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Polaronic quasiparticles in the valence-transition compound $\text{TmSe}_{1-x}\text{Te}_x$

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Exotic quasiparticle states have been proposed in mixed-valent compounds exhibiting valence transitions. However, clear spectroscopic evidence identifying these states has remained elusive. Using synchrotron-based hard x-ray and extreme ultraviolet photoemission spectroscopy, we have probed the Tm 3d and 4f emissions in $\text{TmSe}_{1-x}\text{Te}_x$, where a Te concentration-dependent semimetal-insulator transition occurs alongside the valence transition. Our photoemission results, which are characteristic of the bulk, track this combined transition across the critical concentration ($x_c = 0.29$). Notably, our results reveal a noninteger valence for the insulating phase and a novel quasiparticle excitation in the semimetallic phase: a Holstein polaron that extends beyond the standard periodic Anderson model.

The proposal that the mixed-valent (MV) compound samarium hexaboride is a strongly correlated topological insulator [1] has prompted extensive studies to clarify its topological nature [2–4]. These efforts have revealed intriguing thermodynamic and transport properties in the bulk [5–9], sparking the search for exotic neutrally charged quasiparticles, such as excitons [10], fractionalized quasiparticles [11], and Majorana fermions [12, 13]. Similar explorations of novel quasiparticle excitations have been extended to other heavy-fermion systems [14, 15]. In particular, the low-energy electronic properties of MV systems have been investigated in relation to changes in the 4f occupation number n_f [16, 17]. Furthermore, it has been suggested that theoretical frameworks beyond the standard periodic Anderson model (PAM) are necessary for heavy-fermion systems undergoing valence transitions [18–25], which could lead to novel quasiparticle states [13]. This has fueled strong interest in identifying such states in MV systems. However, no clear spectroscopic evidence of these quasiparticles has yet been observed under ambient conditions.

The MV compound $\text{TmSe}_{1-x}\text{Te}_x$ offers a unique platform to study the evolution of electronic states as a

function of chemical pressure using photoemission spectroscopy (PES). The underlying conceptual view of the electronic states of $\text{TmSe}_{1-x}\text{Te}_x$ is as follows: The MV character sits on the Tm ion, which lies between Tm^{2+} ($4f^{13}$) and Tm^{3+} ($4f^{12}$) (Suppl. Sec. I [26]). Both chalcogens (Se and Te) accept approximately two electrons from Tm to form a (almost) closed shell. An additional electron from the Tm^{3+} ion is transferred to the Tm 5d conduction band. When Se is replaced with Te, the lattice expands while retaining the fcc crystal structure and the periodicity of the Tm ions. Transport and magnetic properties corroborate this analogy because the behavior of $\text{TmSe}_{1-x}\text{Te}_x$ at ambient pressure is smoothly related to that of TmSe under hydrostatic pressure [38, 39]. A semimetal-insulator transition should occur between TmSe and TmTe [40], causing a drastic change in the 4f bonding properties at ambient pressure (Suppl. Sec. I [26]). Such changes in the electronic environment may be expected to give rise to novel quasiparticle excitations. However, systematic spectroscopic studies of $\text{TmSe}_{1-x}\text{Te}_x$ as a function of x that reveal the underlying electronic structure changes are still lacking.

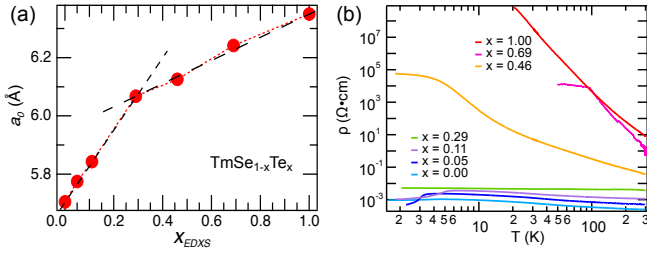


Figure 1. Structural and electrical properties of $\text{TmSe}_{1-x}\text{Te}_x$. (a) Lattice parameter a_0 as a function of the Te content x_{EDXS} . The two fitted dashed lines with different slopes indicate two phases and a transition at $x_{\text{EDXS}} = 0.29$. (b) Temperature- and Te concentration-dependent resistivity data, indicating semimetallic behavior for $x = x_{\text{EDXS}} \leq 0.11$ and semiconducting behavior for $x \geq 0.46$.

Here, we report on the evolution of the electronic structure of $\text{TmSe}_{1-x}\text{Te}_x$ across the valence and semimetal-insulator transition, as determined through core- and valence-electron emissions using synchrotron-based hard x-ray and extreme ultraviolet (XUV) PES [46–48]. Our results firmly establish a bulk electronic transition at $x = 0.29$ between the semimetallic and insulating electronic phases, which have distinct noninteger valences. Most interestingly, the semimetallic phase is characterized by a conspicuous asymmetric Tm $4f$ emission near E_F , which we attribute to a polaronic $4f$ quasiparticle state.

Experiment—Single-crystalline $\text{TmSe}_{1-x}\text{Te}_x$ samples were grown using the Bridgman method with Tm flux (Suppl. Sec. II [49]). The Te content x was determined by energy-dispersive x-ray spectroscopy (EDXS). Synchrotron-based hard x-ray photoemission spectroscopy (HAXPES) and high-resolution XUV photoemission spectroscopy were performed at ALS MERLIN, BESSY II ¹³, DIAMOND I09, PETRA III P22 and P04, and SOLEIL TEMPO. Photoemission spectra were taken from cleaved (001) surfaces, typically within six hours after cleavage under ultrahigh vacuum, in a temperature range from 2 K to 110 K (Suppl. Sec. III [53]).

Structural and electrical properties—Figure 1(a) shows the relationship between the measured lattice constant, a_0 , and the composition ratio, x_{EDXS} , as determined by EDXS. Hereafter, x_{EDXS} is referred to as x (Suppl. Tab. I [55]). The two fitted lines indicate two different regimes with distinct slopes. Since x and a_0 can be considered external pressure and volume, respectively, the different slopes indicate different compressibilities. Samples with lower x values are more compressible, which is consistent with previous results [40]. The intersection of the two fitted lines occurs at $x_c = 0.29$, indicating a phase transition.

The resistivity data in Fig. 1(b) exhibit behavior consistent with that reported in the literature [56, 57]. For $x \leq 0.11$, resistivity increases by about an order of mag-

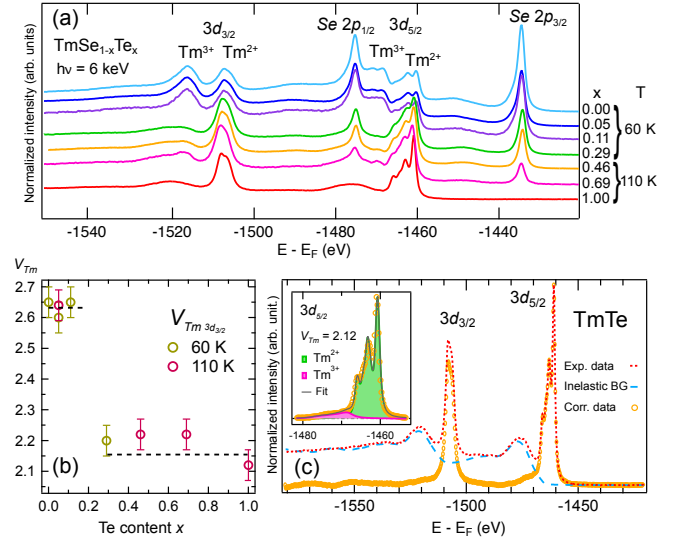


Figure 2. Valence transition of $\text{TmSe}_{1-x}\text{Te}_x$ from bulk-sensitive core-level spectroscopy. (a) Se $2p$ and Tm $3d$ photoemission spectra as a function of x . The distinct Tm^{2+} and Tm^{3+} ionization peaks of the Tm $3d$ emissions are indicated. (b) Tm valence (V_{Tm}) as a function of x , extracted from the Tm $3d$ spectral weights of the Tm^{2+} and Tm^{3+} emissions. The dashed horizontal lines indicate two phases with non-integer valences and a transition at $x_c \approx 0.29$. (c) Tm $3d$ spectral analysis for V_{Tm} determination of TmTe ($x = 1$). The intrinsic spectrum (orange circles) is obtained by subtracting an inelastic background (blue dashed line) from the original spectrum (red dotted line). Inset: Fitted spectral Tm^{2+} and Tm^{3+} contributions (green and pink areas), yielding $V_{\text{Tm}} = 2.12$.

nitude as temperature decreases, but remains low. This corresponds to the behavior of TmSe ($x = 0$), which is classified as a semimetal. The absolute electrical resistivity is low while the optical reflectivity is high; the material exhibits characteristic conduction band plasma effects at room temperature [58]. For $x \geq 0.46$, the resistivity increases more dramatically with decreasing temperature, indicating semiconducting or insulating behavior. At $x = 0.29$, the temperature dependence of the resistivity is flat, representing intermediate behavior. Taken together, the data establish a semimetal-insulator transition in $\text{TmSe}_{1-x}\text{Te}_x$ at $x_c = 0.29$.

Mixed valence and valence transition—In rare-earth systems, the electronic properties at the surface can differ substantially from those in the bulk [59–61]. We used HAXPES to probe the bulk valence properties and measured the insulating samples ($x \geq 0.46$) at a higher temperature to avoid sample charging. Figure 2(a) shows representative spin-orbit-split Tm $3d$ and Se $2p$ core-electron emissions (Suppl. Sec. III [53]). The Tm $3d_{5/2}$ and $3d_{3/2}$ peaks each consist of two ionization peaks, corresponding to Tm^{2+} and Tm^{3+} due to the MV character.

The Tm valence V_{Tm} is calculated from the integral spectral weight of Tm^{2+} and Tm^{3+} . To estimate the

Tm³⁺ spectral weight, the two Se 2*p* peaks and the inelastic background must be removed since the latter is strongly reduced in samples with $x \geq 0.29$, as shown in Fig. 2(a) for the 3*d*_{3/2} peaks. Figure 2(b) shows the V_{Tm} values obtained after subtracting these contributions (Suppl. Sec. IV [62]). The V_{Tm} values differ significantly between semimetallic and insulating samples, while remaining almost constant between the samples of the same phase. This x -dependent V_{Tm} behavior is consistent with magnetic susceptibility measurements [40, 57], which do not show any integer V_{Tm} for Tm monochalcogenides. The V_{Tm} values for the semimetallic and insulating samples are around 2.65 and 2.15, respectively (indicated by the dashed lines), corresponding to $n_f = 12.35$, and $n_f = 12.85$, respectively. Unlike the Sm valence in SmB₆ [60, 61, 74], we do not observe a clear temperature dependence in V_{Tm} , as exemplified by the two data points for $x = 0.05$ in Fig. 2(b). V_{Tm} in the insulating phase is often considered to be divalent [75, 76], but our data clearly indicate a non-integer value.

A reliable value of V_{Tm} in the insulating regime can be obtained for TmTe ($x = 1$) [Fig. 2(c)] because the loss function can be unambiguously determined using the Te 3*p* core-level spectra (Suppl. Sec. IV [62]). Consequently, the inelastic background (cyan dashed line) can be removed, and the intrinsic Tm 3*d* spectrum can be retrieved (orange circles). From the intrinsic spectrum [inset in Fig. 2(c)], V_{Tm} is evaluated using multiplet ligand and field theory calculations [77]. Our fitting results yield a non-integer $V_{\text{Tm}} = 2.12 \pm 0.05$, which is consistent with bulk-sensitive magnetic susceptibility and spectroscopic measurements [57, 75, 78, 79]. Since our bulk-sensitive data were obtained on freshly cleaved surfaces, the non-integer V_{Tm} cannot be due to contamination [46].

We attribute the observed noninteger valence ($V_{\text{Tm}} > 2$) of the insulating phase of TmSe_{1- x} Te _{x} ($x \geq 0.29$) to the hybridization of the Tm 4*f* states with Tm 5*d*/6*s* states. Specifically, our density functional theory (DFT) analysis of TmSe shows that the hybridization shifts from Tm 4*f*–5*d* to Tm 4*f*–6*s* as the lattice constant increases (Suppl. Sec. IV [62]) [80]. This suggests that Tm 4*f*–6*s* hybridization dominates the contribution to noninteger valence in the insulating regime of TmSe_{1- x} Te _{x} .

4*f* multiplet structure and spectral gap—Our focus now turns to the Tm 4*f* emissions near E_F . Figure 3(a) shows the complete 4*f* multiplet structure of TmSe ($x = 0$), as recorded using XUV and hard x-ray excitations. Due to the 4*f*¹³ and 4*f*¹² contributions to the ground-state wave function, the 4*f*¹² and 4*f*¹¹ final states are accessible after removing a 4*f* electron in the photoemission process. The green and pink vertical bars indicate the calculated atomic multiplet lines for the corresponding transitions [81]. The XUV spectrum ($h\nu = 70$ eV) exhibits a more intricate peak structure than the hard x-ray spectrum ($h\nu \approx 6$ keV) due to the presence of surface 4*f* peaks (Suppl. Sec. V [82]). Apart from these sur-

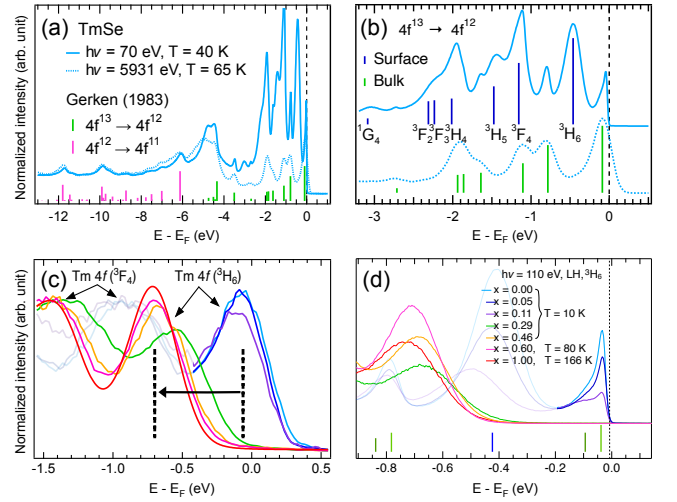


Figure 3. Tm 4*f* multiplet structure of TmSe_{1- x} Te _{x} in XUV-PES and HAXPES. (a) Overview 4*f* spectra of TmSe ($x = 0$) as recorded with surface- and bulk-sensitive photoemission spectroscopy. Calculated multiplet lines for the 4*f*¹² (green bars) and 4*f*¹¹ (pink bars) final states are indicated. (b) Corresponding zoomed-in near- E_F 4*f*¹² final-state spectra. Surface and bulk spectral contributions are indicated by blue and green bars, respectively. (c) Tm 4*f* spectra of TmSe_{1- x} Te _{x} as a function of x , obtained by HAXPES. Black dashed vertical lines mark the position of the leading ³H₆ emission in the metallic and insulating regimes, indicating a spectral gap of ≈ 0.6 eV. (d) Corresponding high-resolution Tm 4*f* spectra obtained by XUV-PES. The measurement parameters are indicated (LH = linear horizontal polarization).

face peaks, however, the peak sequence and positions of the XUV and hard x-ray 4*f* spectra are consistent. Figure 3(b) shows an enlarged view of the 4*f* spectra of the $f^{13} \rightarrow f^{12}$ transition. While the surface peaks (indicated by blue vertical bars) dominate the XUV spectrum, they are absent from the HAXPES data. The surface peak closest to E_F is located at approximately -0.4 eV on the freshly cleaved surface and shifts to lower energies over time [Suppl. Fig. S4(b)].

Figures 3(c) and 3(d) show the evolution of the first two bulk 4*f* emissions: ³H₆ and ³F₄. The position of the leading ³H₆ peak determines the size of the possible energy gap. To highlight the spectra of the insulating samples, the part of the spectra of the semimetallic samples below the leading ³H₆ peak is shown faintly (Suppl. Sec. III [53]).

Figure 3(c) provides a medium-resolution HAXPES view. In the semimetallic regime ($0 \leq x \leq 0.11$), the ³H₆ peak appears at about -50 meV, while in the insulating regime ($0.46 \leq x \leq 1$), the ³H₆ peaks are located below -0.5 eV. The energy separation of the ³H₆ peaks is maximal (≈ 0.6 eV) between TmSe ($x = 0$) and TmTe ($x = 1$), reflecting the complete semimetal-insulator transition in the bulk. As x increases, the ³H₆ peak broadens up to $x_c = 0.29$ and then narrows again for larger $x > x_c$.

At x_c , the spectral weight largely fills the gap region, confirming that this Te concentration corresponds to the semimetal-insulator transition point.

Figure 3(d) shows the corresponding high-resolution XUV view (Suppl. Sec. III [53]). The XUV photoemission peaks are sharper than the HAXPES peaks in Fig. 3(c), but their positions are similar, identifying them as bulk emission features. The 3H_6 peak in the insulating compound TmTe ($x = 1$) is located at about -0.7 eV, indicating that the band gap is greater than 0.7 eV [83]. In the semimetallic region, the shapes and intensities of the 3H_6 peaks are found to be asymmetric and varying.

4f fine structure in the semimetallic phase—To probe these asymmetric line shapes with minimal thermal broadening and reduced spectral weight of the surface multiplet peaks, we performed low-temperature ($T = 2$ K) high-resolution XUV photoemission measurements at different light polarizations. The results are shown in Fig. 4(a) (Suppl. Sec. III [53]). The 3H_6 and 3F_4 emissions become more asymmetric as x increases. Each peak appears to consist of two bulk emission components, B1 and B2, as indicated by the vertical green bars. Asymmetric 3H_6 peak shapes are also seen in the high-resolution HAXPES spectra for $x = 0.05$ and 0.11 [Fig. 4(b)], confirming the characteristic line shape as a bulk effect. As x increases, spectral weight appears to transfer from the high-energy B1 component to the low-energy B2 component.

DFT+DMFT calculations with an on-site Coulomb interaction of 6 eV and a Hund's coupling of 1 eV are unable to capture the observed spectral weight transfer (Suppl. Sec. VI [84]). This suggests the presence of additional interactions, beyond the standard PAM. One candidate is the on-site $4f$ - $5d$ Coulomb interaction [21, 23–25] or $4f$ - $5d$ screening interaction [13, 18], which are estimated to be on the order of 1 eV [90, 91]. This interaction becomes relevant when a $4f$ photohole is created because the localized hole behaves as an impurity potential relative to the $5d$ electrons. Depending on the $5d$ bandwidth, the binding energy of an impurity-bound state resulting from the $4f$ - $5d$ interaction would be slightly smaller than the interaction itself. Consequently, occupying or emptying this bound state could give rise to two-peak structure with an asymmetric line shape of which separation would be on the order of 1 eV, which is significantly larger than the experimental observation.

Electron-phonon coupling [92], which is often overlooked in photoemission studies of heavy-fermion systems, is an interaction with a more consistent energy scale. When a localized Tm $4f$ photohole is created, nearby Se^{2-} or Te^{2-} anions can be attracted to form a Holstein polaron. Polaronic sidebands are clearly visible in ARPES spectra of low-carrier-density systems, such as electron-doped SrTiO_3 [93] and TiO_2 [94, 95], whereas in metallic systems, polaronic spectral signatures are typically suppressed due to rapid screening by con-

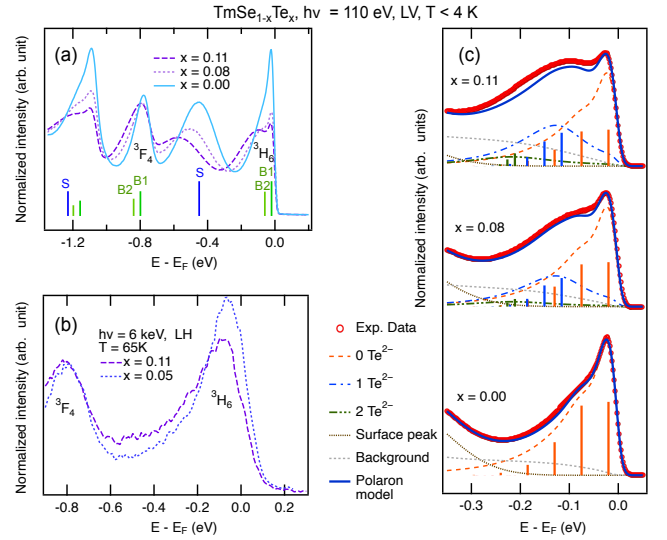


Figure 4. Tm $4f$ near- E_F fine structure of $\text{TmSe}_{1-x}\text{Te}_x$ in the semimetallic regime ($x \leq 0.11$) in XUV-PES and HAXPES. (a) Low-temperature high-resolution XUV-PES Tm $4f$ spectra. The asymmetric 3H_6 and 3F_4 emissions, as well as the bulk and surface emission features, are labeled. Measurement parameters are indicated (LV = linear vertical polarization). (b) High-resolution HAXPES Tm $4f$ spectra focusing on the 3H_6 emission. Measurement parameters are indicated (LH = linear horizontal polarization). (c) Low-temperature high-resolution XUV-PES Tm $4f$ spectra focusing on the 3H_6 emission (red circles), plus fitted lineshapes using a Holstein polaron model (blue lines). The spectral decomposition into phonon exciton peaks for Tm(Se,Te) $_6$ octahedra with 0, 1, and 2 Te ions (orange, blue, and green vertical bars and dash-dotted lines), a surface emission feature (gray dotted line), and an inelastic background (gray dashed line) is indicated. Same measurement parameters as in (a).

duction electrons. In heavy-fermion systems [96], however, this screening can be significantly slowed due to the large effective mass of quasiparticles. Moreover, local spatial dynamics seem beneficial for polaron formation in $\text{TmSe}_{1-x}\text{Te}_x$. Conduction electrons must hop from a next-nearest-neighbor site to screen a Tm $4f$ hole, while a polaron can form more readily through the displacement of nearest-neighbor anions.

Figure 4(c) shows the spectral function fits of the Tm $4f$ near- E_F spectra in the metallic regime ($0 \leq x \leq 0.11$) using a Holstein polaron model for the localized f electron [97]. For $x = 0$ [Fig. 4(c), bottom], the spectrum is a sum of a dressed peak closest to E_F (“B1 component”) and multiple phonon excitation peaks (“B2 components”) with an equal energy separation, which corresponds to the characteristic phonon energy. The intensity of each phonon excitation peak relative to the dressed peak follows a Poisson distribution, $g^p/p!$, where g is the electron-phonon coupling and p is the number of created phonons. The experimental Tm $4f$ spectrum is well reproduced with a dressed-peak energy $\varepsilon_f = -20$ meV, a phonon

energy $\omega_0 = 55$ meV, and an electron-phonon coupling $g = 0.95$, when lifetime and experimental broadening, as well as a background and the Fermi cutoff, are included [98–100].

To model the substitution of Se with Te ($x = 0.08, 0.11$), we assume that polarons are localized in a $\text{Tm}(\text{Se}, \text{Te})_6$ octahedron with N Te^{2-} ions. The probability or spectral weight of this configuration is given by the binomial distribution $\binom{6}{N} x^N (1-x)^{6-N}$. Substitutional Te^{2-} -ion doping results in reduced screening by conduction electrons, an increased average ion mass, and a decreased average chalcogen ionicity. These changes should lead to reduced values of ε_f , ω_0 , and g . Indeed, we can reproduce the Tm $4f$ spectra for $x = 0.08$ and $x = 0.11$, if we assume relative parameter reductions per Te^{2-} ion of $\delta\varepsilon_f = -95$ meV, $\delta\omega_0 = -20$ meV, and $\delta g = -0.2$ [Fig. 4(c), middle and top]. These spectra are characterized by a peak-dip-hump structure, where the parameter $\delta\varepsilon_f$ is critical for modeling the hump. Therefore, we emphasize that the size of $\delta\varepsilon_f$ is consistent with the observed Tm $3d$ core-level shift between TmSe and TmTe of 0.66 eV, which corresponds to approximately $6\delta\varepsilon_f$. Thus, our spectral function fitting with the relatively simple polaron model suggests that the spectral Tm $4f$ fine structure near E_F is caused by electron-phonon interaction.

Conclusion—Our combined XUV-PES and HAXPES study of the MV compound $\text{TmSe}_{1-x}\text{Te}_x$ over the full composition range ($0 \leq x \leq 1$) reveals a transition in the bulk electronic structure at $x_c = 0.29$ between phases with distinct noninteger valences and distinct semimetallic *versus* insulating characters. The key novel finding is a peak-dip-hump spectral structure near E_F in the semimetallic phase ($x \leq 0.11$), which a Holstein polaron model can reproduce. This result highlights the importance of electron-phonon interactions in MV systems and the need for more comprehensive theoretical models to describe them.

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Supplementary materials: Polaronic quasiparticles in the valence-transition compound $\text{TmSe}_{1-x}\text{Te}_x$

S I. OVERVIEW OF THULIUM MONOCHALCOGENIDES

$\text{TmSe}_{1-x}\text{Te}_x$ exhibits two prominent features: (1) an antiferromagnetic mixed-valent (MV) ground state¹, and (2) a metal-insulator transition (MIT) that encompasses a bosonic exciton-condensation phase during the transition²⁻⁵. The ground state of most $\text{TmSe}_{1-x}\text{Te}_x$ is characterized by trivalent ($V_{\text{Tm}} = 3$) and divalent ($V_{\text{Tm}} = 2$) configurations, both uniquely magnetic ($J \neq 0$)^{6,7}. V_{Tm} can be converted to the number of $4f$ electrons (n_f), thereby estimating the number of other outermost shell electrons (n_c). For Tm^{3+} (Tm^{2+}), the occupation of the $4f$ states is $n_f = 12$ ($n_f = 13$), while that of the conduction state is $n_c = 1$ ($n_c = 0$) with the formal configuration described as $f^{12}c^1$ ($f^{13}c^0$). By Hund's rule, the former and the latter have the $J = 6$ and $J = 7/2$ symmetry for the ground state, respectively.

Anion-replacement of Se by Te induces the lattice expansion together with the increase of the radius of Tm cations^{8,9}. This indicates the decrease of V_{Tm} , namely toward the divalence³. Semimetallic TmSe shows $V_{\text{Tm}} = 2.65 \pm 0.05$ ($n_f = 12.35 \pm 0.05$), which indicates smaller $a_0 = 5.705 \text{ \AA}$ at room temperature^{10,11}, whereas insulating TmTe shows $V_{\text{Tm}} = 2.05 \pm 0.05$ ($n_f = 12.95 \pm 0.05$), which reflects greater $a_0 = 6.35 \text{ \AA}$ ^{11,12}. Consequently, during the MIT from TmSe to TmTe, a substantial charge redistribution will happen from the conduction electron states n_c to the localized $4f$ states n_f . It is not intuitive how such an insulating state can show the intermediate valence. Even in the most bulk-sensitive L_3 -edge fluorescence-yield x-ray absorption result, Tm^{3+} contributions do appear as a shoulder¹³.

Unlike the other MV compounds, long-range magnetic orderings occur in both semimetallic and insulating phases. Type-I antiferromagnetic (AFM) ordering appears in TmSe at $T_N = 3.2 \text{ K}$ ¹ while antiferroquadrupolar and type-II antiferromagnetic orderings occur in TmTe at $T_Q = 1.8 \text{ K}$ and $T_N = 0.23 \text{ K}$, respectively¹⁴. Due to the presence of both spin and valence fluctuations at low temperatures, scattering studies on TmSe and TmTe have revealed distinctive features below T_N , which have not been observed in other MV Ce, Sm, and Yb compounds and a metallic Ce system with a long-range magnetic ordering¹⁵⁻¹⁷. The major difference of $\text{TmSe}_{1-x}\text{Te}_x$ is that the total number of electrons per unit cell is odd ($N = 13$), whereas for other MV materials this number is even¹⁸. Moreover, the crystal field splittings are not considered in this study since they are smaller than 10 meV, which even in transport measurements is barely detectable^{14,19}.

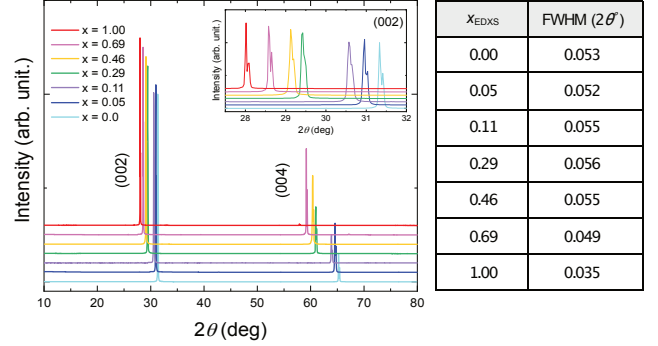


Figure S1. (Color online) X-ray diffraction patterns for the $\text{TmSe}_{1-x}\text{Te}_x$ single crystals.

S II. SINGLE CRYSTAL SYNTHESIS AND TE/SE RATIO CHARACTERIZATION

Single crystals of $\text{TmSe}_{1-x}\text{Te}_x$ were grown by Bridgman method. The raw materials of Tm pieces (Alfa aesar 99.9%), Se grains (Kojundo chemical, 99.999%), and Te lumps (Alfa aesar 99.9995%) were weighed in a molar ratio of $\text{Tm}:\text{Se}_{1-x}\text{Te}_x = 0.6 : 0.4$. This method with self-flux Tm enables single crystal growth of $\text{TmSe}_{1-x}\text{Te}_x$, which has a very high melting point of about 2500 °C, at low temperatures. It has been known that the single crystal growth method at a low temperature has the advantage of reducing the number of crystal defects that otherwise may occur more frequently at a high temperature. The weighed materials were placed in a clean tungsten crucible baked at 2200 °C. The crucible and the lid were then welded with an arc welder to prevent the volatility of the materials, especially Se and Te. The welded tungsten crucible was mounted in a high vacuum electric furnace consisting of a tungsten meshed heater with temperature stability of $\pm 0.1^\circ\text{C}$. The single crystals were grown at 2000 °C and the typical size was from $1 \times 1 \times 0.5$ to $3 \times 3 \times 0.5 \text{ mm}^3$.

The x-ray diffraction (XRD) patterns of $\text{TmSe}_{1-x}\text{Te}_x$ single crystals were obtained using a PANalytical Empyrean diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda_{K-\alpha_1} = 1.54060$ and $\lambda_{K-\alpha_2} = 1.54443 \text{ \AA}$). As shown in Fig. S1 (Left), only (00 l) diffraction pattern was clearly observed, and as the amount of Te substitution increased, the peak positions shifted to a low angle due to an increase in the lattice constant. The lattice constant a_0 calculated by (00 l) peaks is listed in Fig. S1 (right), and the lattice constant increases as the amount of Te increases. The parent TmSe single crystal grown by our single crystal method, which prevents the volatility of Se, can exclude the sample inhomogeneity that may occur due to the Te substitution and Se defects. This is supported by

the fact that the temperature dependence of the electrical resistivity of a few single crystals obtained from the same ingot was almost identical. As demonstrated in the inset to Fig. S1 (Right), the homogeneous TmSe single crystal shows a very narrow (002) peak with FWHM = 0.0526 °. Since the substitution by Te in TmSe may lead to inhomogeneity, FWHM of the XRD (002) peak for the substitution system $\text{TmSe}_{1-x}\text{Te}_x$ was evaluated and is listed in Fig. S1 (Right). The FWHM for each x is also very small and approximately equals that of TmSe, indicating that Te-substitution did not result in crystal inhomogeneity. Another evidence for the crystal homogeneity is that the temperature dependence of the electrical resistivity of a few single crystals (Fig. 1) extracted from the same ingot is approximately the same. Therefore, the $\text{TmSe}_{1-x}\text{Te}_x$ single crystals used in this study did not cause inhomogeneity due to Te substitution. At a few single-crystal near the MIT, *i.e.*, at $x_{\text{EDXS}} = 0.11$ and 0.29, we have sometimes found some pieces with slightly different Te concentrations compared to the other pieces synthesized at the same batch, but all their spectral features were fitting the general trends between $x_{\text{EDXS}} = 0.05$ and 0.46. Thus, all of them fit the general trend upon x .

The composition ratio x_{EDXS} of each element in a single crystal of $\text{TmSe}_{1-x}\text{Te}_x$ was determined by Energy-Dispersive X-ray Spectroscopy (EDXS) and scarcely by Inductively Coupled Plasma (ICP) marked with * as shown in Table I. The table shows the results of the compositional analyses of the grown $\text{TmSe}_{1-x}\text{Te}_x$ crystals, revealing significant deviations between the nominal values x_{nominal} , corresponding to the pregrowth mixing ratio, and the actual values x_{EDXS} measured by EDXS. Such a discrepancy is common in crystal growth for multicomponent crystals²⁰. Our x_{nominal} values are close to the x values reported in Ref.²¹ when comparing values for similar lattice constants a_0 .

x_{nominal}	0.0	0.125	0.25	0.4	0.5	0.66	1.0
x_{EDXS}	0.0	0.05	0.11	0.29	0.46	0.69*	1.0
a_0 (Å)	5.705	5.775	5.843	6.068	6.126	6.242	6.366

Table I. Nominal and measured Te contents x_{EDXS} and lattice constants a_0 of $\text{TmSe}_{1-x}\text{Te}_x$

a_0 can be tuned quite continuously with varying x except for the range of $5.85 \text{ Å} < a_0 < 6.05 \text{ Å}$ ^{3,22}. This exceptional range (miscibility gap) is near MIT, which might be an unstable phase region for crystal growth. Such isostructural first-order transition has been studied in Sm monochalcogenides as well²³. At $x = 0.29$ ($a_0 = 6.068 \text{ Å}$). The reported activation gap values were 180 meV for $x \sim 0.29$ ($a_0 = 6.07 \text{ Å}$)²², and 110 meV for $x \sim 0.46$ ($a_0 = 6.14 \text{ Å}$)²¹.

S III. EXPERIMENTAL AND NORMALIZATION

Presumably, due to a strong charging effect, obtaining photoemission spectra of those insulating samples at $T < 70 \text{ K}$ was impossible. For this reason, the data for these insulating samples were collected at 110 K. Additionally, the intensity of the incident light was varied, which allowed us to exclude any detectable charging at this higher temperature. All XUV 4*f*-electron spectra were taken in normal emission and angle-integrated over more than 40° along the analyzer slit direction, while HAXPES data were taken with the transmission lens mode of the electron analyzers. The 4*f* multiplet lines result from the transition from the ground state to the one-electron removal final state. Each multiplet line represents a specific photohole state among different final state configurations, resulting in different net Coulomb interactions⁷. The closer the state is to E_F , the less energy is required to create it.

Hard x-ray photoelectron spectroscopy (HAXPES) were performed with $h\nu = 6 \text{ keV}$ at the beamline P22 of PETRA III using a Phoibos 225HV electron analyzer²⁴ with the total energy resolution (ΔE) of 340 meV (Figs. 2, 3(c) and S2) and $\Delta E = 270 \text{ meV}$ (Fig. 4(d)). After cooling the cryostat with LHe, the base pressure was below $5.0 \times 10^{-10} \text{ mbar}$. Theoretically, the kinetic energy of 3*d* photoelectrons produced with $h\nu = 6 \text{ keV}$ has an inelastic mean free path of 6 nm. The core-level spectra in Fig. 2 are normalized to the total spectral weight of Tm 3*d*_{3/2} after removing the Shirley background. The 4*f* spectra in Fig. 3(c) and Fig. 4(d) are normalized with respect to the intensity of 3F_4 , and the 3F_4 peaks in the semimetallic phases are faintly displayed to emphasize the 3H_6 peaks in the insulating states.

Additional measurements (see Fig. 3(a)) have also been performed at the beamline I09 of DIMOND (Didcot) equipped with the VG Scienta EW4000 analyzer using energy resolution of $\Delta E = 250 \text{ meV}$ at $h\nu = 5931 \text{ eV}$. The base pressure was better than $5.0 \times 10^{-10} \text{ mbar}$.

The high-energy-resolution photoemission spectroscopy (HR-PES) was carried out at the beamline MERLIN of ALS (Berkeley) with the energy resolution $\Delta E \leq 30 \text{ meV}$ at $h\nu = 70$, and 110 eV using the VG Scienta R8000 analyzer (Fig. 3(a-b, d), and Fig. S4(b-c)). The base pressure was lower than $7.0 \times 10^{-11} \text{ mbar}$. The 4*f* spectra of Fig. 3(d) are normalized to match the intensities around $E - E_F = -3 \text{ eV}$ and -3.5 eV for metallic and insulating samples, respectively. Moreover, the surface 3H_6 and bulk 3F_4 peaks are rendered faint to focus on the 3H_6 peaks.

The high-resolution spectra at $T \approx 2 \text{ K}$ shown in Fig. 4(a-b) were achieved using the one-cube ARPES setup, where a Scienta-omicron DA30 analyzer installed at the UE112-PGM2b beamline of the BESSY-II. The total energy resolution was $\Delta E \leq 28 \text{ meV}$ at $h\nu = 110 \text{ eV}$. The base pressure was lower than $1.0 \times 10^{-10} \text{ mbar}$. The 4*f* spectra in Fig. 4(a) are normalized with respect to

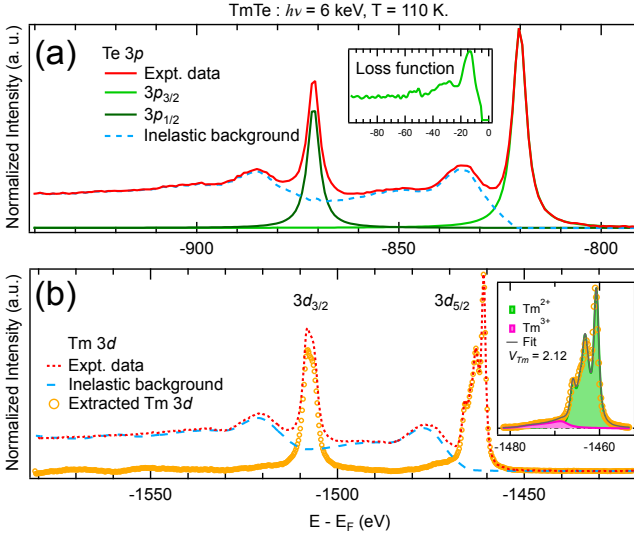


Figure S2. HAXPES core-level study of TmTe (a) Simple Te 3*p* core-level spectrum (red) is utilized to extract the full line shape of the energy loss function of photoelectrons (inset), which can generate the inelastic background shape (cyan dashed line). (b) By deconvoluting the loss function out of the experimental spectrum, we extract the intrinsic Tm 3*d* spectrum (orange circles). (b, inset) With the intrinsic one, the Tm³⁺ and Tm²⁺ contributions are identified (pink and green areas, respectively), which gives a non-integer $V_{\text{Tm}} = 2.12$ even in the insulating states.

the intensity at $E - E_F \approx -3$ eV.

The PES spectra for $x = 0.29$ and 0.46 in Fig. S4(c) were measured at $T = 40$ K at the beamline TEMPO of SOLEIL (Gif-sur-Yvette) using a MBS A1 analyzer with the total resolution $\Delta E = 40$ meV at $h\nu = 110$ eV. The base pressure was better than 5.0×10^{-10} mbar. The 4*f* spectra in Fig. S4(c) are normalized to the intensity of 3F_4 peaks.

Soft x-ray core-level spectroscopy in Fig. S4 (a) was performed at the BL P04 of PETRA III (Hamburg) using $h\nu = 1800$ eV with $\Delta E \leq 400$ meV where the ASPEHRE III endstation is equipped with a Scienta-Omicron DA30 analyzer. The base pressure was better than 2.0×10^{-10} mbar.

S IV. V_{Tm} ESTIMATION

A. valence of TmTe

We demonstrate our analysis procedures to obtain V_{Tm} for insulating states. The Quanty program was used for the multiplet structure of the Tm core-level²⁵ and deconvolute the loss function to remove the inelastic background (BG). The loss function describes various extrinsic energy losses of photoelectrons due to the inelastic scatterings while escaping from the sample. The inelastic BG is the result of a convolution of intrinsic core-level

spectral functions and a loss function.

The simple peak structure of Te 3*p* is used to deduce the loss function Fig. S2 (a, inset), which enables to generate the inelastic BG (cyan-dashed line). By deconvoluting the loss function out of the experimental Tm 3*d* core-level spectrum, the inelastic BG is filtered out whereby the intrinsic 3*d* spectrum is extracted (orange circles in Fig. S2 (b)). From the intrinsic spectrum, V_{Tm} are evaluated using the multiplet ligand field theory calculations (inset of Fig. S2 (b))²⁵. Our fitting results clearly show the non-integer $V_{\text{Tm}} (= 2.12)$, which is consistent with a few bulk-sensitive magnetic susceptibility and spectroscopic results^{3,8,11,26}. Such intermediate valence indicates an interaction between 4*f* and non-5*d* states also exists in the insulating phase. Since our bulk-sensitive data were taken on freshly cleaved surfaces, it would be very challenging to attribute the non-integer valencies to the contamination²⁷.

B. V_{Tm} estimation for the semimetallic samples

The general idea relies on fitting the experimentally measured Tm 3*d* core level spectrum to the sum of 2+ and 3+ components, while the components themselves are obtained within atomic multiplet calculation:

$$\chi^2(\alpha_2, \alpha_3) = \int (I_{\text{exp}}(E) - I_{\text{mod}}(E))^2 dE \rightarrow \min, \\ \text{with } I_{\text{mod}}(E) = \alpha_2 I_{\text{mod}}^{2+}(E) + \alpha_3 I_{\text{mod}}^{3+}(E) \quad (\text{S1})$$

The required valence is then given by

$$v = \frac{2\alpha_2 + 3\alpha_3}{\alpha_2 + \alpha_3}. \quad (\text{S2})$$

Since the 4*f* electrons are well shielded, the strength of the crystal field (CF) for the rare earth elements can be disregarded altogether because of the experimental resolution and purpose of this calculation²⁸⁻³⁴. For the same reason, we can safely neglect the CF effects in the *d*-shell, since the 3*d* core orbitals are even more localized than the 4*f* valence levels. Therefore, to properly describe the experimental line-shape of the XPS spectrum it suffices to account in the Hamiltonian for the spin-orbit interaction in the 3*d*- and 4*f*-shells and for the Coulomb repulsion between 3*d* and 4*f* electrons^{35,36}:

$$\hat{H} = \hat{H}_{\text{Coul}}^{dd} + \hat{H}_{\text{Coul}}^{df} + \hat{H}_{\text{Coul}}^{ff} \\ + \zeta_{3d} \hat{\mathbf{L}}_{3d} \cdot \hat{\mathbf{S}}_{3d} + \zeta_{4f} \hat{\mathbf{L}}_{4f} \cdot \hat{\mathbf{S}}_{4f}. \quad (\text{S3})$$

For example, the Coulomb term $\hat{H}_{\text{Coul}}^{ff}$ can be relatively simply expressed as

$$\hat{H}_{\text{Coul}}^{ff} = \frac{1}{2} \sum_{p,q,u,t} \sum_{k=0}^l a_k(p, q, u, t) F_{ff}^{(2k)} \hat{f}_p^\dagger \hat{f}_q^\dagger \hat{f}_u \hat{f}_t, \quad (\text{S4})$$

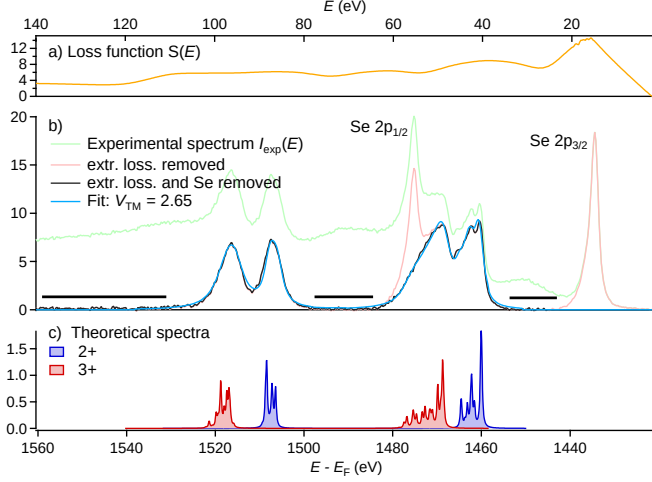


Figure S3. Extracting pure Tm 3d core-level. (a) The loss function without the leading delta peak at $E = 0$. (b) The process of deconvolution of the extrinsic losses and removal of Se 2p peak. (c) Theoretical spectra for Tm^{2+} and Tm^{3+} were used to fit the deconvoluted data.

where the outer sum runs over the $7 \times 2 = 14$ $4f$ spin-orbitals, a_k are known constants determined by the angular part of the $4f$ -states, so that $\hat{H}_{\text{Coul}}^{ff}$ is fully determined by the four Slater integrals, $F_{ff}^{(0)}, F_{ff}^{(2)}, F_{ff}^{(4)}, F_{ff}^{(6)}$, which in turn depend on the radial part of the one-particle $4f$ -states. Similarly, the f - d part depends on five other parameters, controlling so-called direct ($F_{df}^{(2)}, F_{df}^{(4)}$) and exchange ($G_{df}^{(1)}, G_{df}^{(3)}, G_{df}^{(5)}$) Coulomb interactions between f - and d -orbitals³⁵.

Eventually, the angle-integrated Tm 3d XPS spectrum can then be approximated by

$$I(E) \sim \sum_i \sum_{\alpha} e^{\frac{-E_{\alpha}}{k_B T}} \sum_{\beta} \left| \left\langle \Psi_{\beta}^{N-1} | \hat{d}_i | \Psi_{\alpha}^N \right\rangle \right|^2 \times \frac{-1}{\pi} \text{Im} \left[\frac{1}{(E_{\beta} - E_{\alpha} - E) + i \frac{\Gamma(E)}{2}} \right]. \quad (\text{S5})$$

Here, the middle sum takes care of the thermodynamic averaging for a finite temperature T , including a possible degeneracy of the initial state $|\Psi_{\alpha}\rangle$. The inner sum accounts for the transition probabilities between the initial N -particle state $|\Psi_{\alpha}^N\rangle$, and the final $N - 1$ -particle state $|\Psi_{\beta}^{N-1}\rangle$, whereas the corresponding lifetimes are given by the function $\Gamma(E)$, which in the current consideration is to be determined from fits to experimental data. The outermost sum runs over the 10 $3d$ spin-orbitals, with $\hat{d}_i$ being the corresponding annihilation operator.

The actual calculations were performed using *Quanty*^{25,37,38}, a program developed by Prof. M. W. Haverkort, which offers a convenient and flexible way to define this quantum mechanical system in second quantization. The values for the spin-orbit couplings and the Slater integrals were obtained using the Cowan

code³⁶. The usual scaling of the atomic Slater integrals down to 74–80% of their atomic Hartree–Fock values was applied to account for intra-atomic screening effects. The resulting theoretical spectra with the realistic lifetime and experimental broadening excluded are shown in Fig. S3 (c).

If it were not for the extrinsic losses and overlap with the Se $2p_{1/2}$ peak, one could have directly used the theoretical spectra in eq. S1 to determine the valency. In practice one first has to determine $I_{\text{exp}}^{\text{no loss}}(E)$ by deconvoluting the losses given by the loss function $S(E)$ and then subtract the Se $2p_{1/2}$ peak:

$$I_{\text{exp}}^{\text{lossy}}(E) = \int_0^{+\infty} I_{\text{exp}}^{\text{no loss}}(E - x) S(x) dx, \text{ where}$$

$$I_{\text{exp}}^{\text{no loss}}(E) = I_{\text{exp}}(E) + I_{\text{exp}}^{2p_{1/2}}(E) + I_{\text{exp}}^{2p_{3/2}}(E) \quad (\text{S6})$$

As shown from Fig. S3 (b), the removal of the Se $2p_{1/2}$ peak from the deconvoluted spectrum $I_{\text{exp}}^{\text{no loss}}(E)$ can be achieved by subtraction of a shifted and scaled copy of Se $2p_{3/2}$ peak.

Since $S(E)$ is a smooth and slowly varying function of energy it can be parametrized using a spline with just a handful of nodes. Optimizing the node positions such that the deconvoluted spectrum becomes maximally close to zero within the three energy ranges marked with the horizontal bars in Fig. S3 (b), the $S(E)$ and the deconvoluted spectrum can be determined.

S V. SURFACE AND BULK ISSUES

According to our analyses, both soft and hard x-ray spectra measured below 65 K give similar V_{TM} on freshly cleaved (001) surfaces (Fig. S4 (a)), but the former shows a slightly higher value. Even with bulk-sensitive HAXPES measurements, severe change in V_{TM} starts to become apparent after 4 - 5 h after the cleaving. Hence, we have measured the Tm 3d core-level spectra for each temperature by cleaving new single-crystalline samples and also using a low-energy resolution setup for quick data acquisition (Fig. 2). We have also checked core-level spectra for several other single-crystalline pieces at the same x and temperature with both XAS and PES to confirm that obtained V_{TM} values are reproduced for each x . Typical aging signature is the reduction of the surface $4f$ multiplet peaks as shown in Fig. S4 (b); moreover, the Tm^{3+} contribution increases with time.

Figure S4 (c) shows $4f$ spectra taken with $h\nu = 110$ eV near the E_F as a function of x , where surface 3H_6 and bulk 3F_4 peaks are weakly rendered. The spectral features are therein mostly consistent with the HAXPES ones shown in Fig. 3 (c): The energy difference in 3H_6 between semimetallic and insulating phases is about 0.6 eV, and $x = 0.29$ shows the largest spectral weight in the gap region. With a further increase of x , the spectral weight in the gap region reduces.

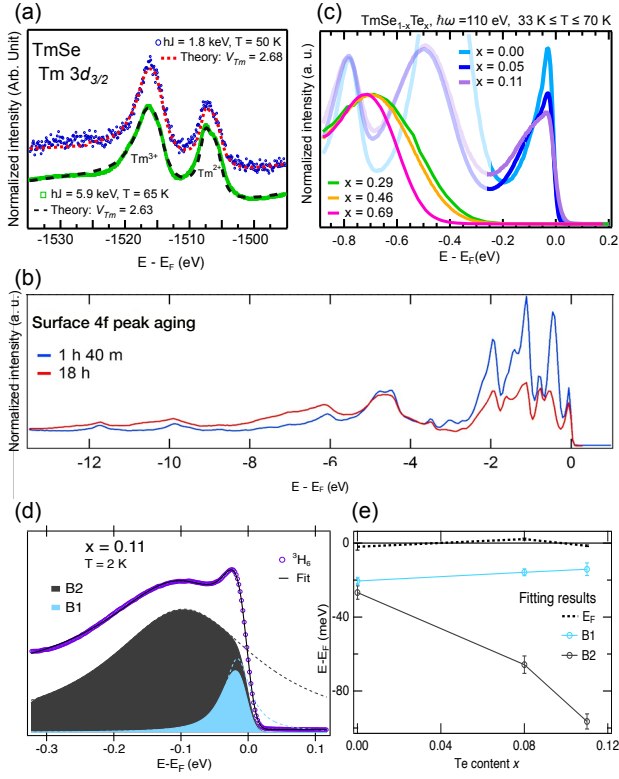


Figure S4. (Color online) (a) The Tm $3d_{3/2}$ core-level spectra were obtained from freshly cleaved surfaces of TmSe with soft and hard x-rays. Estimated V_{Tm} is almost identical disregarding the probing depth of our method, which indicates that both surface and bulk are mixed-valent states. (b) XUV-PES spectra show the aging effect on the $4f$ spectra. Surface $4f$ peaks are shown in (a) decrease in intensity with aging. (c) High-resolution PES spectra taken at $h\nu=110$ eV reveal the same energy difference in the 3H_6 peaks between semimetallic samples and insulating samples like the HAXPES data. (d) Line decomposition of 3H_6 . The asymmetric shape is due to the two-peak structure of each bulk multiplet peak. For example, the 3H_6 peak for $x = 0.11$ consists of a sharp peak (B1) and a broad peak (B2). As x increases, the spectral weight of the B1 at E_F decreases relative to that of the B2, colored in cyan and black, respectively. (e) Energy difference between B1 and B2, increasing with x . The energy position of B1 remains almost the same, but B2 shifts to lower energies, as indicated by the arrows in (a), up to -96 meV.

The main differences between XUV and hard X-ray data are found in the $x = 0.29$. In the HAXPES, the 3H_6 peak appears at $E-E_F = -0.52$ eV, whereas in the XUV spectra at -0.62 eV (Fig. S4(c)). Depending on the cleaved surface the $4f$ peak of $x = 0.29$ appears at different energies in the range of ± 0.1 eV. However, the $x = 0.29$ certainly shows the highest spectral weight in the gap region (-0.7 eV $< E-E_F < 0.0$ eV). As a result, one can conclude that a substantial decrease in the spectral weight happens inside the gap region upon x among insulating states.

Figure S4(d) shows that the 3H_6 emission for $x = 0.11$

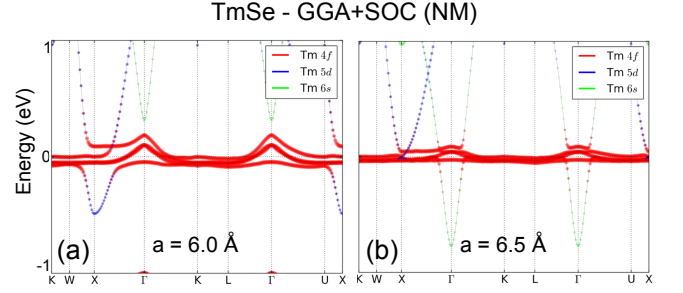


Figure S5. DFT results with GGA+SOC scheme in nonmagnetic phase of TmSe. As a function of the lattice parameter, the minimum of the conduction band appears at different high symmetry points.

consists of a sharp peak at about -14 meV and a broad peak at lower than -96 meV whose splitting is too large to be attributed to crystal-field splitting in Tm monochalcogenides¹⁹. Note that as x increases, the sharp peak B1 is suppressed, while the broad peak B2 becomes relatively more intense and shifts to lower energies, as indicated by the downward arrows [see also Fig. 4(a)]. The peak positions of B1 and B2 as a function of x are plotted in Fig. S4(d). The energy difference between B1 and B2 increases from 6 meV to 82 meV for a 2% lattice expansion from $x = 0$ to $x = 0.11$.

S VI. COMPUTATIONAL DETAILS OF DFT AND DFT+DMFT

Our detailed investigation of the band structure of $TmSe_{1-x}Te_x$ will be published elsewhere. Here, we briefly mention our theoretical results based on the density functional theory and also with dynamical mean-field theory (DFT+DMFT) scheme, which explains the electronic structure of strongly correlated systems well. In the DFT part, we have employed the all-electron full-potential linearized augmented plane wave (FLAPW) band method implemented in the WIEN2K package³⁹. A generalized gradient approximation (GGA) functional was chosen for exchange-correlational functional. The spin-orbit coupling (SOC) is included as the second variational method. Since antiferromagnetic ordering temperature T_N is very low (3.5 K) and ARPES measurements were mostly done above T_N or without sufficient energy resolution to probe the effect, we focus on a paramagnetic phase in this study. Based on the DFT with GGA+SOC scheme, we obtained a similar band structure of TmSe in Ref.⁴⁰.

The band structure of $TmSe_{1-x}Te_x$ is expected to have an indirect gap E_g between the conduction $5d$ band minimum (at X) and the valence $4f$ band maximum (at Γ)^{40,41}. TmSe is predicted to be a semimetal with $E_g < 0$, whereas TmTe is expected to be an insulator^{12,22}. Hence, by analyzing the x -dependence, which is equivalent to the a_0 dependence, one can study the evolution of the

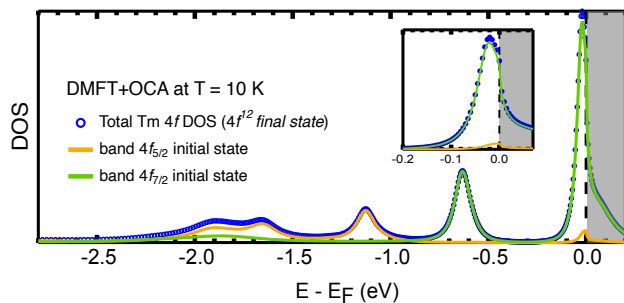


Figure S6. Our DFT+DMFT (OCA impurity solver) results reproduce the bulk multiplet peaks for the $4f^{12}$ final state at 10 K, but the two-peak structure is absent.

energy gap, which is composed of $5d$ and $6s$ band dispersion. The GGA+SOC calculations show a metallic phase in the range of a_0 that we studied. (The on-site Coulomb repulsion U is required to obtain the insulating phase.) We found that the paramagnetic results explain the position of the conduction band minimum observed in the ARPES data.

As shown in Fig. S5, the conduction $5d$ and $6s$ bands shift noticeably in opposite directions. As a_0 increases, the conduction $5d$ band gradually moves above E_F while the $6s$ band shifts downward. In the range of $6.1 \text{ \AA} < a \leq 6.5 \text{ \AA}$, the conduction $6s$ band is present below E_F . Thus, Tm $4f$ - $5d$ hybridization changes into Tm $4f$ - $6s$

hybridization as a_0 increases. This trend is also found in the hypothetical SmO system⁴².

In our PES spectra, no conduction band is observed in the insulating phase ($x = 0.69$), and there is almost no energy shift of the conduction $5d$ band minimum in the metallic samples ($0 \leq x \leq 0.11$). Since GGA+SOC does not properly account for strong electronic correlations, we utilize the GGA+SOC+ U scheme in the paramagnetic phase (not shown). When on-site Coulomb repulsion U ($= 6 \text{ eV}$) is included, a band gap opens and generally increases with a_0 but the gaps often close at certain lattice parameters.

Neither GGA+SOC nor GGA+SOC+ U schemes fully explain the evolution of the $4f$ states, indicating the need for advanced calculations that incorporate dynamic correlation effects beyond static ones. So far, no ARPES studies have observed the presence of $6s$ character below E_F , suggesting that it may lie just above the E_F in the experiment.

Using the DFT results, we also performed DFT+DMFT calculations similar to Ref.⁴³ and analyzed the bulk $4f^{12}$ final state peaks. To solve the impurity solver, we used the vertex-corrected one-crossing approximation (OCA), in which the full atomic interaction matrix was taken into account³⁶. The Coulomb interaction $U = 6.0 \text{ eV}$, and the Hund's coupling $J = 1.0 \text{ eV}$ were used for the DFT+DMFT calculations. Overall $4f^{12}$ final state peaks are nicely reproduced (Fig. S6), but the fine structure of B1 and B2 has been absent.

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