Photoemission Study of Rare-Earth Ditelluride Compounds

(ReTe$_2$ : Re = La, Pr, Sm, and Gd)

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Abstract

We studied the electronic structure of rare-earth ditelluride (ReTe$_2$: Re = La, Pr, Sm, and Gd) using photoemission spectroscopy. From the x-ray photoelectron spectroscopy (XPS) study of the 3d core levels of rare-earth elements, we found that all the rare earth elements are trivalent. We have also made theoretical calculations using the Gunnarsson and Schönhammer approximation and multiplet calculations for the rare earth elements to find that the La and Gd 3d peaks are well explained using our calculations. There is no considerable change in the line-shape of the Te 3d peaks depending on different rare earth elements. On the other hand, valence band spectra
studied with the ultraviolet photoelectron spectroscopy (UPS) show a small change in the Te $p$ band depending on rare-earth elements. According to the UPS data, LaTe$_2$ has very low carrier density at the Fermi level while SmTe$_2$ and PrTe$_2$ show strongly metallic band structure effects near the Fermi level.

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I. INTRODUCTION.

One of the abiding interests in materials science is the synthesis and characterization of new materials that locate near the metal-insulator boundary. Such materials exhibit some of the most important properties of condensed matter physics; for example the high-$T_c$ superconductivity, a commensurate and incommensurate charge density wave, the mixed-valency effect, and Mott-Hubbard transitions.

Rare-earth dichalcogenides (ReX$_2$, Re = Rare-earth, $X$ = Se, Te) have drawn attentions because they might have a charge density wave (CDW) transition like NbSe$_3$. To date, however, DySe$_{1.85}$ is the only one known to have such a CDW instability among the rare-earth dichalcogenides. Interestingly, most ReX$_2$ compounds have a strong two dimensional character in physical properties arising from their tetragonal Cu$_2$Sb-type structure. This structure are based on two motifs. One is a corrugated cubic layer of rare-earth elements and Te atoms, and the other is a planar square lattice sheet of chalcogen atoms. The orbitals of the 4-fold coordinated chalcogens in the sheet are expected to broaden into dispersive bands inducing metallic behavior along the basal plane.

II. EXPERIMENTS.

We made ReX$_2$ samples (Re = La, Pr, Sm, and Gd) as described elsewhere. The crystal structure of all the samples was checked by x-ray analysis. In order to obtain clean surface for photoemission spectroscopy measurements, we scraped the samples in situ. Photoelectron spectra were taken by a HA-150 concentrical hemispherical analyser, which is attached to a ultra high vacuum (UHV) system, of the VSW Scientific Instruments, England. During the experiments pressure was better than $2 \times 10^{-10}$ mbar. We used Al-$K\alpha$ ($h\nu = 1486.6$ eV) for the measurement of rare earth $3d$ and Te $3d$ peaks, and He I and He II ($h\nu = 21.2$ and 40.8 eV respectively) for the measurement of rare earth $4f$ and valence band spectra. O 1$s$ and C 1$s$ signals were used to ensure that sample surface was clear of other contaminants.
For the UPS experiments we did not observe any C and O related peaks. However, in the case of XPS C 1s and O 1s core-level peaks were detected. These C and O peaks, we think, came from the sample holder since a wider sample area was usually covered by the X-ray source than the He discharge lamp. Therefore, we calibrated all core level spectra against the C 1s peak.

III. RESULTS AND DISCUSSION.

Figure 1 shows the 3d core-level spectra of LaTe$_2$, PrTe$_2$, SmTe$_2$, and GdTe$_2$, which are typical of rare earth compounds. In all four spectra, we can see double peak structures due to the spin-orbit splitting of $3d_{5/2}$ and $3d_{3/2}$, and their satellites as in other rare earth compounds. That the 3d core-level spectra are very similar to each other suggests that all the rare earth elements should be trivalent.

The LaTe$_2$ data in figure 1(a) show a double-peak structure due to spin-orbit splitting like other rare earth compounds. The secondary loss peak near 870 eV is due to an inelastic scattering process. As in other rare earth samples, we think that the main peaks and satellite are $3d^4f^0$ and $3d^4f^1$ peaks, respectively (underline denotes a hole state). In the formulation of Gunnarsson and Schönhammer (GS), the Anderson impurity hamiltonian (AIH) can be written as:

$$H = \sum_{k\sigma} \epsilon_{k\sigma} a_{k\sigma}^{\dagger} a_{k\sigma} + \epsilon_f \sum_{m\sigma} a_{m\sigma}^{\dagger} a_{m\sigma}$$

$$+ U_{ff} \sum_{(m\sigma)(m'\sigma')} n_{m\sigma}^{\dagger} n_{m'\sigma'}^{\dagger} + \left[ \sum_{km\sigma} V_{km} a_{m\sigma}^{\dagger} a_{k\sigma} + \text{h.c.} \right]$$

$$+ \left[ \epsilon_c n_c + U_{fc} (1 - n_c) \sum_{m\sigma} a_{m\sigma}^{\dagger} a_{m\sigma} \right]$$

It contains a conduction band with energy dispersion $\epsilon_{k\sigma}$, and an impurity atom level of degeneracy $N_f$ with the energy $\epsilon_f$ corresponding to the total energy difference between consecutive $f$-occupations when hybridization and $f$-coulomb correlation energies are ignored. $U_{ff}$ is the on-site $f$-$f$ Coulomb repulsion which is the energy needed for the formation of two non-interacting $f^{n-1}$ and $f^{n+1}$ states. $V_{km}$ is a hopping matrix element between the
orbital and a conduction state. The term in the second square brackets is considered in order to describe the excitations of a deep core level at an energy $\varepsilon_c$, where $U_{fc}$ is the attraction energy between an $f$ state and the core hole, $n_c$ the electron occupation in the core level. Calculations of core level XPS spectral functions using the AIH model Hamiltonian shows that the satellite structure depends strongly upon the hybridization strength. According to the calculations, the satellite of La 3$d$ at the lower binding energy side is well screened 3$d$ peaks by charge transferred electrons from ligands. For the model calculations using the Gunnarsson and Schönhammer approximation, we used the following set of model parameters; hybridization parameter $V = 0.04$ eV, correlation energy between rare-earth 4$f$ electrons $U_{ff} = 5.0$ eV, core-$f$ coulomb attraction interaction $U_{fc} = 6.7$ eV, 4$d$ core level binding energy $\varepsilon_f = 836.4$ eV, and spin-orbit splitting $\varepsilon_{5/2}^{d} = 16.8$ eV. Using this set of model parameters, we found that the experimental La 3$d$ line shape can be well explainable. Table I shows the summary of these fitting results.

Figures (b) and (c) show the Pr and Sm 3$d$ core level spectra of a double peak structure due to the spin orbit splitting ($\varepsilon_{Pr}$ 3$d_{5/2} = 933.6$ eV, $\varepsilon_{Pr}$ 3$d_{3/2} - S$ = 19.9 eV, $\varepsilon_{Sm}$ 3$d_{5/2} = 1083.6$ eV, and $\varepsilon_{Sm}$ 3$d_{3/2} - S$ = 26.8 eV). We can also see a secondary loss peak near 975 eV which is due to inelastic scattering of Pr 3$d$ spectrum. Additional surface satellite peaks are shown at the lower binding energy side of 3$d$ peaks in SmTe$_2$. For both Pr and Sm, a new structure appears at the higher binding energy side of 3$d_{3/2}$. As to the origin of this structure, we think that there are two possible explanations. One is a 4$f$ induced multiplet effect like Gd 3$d$ multiplet and the other is a stoichiometric effect.

Figure (d) shows the Gd 3$d_{5/2}$ and 3$d_{3/2}$ peaks of GdTe$_2$. These data exhibit main and satellite structures as in the trivalent Gd compounds. One note that the satellite peak appears at a higher binding energy for the trivalent Gd compounds than the main peak corresponds to the 4$f^7 \rightarrow 3d^9 4f^7$ electronic configuration.

In figure 2, we show the x-ray photoelectron spectra of Te 3$d$ of LaTe$_2$, PrTe$_2$, SmTe$_2$, and GdTe$_2$. We note that the position and the full width at half maximum (FWHM) of the peaks appear to have almost the same values for all rare earth compounds. This similarity
in the Te 3d spectra, we think, supports the foregone conclusion that all the rare earth elements have the same 3+ valence. In that case, the Te ligands would have a similar chemical valency. On the other hand, a careful inspection reveals that the line width of the Te 3d is slightly broader than in typical Te semiconductors. It is likely to be due to the probably two chemical phases of Te in ReTe2. As we noted before, ReTe2 is a strongly two dimensional material. There are two crystallographically different sites for Te atoms in the structure. One of Te atoms sits in the corrugated cubic layer of rare earth and Te atoms, and the other one in the planar square lattice sheet of Te atoms. Therefore, we expect that Te atoms at the two different sites would experience different chemical environments leading to a slight difference in the Te 3d spectra. The curve fitting results are summarized at table II.

Figure 3 is the valence band spectra of rare earth ditellurides taken with a He I ($h\nu = 21.2$ eV) discharge lamp. Experiments using a He II source produce more or less similar data when the background is properly subtracted off. The valence band spectra with the He I and He II sources also attest to the quality of the samples since these spectra do not show any O and C related structure.

In figure 3, the Fermi level of each spectrum and the spectral position were determined using the Fermi edge of Ag valence band measured at the same experimental cycle as the ReTe2 data. These valence band spectra taken with the He discharge lamp reflect mainly the Te 5p-band because the photoionization cross-section of rare earth 4f is much smaller than that of the Te 5p-band. Furthermore, in the case of Gd and Sm the 4f level locates far below the Fermi level.

In the valence band spectra of rare earth ditelluride, one can see that there is a slight change in the Te p band depending on rare earth elements. Interestingly enough, the spectrum of LaTe2 shows a very low carrier density at the Fermi level indicative of a semiconducting character. This semiconducting character is also consistent with the satellite structures of the La 3d core level. However, the semiconducting behavior contradicts the results of band calculations. The electronic structure of LaTe2 was obtained using a tight-bind model.
first principle calculations\textsuperscript{12}, and a precise one electron FLAPW method\textsuperscript{15}. Unlike the experimental finding, all the band calculations agree that LaTe\textsubscript{2} is metallic with a majority contribution at the Fermi level coming from the 5\textit{p} of Te square sheet in the tetragonal \textit{c}-plane.

The spectra of Sm and Pr valence band have almost the same line shape and slightly broader bands than the La band. From the data, we conclude that Sm and Pr samples are strongly metallic. The Gd sample also shows a slightly metallic behavior with a relatively small fermi edge.

\section*{IV. SUMMARY}

We have presented the core level and valence band spectra of ReTe\textsubscript{2} (Re = La, Pr, Sm, and Gd), which have a strong two dimensional character.

In the x-ray photoelectron spectroscopy (XPS), the 3\textit{d} core level spectra of rare earth elements in figure 1 show that all the rare earth elements are trivalent. In the case of La 3\textit{d} core levels, main peaks and their satellites denoted as 3\textit{d}4\textit{f}\textsubscript{0} and 3\textit{d}4\textit{f}\textsubscript{1} are well described within the formulation of Gunnarsson and Schönhammer for the Anderson impurity Hamiltonian. According to our calculations, the satellites arise from the hybridization of \textit{f} electrons with ligand Te \textit{p} level. The 3\textit{d} structures of Gd, Pr, and Sm are interpreted as arising from multiplet effects due to \textit{f} electrons in a photoemission process. In particular, the Gd 3\textit{d} peaks are in good agreement with the calculated 3\textit{d} XPS of 4\textit{f}\textsuperscript{7} ion corresponds to the 4\textit{f}\textsuperscript{7} \rightarrow 3\textit{d}\textsuperscript{9}4\textit{f}\textsuperscript{7} electronic configuration. The Slater’s integrals for Gd\textsuperscript{3+} are calculated using a Hartree-Fock-Slater program.

In the Te 3\textit{d} core levels from the XPS, we have not found any considerable change in the line-shape of the Te 3\textit{d} peaks depending on different rare earth elements within the resolution of our set-up. However, there is also an evidence of the two chemical phases of Te.

Valence band spectra studied using UPS show that there is a slight change in the Te
$p$ band depending on rare-earth elements. Our data show that LaTe$_2$ has very low carrier density at the Fermi level in contrast to the prediction of band calculations. On the other hand, Sm and Pr samples show strongly metallic band structure effects near the Fermi level in our data.

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### Tables

#### Table I. Values of binding energy, spin-orbit splitting, and line width of rare earth elements of ReTe$_2$. The results of LaTe$_2$ is obtained from GS calculation, and the values of GdTe$_2$ get from Hatree-Fock-Slater multiplet calculation.

| Sample  | $\varepsilon_{5/2}$ | $L - S$ splitting | FWHM | $V$ | $U_{ff}$ | $U_{fc}$ |
|---------|---------------------|-------------------|-------|-----|---------|---------|
| LaTe$_2$| 836.4               | 16.8              | 2.7   | 0.04| 5.0     | 6.7     |
| PrTe$_2$| 933.6               | 19.9              | 3.9   |     |         |         |
| SmTe$_2$| 1083.6              | 26.8              | 3.6   |     |         |         |
| GdTe$_2$| 1187.7              | 32.5              | 5.3   |     |         |         |

#### Table II. Curve fitting results of Te 3$d$ of ReTe$_2$ compounds. $\varepsilon_{5/2}$, $L - S$, L-W, and G-W represent the binding energy of 3$d_{5/2}$, spin orbit splitting, lorentzian width, and gaussian width, respectively. All values are given in the unit of eV. Binding energy, $L - S$ splitting, and lorentzian width are free parameters in our model calculations. We used the Gaussian width as an instrumental resolution.

| Sample  | $\varepsilon_{5/2}$ | $L - S$ | L-W | G-W |
|---------|---------------------|---------|-----|-----|
| LaTe$_2$| 572.37              | 10.4    | 1.1 | 1.0 |
| PrTe$_2$| 572.28              | 10.3    | 1.1 | 1.0 |
| SmTe$_2$| 572.32              | 10.4    | 1.1 | 1.0 |
| GdTe$_2$| 572.27              | 10.4    | 1.1 | 1.0 |
FIGURES

FIG. 1. Photoemission spectra of rare-earth 3d core level in (a) LaTe$_2$, (b) PrTe$_2$, (c) SmTe$_2$, and (d) GdTe$_2$ taken with Al-K$\alpha$ ($h\nu = 1486.6$ eV) source. X-ray satellite contribution are subtracted off the raw data. The raw data are given by filled circle, dashed line the background, and the solid lines in (a) and (d) are fitting results using the GS approximation and multiplet calculations, respectively.

FIG. 2. Te 3d core level spectra of rare-earth ditellurides in LaTe$_2$, PrTe$_2$, SmTe$_2$, and GdTe$_2$ taken with Al-K$\alpha$ ($h\nu = 1486.6$ eV) source. Filled circles represent the raw data, and the solid lines the curve fitting results. X-ray satellite contribution is subtracted off the raw data.

FIG. 3. Valence band spectra of rare earth ditellurides; LaTe$_2$, PrTe$_2$, SmTe$_2$, and GdTe$_2$, taken with a He I ($h\nu = 21.2$ eV) discharge lamp. All spectra are normalized by a maximum peak height, and the Fermi level is marked by the vertical line. Fermi edge is clearly seen in the data of PrTe$_2$, SmTe$_2$, and GdTe$_2$. 

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Fig. 1

Intensities [arb. units]

Binding Energy [eV]

(a) $\text{LaTe}_2$

Secondary loss peak

(b) $\text{PrTe}_2$

Secondary loss peak

(c) $\text{SmTe}_2$

Surface

(d) $\text{GdTe}_2$

Multiplet

Plasmon

3d $3/2$ $5/2$

3d $3/2$ $5/2$

3d $5/2$

3d $5/2$

3d $5/2$

3d $5/2$

3d $5/2$

3d $5/2$

3d $5/2$

3d $5/2$

3d $5/2$

3d $5/2$

3d $5/2$
Fig. 2
Fig. 3