

Evidence for Quasilocalized $5f$ Electronic States in $\text{USb}_x\text{Te}_{1-x}$

B. Reihl, N. Mårtensson, P. Heimann, and D. E. Eastman
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

and

O. Vogt

Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule, Ch-8093 Zürich, Switzerland
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We have studied the " $5f, 6d$ " electron states of the system $\text{USb}_x\text{Te}_{1-x}$ (100) using photoemission spectroscopy with synchrotron radiation. In contrast with the generally accepted picture of uranium chalcogenides and pnictides, we find for UTe that the main $5f$ level lies 0.75 eV below E_F rather than at E_F and that $6d$ states exist at E_F . Our results may be explained with a model having a correlated quasilocalized $5f^{3-\delta}$ ($\delta = 0-0.5$) level resonant with broader $6d$ bands rather than bandlike $5f$ levels.

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The generally accepted picture¹⁻³ of the electronic structure of *all* uranium monochalcogenides and pnictides (UX, X = group-V or -VI element) is one of a ~ 2 eV wide " $f-d$ " conduction band with very narrow occupied $5f^n$ ($n \cong 2-3$ electrons) bands [full width at half maximum (FWHM) ≤ 0.5 eV] at the Fermi level E_F and $\sim 3-5$ eV anion-derived valence bands several eV below E_F . The occurrence of essentially the same " $5f, 6d$ " electronic structure for both uranium pnictides and chalcogenides is, however, questionable in view of their different formal U valence configurations, likely $5f$ correlation effects, and their quite different magnetic properties.¹⁻³ We report high-resolution photoemission measurements using single crystals for the system $\text{USb}_x\text{Te}_{1-x}$ ($0 \leq x \leq 1$) which show detailed " $5f, 6d$ " conduction-band features. This system exhibits an unexpected behavior, with UTe being quite different from USb and the generally accepted picture of UX compounds. We discuss possible descriptions of our results, and conclude that correlation effects are more important than previously believed via band calculations and that this system can be described with a correlated, quasilocalized $5f^{3-\delta}$ ($\delta = 0-0.5$) level which is in resonance,³ i.e., hybridized, with itinerant $6d$ bands.

Measurements were performed with a two-dimensional display-type analyzer⁴ with use of synchrotron radiation at the Synchrotron Radiation Center, Stoughton, Wisconsin. This system was operated with an energy resolution of 0.1 eV in either an angle-integrated mode with a full 86° acceptance cone of emission angles and typical counting rates of $\geq 10^5$ /sec, or in an angle-resolved mode with an angular resolution of 6° full angle.

Single crystals of $\text{USb}_x\text{Te}_{1-x}$ ($x = 0.0, 0.7, 0.8$, and 1.0) of dimensions $\sim 3 \times 3 \times 5$ mm³ were cleaved along their (100) planes in a 1×10^{-10} Torr vacuum. Low-energy electron-diffraction (LEED) patterns always showed a regular $p(1 \times 1)$ pattern with no observable steps (e.g., split LEED spots) on the surface. The preparation of the single crystals is described elsewhere.⁵ A microprobe analysis showed that stoichiometries are off by less than 1%.⁶ Measurements were performed in a vacuum of 10^{-11} Torr, in which samples stayed clean for several hours during the measurements, as monitored by Auger spectroscopy and by the oxygen $2p$ signal in photoemission.

Photoemission angle-integrated energy distribution curves (EDC's) are shown in Fig. 1 for USb(100), $\text{USb}_{0.7}\text{Te}_{0.3}$ (100) and UTe(100) for $h\nu = 45$ eV, a photon energy sufficiently high to make the " $5f, 6d$ " conduction-band emission intensity much greater than the " s, p " valence-band emission. A narrow " $5f, 6d$ " conduction band is observed just below E_F together with broader " s, p " valence bands at lower energies with band widths as indicated. These s, p bands are seen more clearly at lower $h\nu$ (not shown). Previous measurements⁷ for $h\nu < 11$ eV show very weak " $5f, 6d$ " emission, but are consistent with our results. An interesting trend is observed for the conduction bands of the system $\text{USb}_x\text{Te}_{1-x}$ on going from USb to UTe, which we have emphasized in Fig. 1 by shifting the respective Fermi energies so as to keep the dominant emission peak labeled *B* at a constant position. Namely, for USb two peaks are seen, *B* at -0.23 eV and *C* at -0.59 eV, and the measured " $5f, 6d$ " conduction-band width is quite small with a full width at half maximum (FWHM) of 0.8 eV. For $\text{USb}_{0.7}\text{Te}_{0.3}$, the bands

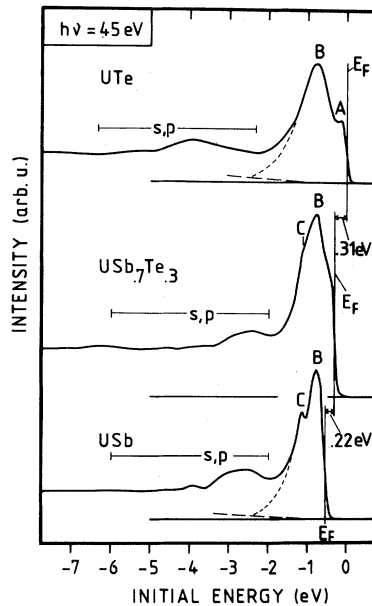


FIG. 1. Energy distribution curves at $h\nu = 45$ eV for USB, $\text{USB}_{0.7}\text{Te}_{0.3}$, and UTe at room temperature. The curves are not normalized. Zero energy corresponds to the Fermi level of UTe. The spectra are aligned so that peaks B coincide. The resulting shifts of E_F for $\text{USB}_{0.7}\text{Te}_{0.3}$ and USB are -0.31 and -0.53 eV, respectively. The $\text{USB}_{0.8}\text{Te}_{0.2}$ spectrum (not shown) is shifted by -0.35 eV relative to E_F of UTe. For USB and UTe, the conduction-band PDOS is obtained (short-dashed line) by subtraction of a secondary-electron background (long-dashed line).

are broadened to 1.1 eV, a shoulder is observed at E_F , and the spectral features B and C have shifted to -0.45 and -0.81 eV, respectively. For UTe, the bands have further broadened to FWHM ~ 1.35 eV, a new spectral peak A appears at -0.13 eV, and peak B has shifted to -0.75 eV; here peak C is not resolved, likely because of increased hole-lifetime broadening (to be discussed below).

These conduction-band photoemission densities of states (PDOS) for $\text{USB}_x\text{Te}_{1-x}$ can be described quite well by a simple rigid-band model which is summarized in Fig. 2 [lattice parameters are nearly constant; USB, 6.197 Å (Ref. 5) and UTe, 6.155 Å (Ref. 6)]. In Fig. 2(a), the PDOS's of USB and UTe are compared. As indicated in Fig. 1, they are obtained after subtraction of a smooth secondary-electron background. The conduction-band PDOS for UTe is taken to contain four conduction-band electrons, as given by the formal valence configuration $\text{U}^{2+}\text{Te}^{2-}$, with two U-derived electrons involved in the filled valence bands.

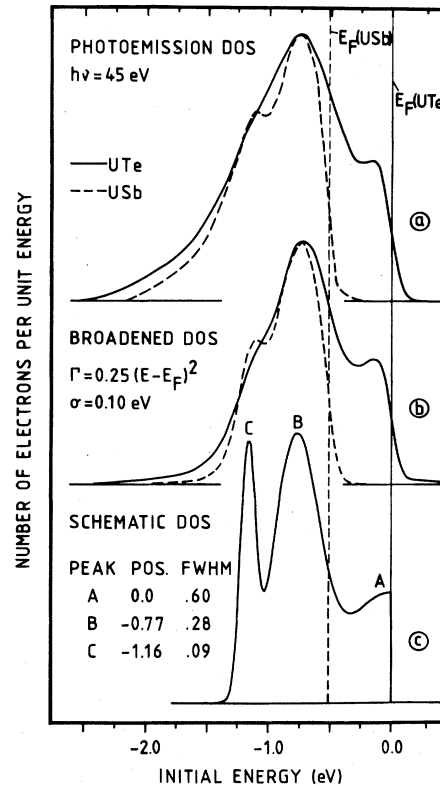


FIG. 2. (a) Conduction-band PDOS's of USB and UTe as obtained from Fig. 1; (b) Lorentzian- and Gaussian-broadened schematic PDOS's; (c) schematic DOS given by a superposition of three Gaussians. All parameters are given in eV. The area under peaks B and C up to the long-dashed cutoff corresponds to 75% of the total area. All curves are normalized to equal maximum peak heights (see text).

The Fermi level position of the USB spectrum is then placed at the cutoff energy position (-0.51 eV) for three conduction-band electrons in the PDOS derived from UTe. This position results in the peaks B of the two spectra coinciding nearly perfectly. A schematic summary of a rigid-band DOS for the $\text{USB}_x\text{Te}_{1-x}$ system is given in Fig. 2(c); here we have used the EDC's of Fig. 1 plus others at lower photon energies so as to resolve optimally peaks A-C. The DOS function was constructed by representing the spectral features A, B, and C by Gaussians with peak positions and FWHM as given in the figure. In Fig. 2(b), we show how the PDOS's of USB and UTe can be derived from this DOS function assuming a common energy-dependent Lorentzian energy broadening⁸ with FWHM $\Gamma(\text{eV}) = 0.25(E - E_F)^2$, and a Gaussian spectrometer resolution with FWHM $\sigma = 0.10$ eV, as determined from the UTe Fermi-level cutoff.

Both the USb and UTe PDOS's are reproduced by this rigid-band model. We note that peak *C* is no longer resolved in the UTe spectrum (cf. Fig. 1) due to an estimated lifetime broadening of $\Gamma = 0.25$ eV at $E = 1.0$ eV.

We have performed two types of photoemission measurements in order to further characterize the conduction-band spectral peaks *A-C* shown in Figs. 1 and 2. First, we have measured the relative intensities (amplitudes) of these peaks as a function of $h\nu$ in the range $10 \leq h\nu \leq 80$ eV (not shown). Such measurements can be used to delineate⁹ “*f*-like” and “*d*-like” features, i.e., “*f*-like” states usually have a delayed onset in their emission intensity with a small emission at low $h\nu$. The result of this study was that the emission intensity ratio I_A/I_B of peaks *A* and *B* in UTe increased by $\sim 30\%$ as $h\nu$ decreased from above 40 eV down to 10 eV, while the intensity ratio I_B/I_C of peaks *B* and *C* in USb decreased by less than 10%. Secondly, we have measured the relative intensities of peaks *A-C* in the range $80 \leq h\nu \leq 130$ eV as $h\nu$ is scanned through the $5d-5f$ threshold around 95 eV. As first observed by Baptist *et al.* (Ref. 2, p. 63) in USb, the $5f$ emission intensity passes through a resonance and becomes very weak ($\times 0.02$) near $h\nu = 92$ eV. Again, this measurement might be expected to delineate *f* and *d* character in the conduction band since “*f*-like” and “*d*-like” states should couple to $5d-5f$ excitations differently. The result of this study is that the intensity ratio I_A/I_B exhibits a resonance with a variation of 30% while the ratio I_B/I_C variation is again less than 10%. Both of these studies suggest that the spectral peak *A* near E_F for UTe contains significant “*d*-like” character, the predominant peak *B* for all three crystals is mainly “*f*-like,” and peak *C* is also mainly “*f*-like,” i.e., very similar in character to peak *B*. We note, however, that the $5f$ partial DOS at E_F might still be substantial in UTe, and vice versa that some $6d$ character in peak *B* cannot totally be excluded. Angularly resolved EDC's show essentially no band dispersion for these $5f$ and $6d$ states.

We now discuss our results in view of previous experimental (see Refs. 1-3) and theoretical (Ref. 2, p. 51, 59, and 78) studies of UX compounds. As mentioned above, the observation of such a different conduction-band DOS for UTe relative to USb and UAs (Ref. 2, p. 117) is both interesting and unexpected in view of past studies. The $5f$ state in UX compounds has been described as an itinerant-electron resonance state¹ within

a one-electron picture, a description which has been supported by band calculations. In this model, all UX compounds have a narrow $5f$ resonance level (~ 2 eV FWHM) at E_F which is partially filled with 2-3 *f* electrons and is spin split to account for the observed magnetic moments. This results in E_F being strongly pinned by a high DOS of spin-up $5f$ states (typically 5-6 electrons/eV at E_F) with a narrow occupied $5f$ band (FWHM ≤ 0.5 eV) and an exchange splitting which is comparable to the occupied bandwidth. It has also been suggested that this *f* resonance at E_F excludes the $6d$ electrons near E_F in the pnictides and the chalcogenides.¹

Our measurements show that, while USb can be described by this $5f$ band model, UTe and $\text{USb}_x\text{Te}_{1-x}$ for $x \leq 0.8$ cannot. [Note that $x = 0.8$ marks⁶ the transition from antiferromagnetism ($x > 0.8$) to ferromagnetism ($x < 0.8$).] Namely, UTe shows “*f*, *d*” bands with FWHM of ~ 1.35 eV which are considerably wider than previously believed and a predominant *f* peak which is *not* at E_F but at 0.75 eV below E_F . The large shift of 0.53 eV in the position of this “*f*-like” peak on going from UTe to USb (e.g., Fig. 1) suggests an average DOS of $1/0.53$, i.e., $n(E) \sim 2$ electrons/eV, within 0.5 eV of E_F , a value which is significantly lower than obtained via a simple *f*-band model.¹ Thus, a subband structure with very wide *f* bands and a relative minimum just below E_F is needed to describe our low DOS results for UTe within such a one-electron model.

Another possible description of our results for the system $\text{USb}_x\text{Te}_{1-x}$ which appears more satisfactory is that correlation effects are more important than given by the above-mentioned calculations and that one has a quasilocalized $5f^{3-\delta}$ ($\delta = 0-0.5$) level which is resonant with $6d$ itinerant states near E_F , but which has a nonzero correlation energy U for accepting an additional *f* electron [but much smaller than the $U \cong 4.5$ eV for the localized $5f$ electrons in UO_2 (Ref. 2, p. 104)]. This level would then correspond to the predominant “*f*-like” *B* and *C* peaks, which reflect multiplet-splitting and/or band-structure effects. In USb [believed to have close to a $5f^3$ configuration⁵ with $\mu_{\text{eff}}^{(\text{calc})} = 3.61 \mu_B$ in Russell-Saunders coupling, in agreement with experiment (Ref. 2, p. 206)] this resonant $5f$ level is located at E_F but becomes shifted downwards by 0.53 eV in UTe because of an additional conduction electron. In this picture, which is consistent with our observed rigid-band behavior, states within ~ 0.5 eV of E_F for UTe which become filled contain

significant $6d$ character. This conclusion is consistent with (i) our rigid-band estimate of ~ 2 electrons/eV near E_F , (ii) with our $h\nu$ -dependent studies of the l character of these levels, and (iii) the observed negative spin polarization⁷ at E_F . Since the paramagnetic moment $\mu_{\text{eff}} = 2.8\mu_B$ in UTe is much smaller than in USb and is inconsistent (Ref. 2, p. 206) with an integer $5f$ configuration, it is suggested that the $6d$ electrons account for the lower moment and that therefore the antiferromagnetic $5f$ - $6d$ coupling in UTe is quite strong.

In summary, we have observed that the " $5f, 6d$ " band structure near the Fermi energy is quite different for UTe and USb, in contrast with previous observations^{1,2,7} and conclusions (see Ref. 2). While the $5f$ electrons in these UX compounds can be described as a resonance state, we find a much broader range of $5f, 6d$ -occupied sharp levels for UTe than previously believed within a one-electron bandlike picture. Consequently, this would require a much larger magnetic exchange splitting in an itinerant- $5f$ -electron band picture. A picture with a correlated, quasilocalized $5f^{3-\delta}$ ($\delta \cong 0-0.5$) level in resonance with $6d$ bands appears to be more satisfactory for describing our photoemission results. It is suggested that additional insight can be obtained via high-resolution, temperature-dependent photoemission studies and also via specific heat studies which sample the ground state of these magnetic materials.

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Note added.—In a subsequent study of single crystal $U_x\text{Th}_{1-x}\text{Sb}$, we have found that U has a quasilocalized $5f^{3-\delta}$ resonant level while Th contributes $6d$ electrons via a filling of states at E_F . These $6d$ electrons appear to be polarized antiparallel to the f moments and account for the decrease of the ordered moment with increasing Th concentration in the range $1 \geq x \geq 0.3$.

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