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## A photoemission and inverse-photoemission study of trigonal Te

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**Abstract.** The valence-band and conduction-band densities of states (DOSS) of trigonal Te have been investigated using ultraviolet photoemission and inverse-photoemission spectroscopy. We find structures at  $-0.8$ ,  $-1.7$ ,  $-3.6$ ,  $-4.6$ ,  $-10.6$  and  $-12.8$  eV, and at  $1.4$ ,  $2.1$ ,  $2.7$ ,  $4.7$ ,  $6.1$  and  $9.5$  eV with respect to the valence-band maximum. Relative energy positions of structures within the valence bands and those within the conduction bands are in good agreement with those in the calculated DOSS on the basis of the empirical pseudopotential theory. Separation between the theoretical valence-band and conduction-band DOSS is, however, narrower by about 1 eV than the experimental results. The Te 4d core-yield spectrum shows intense and sharp doublets at the 4d core-absorption threshold. These structures are assigned to the spin-orbit doublets of the Te 4d core excitons with a comparatively long lifetime and a fairly localized nature.

### 1. Introduction

A crystal of trigonal Te consists of helical chains arranged in a hexagonal array. The unit cell is composed of three atoms of a helix as shown in figure 1 [1]. Two of the four 5p electrons per atom are used in forming covalent bonds with the two nearest neighbours in the chain, while the other two form lone-pair orbitals pointing toward neighbouring chains. The interaction between atoms in neighbouring chains is comparatively weak and often believed to be of van der Waals character.

The density of states (DOS) of valence bands of trigonal Te has been investigated by means of ultraviolet and x-ray photoemission spectroscopy [2–6] (UPS and XPS). The UPS [2, 3] and XPS [2, 4–6] spectra exhibited a prominent peak at  $-2$  eV, two peaks between  $-3$  and  $-6$  eV and also two broad peaks between  $-8$  and  $-16$  eV with respect to the valence-band maximum (VBM). These peaks were attributed to the 5p lone-pair, 5p-like bonding and 5s states, respectively. Weak conduction-band structures were also reported at 5.4, 5.8 and 6.1 eV above the VBM from experiments on the excitation-photon-energy (3–12 eV) dependences of energy distribution curves and their second energy derivatives [3]. The Te 4d core-absorption spectrum has been discussed in conjunction with the DOS of conduction bands, taking into account the final-state interaction [7].

The band-structure calculations for trigonal Te [8–17] have been performed on the basis of tight-binding [8, 15], Korringa–Kohn–Rostker [10], modified augmented plane-wave [11], pseudopotential [9, 12–15], orthogonalized plane-wave [16] and vector-charge-density [17] methods. The valence-band DOS accomplished by the empirical pseudopotential calculation

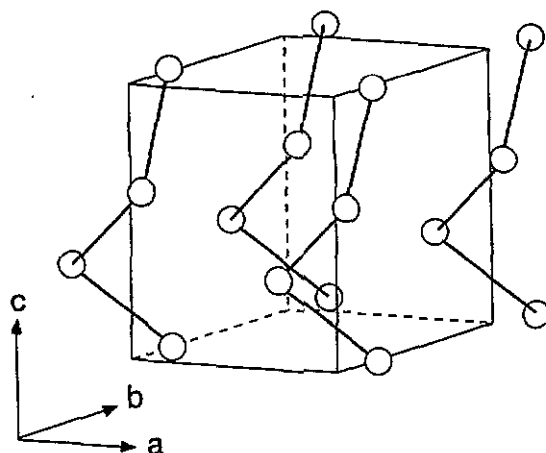


Figure 1. The crystal structure of trigonal Te. The unit cell consists of three atoms of one helix.  $a$ ,  $b$  and  $c$  represent the crystal axes.

[15] was in an excellent agreement with the experimental photoemission spectrum. Little comparison, however, was made between the theory and experiment on the conduction-band DOS, because the direct experimental information was fairly limited.

In this paper, we present valence-band and conduction-band spectra of trigonal Te measured by means of ultraviolet photoemission and inverse-photoemission spectroscopy (UPS and IPES). The UPS spectra are fully consistent with the earlier results [2–6]. The IPES spectrum reveals, for the first time, a measure of the conduction-band DOS, in particular, the energy positions and widths of the 5p-like antibonding bands and higher-lying 5d-like bands. In addition, we show that *in situ* measurements of the UPS and IPES spectra realize a connection of these two spectra at the Fermi level in the band gap and provide a whole DOS spectrum [18]. This makes it possible to discuss relative energy positions of experimental DOS peaks derived from the 5s, 5p and 5d states in comparison with the calculated DOS. We also report the Te 4d core-yield spectrum measured with high resolution. Intense and sharp doublets near the 4d core threshold are assigned to the Te 4d core excitons. A newly resolved structure near the threshold reveals a dominant source for the earlier discrepancy between the splitting energies of the 4d core-yield and 4d core-level photoemission spectra.

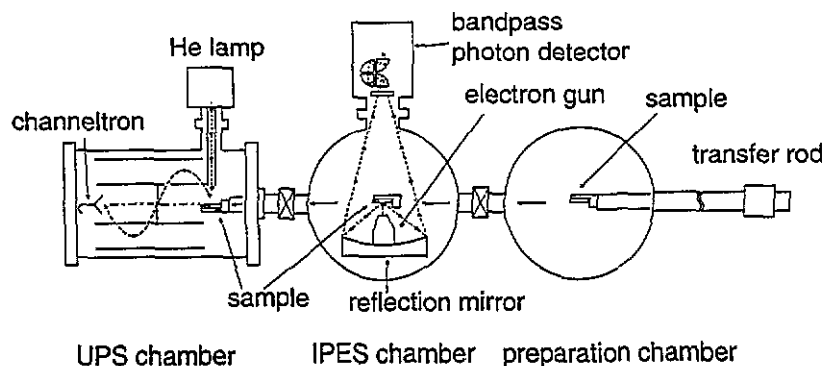


Figure 2. A schematic illustration of the apparatus used for UPS and IPES.

## 2. Experimental details

The UPS and IPES [19] spectrometers employed in the present study are schematically shown in figure 2. The UPS spectrometer connected with the IPES apparatus consists of a He discharge lamp and a double-stage cylindrical-mirror analyser. The energy resolution was set to be 0.2 eV. The working pressure under the operation of the discharge lamp was  $3 \times 10^{-9}$  Torr, though the base pressure was  $4 \times 10^{-10}$  Torr. The IPES spectrometer contains an electron gun of Erdman-Zipf type with a BaO cathode mounted on the symmetry axis of an Al mirror coated with an MgF<sub>2</sub> film to improve the reflectivity. Light emitted from the sample is focused onto the first dynode of the photomultiplier after passing through an entrance window of SrF<sub>2</sub> crystal. The acceptance angle of the light is about  $0.8\pi$  sr. All components are mounted in an ultrahigh-vacuum chamber under the base pressure, below  $5 \times 10^{-10}$  Torr. The overall energy resolution is 0.56 eV [19]. The energy calibration of the UPS and IPES apparatus was experimentally performed using the spectra of polycrystalline Au film. The UPS and IPES spectra were connected at the Fermi level, by measuring these spectra *in situ* for the same sample surface.

Synchrotron-radiation (SR) experiments were performed on the beamline 2 at the Institute for Solid State Physics, University of Tokyo (SRL-ISSP). A combination of a modified Rowland-type monochromator and a double-stage cylindrical-mirror analyser was used to obtain angle-integrated photoemission spectra of core levels and valence bands as well as constant-initial-state (CIS) spectra. The Te 4d core-absorption spectra were measured by total-yield mode. The CIS and total-yield spectra were normalized to the monochromator output. The resolution of the monochromator was set to be 0.1 eV at 50 eV.

All energies of the core-level, valence-band and conduction-band spectra were defined with respect to the VBM determined by extrapolating the steep leading edge of the highest valence-band peak to the baseline.

Samples used were undoped Te single crystals with a trigonal form. The clean surfaces were prepared *in situ* by scraping with a diamond file for UPS and IPES measurements, and by cleavage for SR measurements. Measurements on surfaces prepared by scraping provide sufficiently angle-integrated spectra. The corresponding UPS and IPES spectra can be reasonably compared with the total DOSS of valence and conduction bands, respectively.

## 3. Results and discussion

Figure 3(a) shows valence-band UPS and conduction-band IPES spectra of trigonal Te. The UPS spectrum measured at the excitation-photon energy of 21.2 eV and the IPES spectrum are connected at the Fermi level of the sample. The SR photoemission spectrum taken at 70 eV is also shown in figure 3(b) (thick dotted curves) to demonstrate the structure around -13 eV. The valence band spectra exhibit structures at -0.8, -1.7, -3.6, -4.6, -10.6 and -12.8 eV with respect to the VBM, in agreement with the results of earlier UPS [2, 3] and XPS [2, 4-6] measurements. On the other hand, the conduction-band spectrum shows prominent structures at 1.4, 2.1 and 2.7 eV, and weak structures at 4.7, 6.1 and 9.5 eV above the VBM.

The solid curves in figure 3(b) exhibit the DOSS of trigonal Te calculated by Joannopoulos *et al* using the empirical pseudopotential method [15]. The energy of the theoretical curves is also referred to the VBM. Calculated valence bands in the energy regions from 0 to -2.5 eV, from -2.5 to -6 eV, and from -8 to -13 eV are derived from the p lone-pair, p-like bonding and s-like states, respectively. Peaks at -3.6 and -4.6 eV have been related

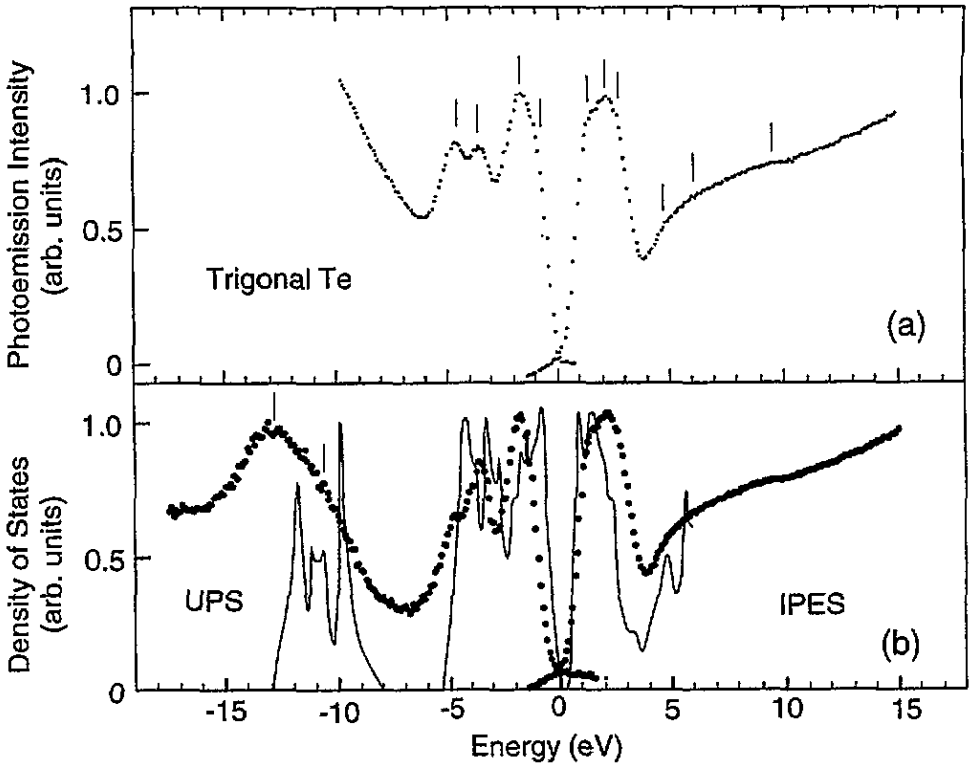


Figure 3. (a) Valence-band photoemission and conduction-band inverse-photoemission spectra of trigonal Te. The two spectra are connected at the Fermi level. Energies are referred to the VBM. Vertical bars mark the DOS features. (b) The calculated DOS of trigonal Te (solid curves; [15]). The valence-band photoemission spectrum measured at 70 eV and the conduction-band inverse photoemission spectrum (thick dotted curves) are also shown for comparison between the theory and experiment.

to interchain and intrachain bonding states, respectively. The amounts of *s* and *d* character in the *p*-like bonding states are around 5–10 and 1–5% in the wavefunctions, respectively. This *p*–*d* mixing is enough to change the bond angle from 90° to 104° without including a strong *s*–*p* admixture [15]. The conduction bands at 0–4 eV and those above 4 eV are due to the *p*-like antibonding and *d*-like states, respectively, though the DOS spectrum is calculated only up to about 6 eV above the VBM.

One can recognize that the theory describes the valence-band spectrum well. In particular, with respect to the relative energy positions of DOS peaks, there appears an excellent agreement between the experiment and theory. To facilitate the comparison with the XPS spectrum, the theoretical DOS was previously convoluted with an energy-dependent broadening function (1.2 eV for the *s*-like bands and 0.7 eV for the remaining bands). Then, the experimental spectrum was placed to make the peak positions match those of the theoretical DOS spectrum [5, 15]. In the present study, however, one notices that all peaks in the theoretical DOS are reproduced shallower in energy than those in the experimental spectrum. In addition, the theoretical widths of the *p*-like bonding and *s*-like bands are narrower than those in the experimental spectrum. Moreover, theoretical intensities of the *p*-like bonding bands are almost equal to those of the lone-pair bands, in contrast to the

experimental spectrum.

Although the calculation has been performed with no direct information on the experimental DOS of conduction bands, the theoretical curve represents fairly well the features of the conduction-band spectrum, including the relative intensities between the p-like antibonding and d-like bands. The relative energy positions of peaks in the theoretical DOS are in good agreement with those in the IPES spectrum. The DOS peaks except for that at 4.7 eV are, however, reproduced on the lower-energy side. In addition, the theoretical width of the p-like antibonding bands is fairly narrow beyond the experimental resolution of the IPES spectrum.

From a comparison between the experimental and theoretical results mentioned above, we point out that the centre-of-mass energy of the p-like bonding and s-like bands should be placed at energies deeper by about 0.4 and 0.8 eV with respect to the VBM, respectively. Then, the bonding-antibonding splitting energy of the p-like bands should be also increased by about 1 eV. An increase of the coupling strength between the hybrid p-like orbitals on different atoms would increase the splitting energy and provide an increase of widths of the p-like bonding and antibonding bands.

Theoretical intensities of the p-like bonding bands, almost equal to those of the p lone-pair bands, may be also reduced by the increase of the coupling between the p-like orbitals, mainly due to the resulting increase of the band width. Weak intensities of the p-like bonding bands compared to those of the p lone-pair bands in both the UPS [2, 3] and XPS [2, 4-6] spectra suggest that the experimental results are independent of the excitation-photon energy and are intrinsic to the DOS features.

Relative intensities of theoretical DOS peaks in the p lone-pair bands are significantly different from those in the experimental spectrum. Such a discrepancy would be improved by fine adjustments of the nearest-neighbour and the second-nearest-neighbour interactions.

Reflecting the ratio of interchain to intrachain atomic distance, 1.31, the spectral shape of the s-like bands in the theoretical DOS is similar to a superposition of DOSs for a one-dimensional chain and a three-dimensional simple cubic lattice [15]. In addition, the bonding-antibonding splitting energy of the s-like bands is in good agreement with the experimental result. The width of the s-like bands is, however, narrower by 3-4 eV compared to the experimental DOS spectrum. A correction of the coupling strength between the neighbouring s orbitals is thus required to increase the dispersion of the s-like bands.

Next, we move to discussions of the Te 4d core-absorption spectrum. The total-yield spectrum is empirically known to be representative of the absorption spectrum in the core-excitation region. Figure 4 shows the 4d core-absorption spectrum of trigonal Te for  $E \perp c$  [20] (dotted curve). In the figure,  $E$  stands for the polarization vector of the light, and the vertical bar represents the energy position of the Te 4d core-absorption threshold (40.83 eV) estimated from the sum of the band-gap energy (0.33 eV) and the Te 4d core-level energy with respect to the VBM. The energies derived from the core-level photoemission spectra are -40.50 and -41.95 eV for the  $4d_{5/2}$  and  $4d_{3/2}$  core levels, respectively, and are in agreement with the results of Shevchik and co-workers [2].

One notices an intense and sharp doublet structure in the energy region from 40 to 43 eV and weak structures above 43 eV. To evaluate accurately the energy positions of structures in the 39-44 eV region, we have calculated the second energy derivatives of the total-yield spectrum, as also shown in figure 4. We find that three structures are clearly resolved as negative peaks at 40.84 (A), 41.04 (B) and 42.30 eV (A'). The splitting energy between A and A' is almost equal to the spin-orbit splitting energy of Te 4d core levels (1.45 eV). In addition, the relative intensity of the doublet A-A' in the total-yield spectrum is close to the 6:4 statistical weight of the initial Te  $4d_{5/2}$  and  $4d_{3/2}$  core states. Thus, we classify the

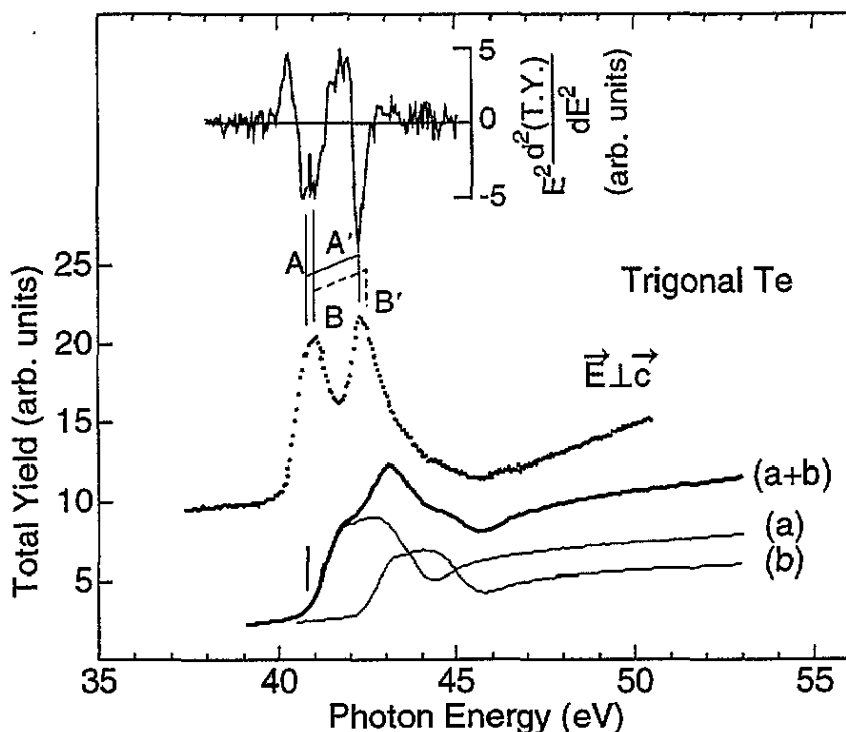


Figure 4. The 4d core-yield spectrum of trigonal Te for  $E \perp c$ . Second energy derivatives of the core-yield spectrum resolve the structures A, B and A' as negative peaks. The vertical bar at 40.83 eV represents the 4d core-absorption threshold. The solid curve (a + b) represents a spectrum constructed by a superposition of two experimental DOS curves (a) and (b) weighted in the ratio of 6:4 and shifted by 1.45 eV. The threshold of the curve (a + b) is adjusted to the 4d core-absorption threshold.

structures as spin-orbit doublets by taking the spin-orbit splitting energy of the Te 4d core levels into account. As concerns the spin-orbit partner of the structure B, we assume that this structure (B') overlaps with the steep drop on the higher-energy side of the structure A'.

The solid curve (a+b) in figure 4 exhibits a DOS spectrum constructed by a superposition of two experimental DOS curves (a) and (b), weighted in the ratio of 6:4 and shifted by 1.45 eV according to the 4d core-level splitting energy. The threshold of the curve (a + b) is adjusted to 40.83 eV. One notices that the initial rise and threshold of the 4d core-yield spectrum are significantly enhanced in comparison with the DOS spectrum. In the energy region above 43 eV, however, there appears a fairly good agreement between the 4d core-yield spectrum and the constructed DOS of conduction bands with respect to the shape and positions of maxima.

Most transitions to the p-like conduction bands are dipole allowed throughout the Brillouin zone as a result of the highly localized character of the initial 4d core states. The assumption of constant average matrix elements is, however, clearly implausible from comparison between the Te 4d core-yield and DOS spectra in figure 4. We believe that the A-A' and B-(B') doublets at the threshold are enhanced as a result of the formation of Te 4d core excitons with a comparatively long lifetime. Such an enhancement due to an

electron-core-hole interaction has been reported also for Si [21], black P [22] and GeS, GeSe, SnS and SnSe [23]. Transitions from the 4d core states to the conduction bands primarily derived from the Te 5p states are dipole-allowed intra-atomic transitions with a strong oscillator strength. The highly anisotropic conduction bands as well as the central-cell part of the d core-hole potential would make the excitation more localized and increase the electron-core-hole coupling [23].

The CIS spectrum for the initial-state energy of  $-1.7$  eV exhibited a prominent resonance at maxima of the corresponding core-absorption spectrum [24]. The amplitude of the resonance was about 50% of the background intensity. This also supports the formation of Te 4d core excitons with a fairly localized nature, since the resonance is assumed to originate mainly from an interference between the direct recombination process of the core excitons and the direct excitation process of the valence electrons [24, 25].

The relative intensity and the splitting energy of the A-A' doublet are very close to the statistical weight of the initial 4d core states and to their splitting energy, respectively. This can be understood as a result of a large spin-orbit splitting energy of 1.45 eV, though a sizeable electron-core-hole exchange energy [26] is expected from the characteristic feature of the intense and sharp doublet.

Judging from comparison of the 4d core-yield spectrum with the DOS curves (a), (b) and (a + b), broad structures in the 43–44 eV and 44–45.5 eV regions are attributed to the final states with p-like antibonding character, while features above 45.5 eV are related to the d-like character. An absence of intense and sharp peak structures suggests that the core-excitation spectrum roughly maps the DOS of conduction bands. We assume that this is the reason why the curve (a + b) describes the spectral features above 43 eV well.

Finally, the absorption spectrum of an evaporated film of crystalline Te has been measured in the Te 4d core-excitation region at room temperature [7]. The spectrum exhibited prominent peaks at 40.95 and 42.30 eV and weak structures on the higher-energy side associated with transitions from the 4d core levels to conduction bands. These features were compared with the DOS of conduction bands and with the calculated multiplet splitting of the  $4d^9 5p^5$  configuration of atomic Te. The discrepancy between the splitting energies of the prominent doublet at 40.95 and 42.30 eV (1.35 eV) and the 4d core levels (1.47 eV) was not explained. In the light of the present results, such a discrepancy is likely to be due to unresolved A and B structures.

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