Band Jahn-Teller effects and Peierls Instability in IrTe$_2$

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Abstract. We report a photoemission spectroscopy study on IrTe$_2$ which exhibits an interesting lattice distortion below 270 K. Ir 4f core-level photoemission spectrum is broadened in going from 300K to 40K. This result indicates the charge moderation of Ir 5d electrons. Angle-resolved photoemission spectroscopy (ARPES) result at 300K shows multi-band Fermi surfaces with six-fold symmetry which are basically consistent with band structure calculations. At the distorted phase, the inner Fermi surfaces become quasi one-dimensional Fermi surface due to the lattice distortion.

1. Introduction

Recently, Pyon et al. [1] and Yang et al. [2] have discovered interesting interplay between lattice distortion and superconductivity in triangular lattice Ir$_{1-x}$Pt$_x$Te$_2$ in which multi-band Fermi surfaces are expected to play significant roles. The parent material IrTe$_2$ exhibits a structural phase transition at $\sim$ 270 K from the trigonal (P3m-1) to the monoclinic (C2/m) structure accompanied by anomalies of electrical resistivity and magnetic susceptibility [3]. When the lattice distortion is suppressed by chemical substitution of Pt or Pd for Ir or intercalation of Pd, IrTe$_2$ becomes superconductors [1][2]. An electron diffraction result by Yang et al. shows that the structural transition is accompanied by superstructure with wave vector of $q = (1/5, 0, -1/5)$. Such superstructure is often observed in charge density wave (CDW) materials [2]. In multi-band Fermi surfaces with Ir 5d and Te 5p orbital degeneracy, the nesting character can be enhanced by orbitally-induced Peierls mechanism [4]. On the other hand, a recent optical study by Fang et al. on single crystal samples shows that there is no gap opening expected for CDW and, instead, band structure is reconstructed over a broad energy scale up to $\sim$ 2 eV [5]. Fang et al. conclude that the structural transition of IrTe$_2$ is not of CDW type but of a novel type driven by Te 5p holes [5].
2. Experimental Results and Discussion

2.1. X-ray Photoemission Spectroscopy

The polycrystalline sample of IrTe$_2$ was prepared as reported in ref. 1. IrTe$_2$ is nonsuperconducting. The x-ray photoemission spectroscopy (XPS) was carried out at 300 K and 40 K using JEOL JPS9200 analyzer. Monochromatic Al K$_\alpha$ (1486.6 eV) was used as x-ray source. The total energy resolution was about 0.6 eV. The base pressure of the chamber was in the $10^{-7}$ Pa range. The binding energy was calibrated using the Au 4f core level of the gold reference sample. We fractured the polycrystalline samples of IrTe$_2$ at 300 K for the XPS measurements.

Ir 4f and Te 3d core-level photoemission spectra of IrTe$_2$ are displayed in Fig. 1. The Ir 4f peak width of IrTe$_2$ slightly increases in going from 300 K to 40 K while the Te 3d peaks do not show any such changes with temperature. The increase of peak width indicates that the density of Ir 5d $t_{2g}$ electrons is modulated in the low temperature phase of IrTe$_2$. Here, it should be noted that the Ir 4f peak width increase of IrTe$_2$ is comparable to that of CuIr$_2$S$_4$ in which the octamer Ir$^{3+}$/Ir$^{4+}$ charge ordering was established [6] and the charge difference between the Ir$^{3+}$ site and the Ir$^{4+}$ site was observed in the Ir 4f XPS [6]. Interestingly, the Ir 4f binding energy of IrTe$_2$ is smaller than that of CuIr$_2$S$_4$ as shown in Fig. 1(a), suggesting that the actual number of Ir 5$d$ electrons of IrTe$_2$ (formally Ir$^{4+}$) is larger than that of CuIr$_2$S$_4$ (formally Ir$^{3.5+}$).

2.2. Angle-resolved Photoemission Spectroscopy

The single crystal samples of IrTe$_2$ were prepared using a self-flux method [1, 5]. The photoemission measurements were performed at beamline 9A, Hiroshima Synchrotron Radiation Center using a SCIENTA R4000 analyzer with circularly polarized light. The total energy resolution was set to 18 meV for excitation energy of $h\nu = 23$ eV. The angular resolution was set to $\sim 0.3^\circ$ that gives the momentum resolution of $\sim 0.015$ Å$^{-1}$ for $h\nu =23$ eV. 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 oriented by ex situ Laue measurements. The spectra were acquired within 8 hours after the cleavage. The binding energy was calibrated using the Fermi edge of gold reference samples. We cleaved the single crystalline samples of IrTe$_2$ at 300 K for the ARPES measurements and then cooled the samples.

Figure 2(a) shows the Fermi surface mapping of IrTe$_2$ at 300 K above the structural transition temperature. The ARPES data are taken at $h\nu = 23$ eV and, for the Fermi surface mapping, the ARPES intensity is integrated within an energy window of $\pm 5$ meV at the Fermi level ($E_F$).
At $h\nu = 23$ eV, the momentum perpendicular to the Ir plane approximately corresponds to $\pi/c$, where $c$ is the out-of-plane lattice constant. Therefore, the center of the hexagonal Brillouin zone is the A point. The direction from the A point to the L (H) point corresponds to the direction of Ir-Ir (Ir-Te) bond. In agreement with the band structure calculations [2, 5], the flower-shaped outer Fermi surface with six-fold symmetry is observed as shown in Fig. 2(a). In addition, the inner Fermi surfaces like six connected beads can be identified although effect of thermal excitations at 300 K tends to obscure the relatively small Fermi pockets. The inner Fermi surfaces observed around the A point at 300 K are roughly consistent with the prediction of the band-structure calculations [2, 5].

The Fermi surface mapping at 20 K well below the transition temperature is displayed in Fig. 2(b). Across the structural transition, the flower shape of the outer Fermi surface does not change appreciably. However, in the region where the outer Fermi surface is close to the inner Fermi surfaces, while the outer Fermi surface is separated from the inner Fermi surfaces at 300 K, the outer Fermi surface overlaps with the inner Fermi surfaces at 20 K. In contrast to the small effect on the outer Fermi surface, the inner Fermi surfaces dramatically change their shapes by the structural transition. At 20 K, two straight portions of Fermi surfaces are observed at 20 K. Such geometry of inner Fermi surfaces at 20 K deviates from the prediction of the calculation. The straight portions are perpendicular to the A-H direction or the direction of
Ir-Te bond. Therefore, both of the Te 5p and Ir 5d orbitals would be involved in the structural transition if the straight Fermi surfaces are driven by orbitally-induced Peierls mechanism [4]. Figures 2(c) and (d) show the wide-range band dispersions along the A-H direction at 300 K and 20 K, respectively. Whereas the band dispersions at 300 K agree with the predictions of the band-structure calculations, those at 20 K deviate from the predictions [2, 5].

3. Conclusion
In conclusion, we have measured the XPS and ARPES spectra of triangular lattice chalcogenide IrTe₂. Ir 4f core-level photoemission spectra show Ir 5d t₂g charge modulation established in the low-temperature phase of IrTe₂. ARPES result at 300K shows multi-band Fermi surfaces with six-fold symmetry which are basically consistent with the band structure calculations. At the distorted phase, the inner Fermi surfaces become quasi one-dimensional by the lattice distortion suggesting that nesting character is enhanced.

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