spectrum between the background-subtracted spectra is indicated by the solid curve with a shaded peak area.

Au 5d bands with the Pt 5d bands leads to the energy shift of the Au/Pt 5d bands since the Pt 5d bands are expected to have lower binding energy than the Au 5d bands. The absence of the core-level energy shift is inconsistent with the former scenario (hole doping in a rigid band manner) and supports the latter scenario, namely that the Pt substitution changes the shape of the valence band constructed from the Au/Pt 5d/6s and Te 5p orbitals, and it cannot be viewed as a simple hole doping to AuTe₂ in a rigid band manner.

The average Au valence close to +2 and the unoccupied Te 5p orbitals indicate that the charge-transfer energy from the Te 5p orbitals to the Au 5d orbitals is negative to stabilize the valence state of Au²⁺(Te₂)²⁻. Namely, the local electronic configuration of the AuTe₆ octahedron is close to d⁸L² (L represents a ligand hole in the Te 5p orbitals) instead of d⁷. Therefore, each Te site accommodates approximately one hole, and the Te 5p holes govern the transport properties and the lattice distortions in AuTe₂. This picture is consistent with the Te-Te dimers in AuTe₂ since the antibonding molecular orbital of the Te-Te dimer can be occupied by the two Te 5p holes from the two Te sites. On the other hand, the band-structure calculations on AuTe₂ with the average structure [21,24] as well as the valence-band spectra indicate that the Au 5d bands are almost fully occupied. To resolve this apparent paradox, strong hybridization between the Au 5d/6s and Te 5p orbitals should be taken into account. Starting from the Au²⁺(Te₂)²⁻ valence state, the hybridization between the Au 5d/6s orbitals and the Te-Te bonding and antibonding molecular orbitals can induce additional charge transfer. Since the Au 5d level in AuTe₂ is much lower than the Ir 5d level in IrTe₂, charge donation from the Te-Te bonding orbital to the Au 5d orbitals can be dominant in AuTe₂, whereas back donation from the Ir 5d orbitals to the Te-Te antibonding orbital would be substantial in IrTe₂. In addition, the Au 6s component can be mixed into the Au 5d bands through the strong Au 5d-Te 5p and Te 5p-Au 6s hybridizations. Therefore, although the “Au 5d bands” constructed from the atomic Au 5d, Au 6s, and Te 5p orbitals are fully occupied, as predicted by the band-structure calculations and observed by the valence-band photoemission experiments, the actual number of atomic Au 5d electrons in AuTe₂ can remain close to nine, which is consistent with the Au²⁺(Te₂)²⁻ valence state. The d⁹ configuration of Au²⁺ is consistent with the Jahn-Teller-like distortion of the AuTe₆ octahedra with two short and four long Au-Te bonds.

Figure 4 shows the Te 3d XAS spectrum of Au₁₋ₓPtₓTe₂ (x = 0 and 0.35). The preedge and main edge structures are clearly observed. The main-edge structure corresponds to the
transformation from the Te 3d core level to the unoccupied Te 4f/Au 6s,6p states. On the other hand, the preedge structure can be assigned to the transition from the Te 3d core level to the Te 5p orbitals, indicating that the Te 5p bands cross the Fermi level and that the Te 5p holes play essential roles in the transport properties. This Te 5p–hole picture is consistent with the XPS and XAS results. In AuTe2, the Te 5p orbitals are partially unoccupied, and the bond formation by the Te 5p holes creates the Te-Te dimers. The Te-Te dimer formation leads to the long and short Te-Te bonds [17,18], which can induce charge modulation of Au through the strong hybridization between the Au 5d and Te 5p orbitals. On the other hand, since all the Te sites belong to one of the Te-Te dimers, each Te site accommodates almost the same amount of Te 5p hole. When Pt is substituted for Au in Au2(Te2)2, Pt ions tend to be 3+ or 4+ and supply electrons to Te-Te antibonding orbitals. Consequently, the local Te-Te dimers are partly broken around the Pt sites, and the superstructure due to the short Te-Te bond (intradimer) and long Te-Te bond (interdimer) is strongly disturbed. In this scenario, disturbed local Te-Te dimers can remain in Au1−xPtxTe2. The remaining Au charge fluctuation and the disordered Te-Te dimers may provide anomalous lattice behaviors to Au1−xPtxTe2 and may contribute to the emergence of superconductivity [5].

IV. CONCLUSION

We have performed photoemission and x-ray absorption measurements on Au1−xPtxTe2 (x = 0 and 0.35) in which the Pt substitution for Au suppresses the lattice distortion in AuTe2 and induces superconductivity. The broad Au 4f core-level peak is consistent with the Au valence modulation in distorted AuTe2. The Au 4f core-level peak gets slightly narrow with the Pt substitution, indicating that small Au 5d charge modulation in distorted AuTe2 is at least partially suppressed by the Pt substitution. The Au 4f and Te 3d core-level binding energies suggest that the average valence state is close to Au2+ (Te2)2−. The Jahn-Teller-like distortion of the AuTe6 octahedra. On the other hand, the valence-band spectra and the band-structure calculations show that the Au 5d bands are almost fully occupied. The two apparently conflicting results can be reconciled by taking account of the strong Au 5d/Au 6s–Te 5p hybridization. The absence of a core-level energy shift with the Pt substitution shows that the simple rigid band picture is not applicable to Au1−xPtxTe2. Although the periodic arrangement of the Te-Te dimers is disturbed by the Pt substitution, the Te-Te dimers and Au valence modulation may partly remain in superconducting Au1−xPtxTe2. The relationship between the possible Au charge fluctuation and the superconductivity should be studied experimentally and theoretically in the future. Another interesting question is whether the Te-Te dimers still remain in Au1−xPtxTe2. If the Pt substitution causes disordering of the dimers instead of breaking, Au1−xPtxTe2 should have highly inhomogeneous electronic states similar to the Fe-based superconductors.

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