

Mixed valency of TmSe

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(Received 13 March 1980)

Vacuum-cleaved single crystals of mixed valence TmSe were studied by x-ray photoemission. The divalent and trivalent part of the Tm $4f$ spectrum were fitted using optical multiplet energies and fractional parentage intensities. From the areas of the divalent and trivalent components we obtained the average valences for samples with four different stoichiometries. Comparison of these results with other estimates of the average valence suggest that the x-ray photoemission spectroscopy data are significantly affected by a divalent surface layer. However, attempts to demonstrate the reality of this layer by varying the take-off angle were inconclusive. It was verified that the Tm^{2+} ground state lies at the Fermi energy, giving a direct proof of the homogeneous character of the mixed valency. The location of this multiplet can therefore be used in general to distinguish between homogeneous and inhomogeneous mixed valency.

The early x-ray photoemission studies of the behavior of mixed-valence systems clearly demonstrated that an "energetic probe" projects the system into integral-valence *final* states.¹ Although it was subsequently found that the ratio of final-state valences corresponds closely to the initial-state average valence,^{2,3} no detailed study of systems in which the initial-state valence could be independently varied was undertaken. The more recent discovery of surface effects on valence in metallic mixed-valence systems^{4,5} calls for a more thorough investigation of the relationship between the properties of the *initial* state and the observations made by photoemission. In this study we restrict our attention to $4f$ spectra because they do not suffer from the additional ambiguity posed by the shake-up excitations which may accompany core-level ionization.

The quantitative analysis of $4f$ multiplet spectra encounters few conceptual, but many practical difficulties. In previous work one was content to use the area under the two final-state spectra after a suitable background subtraction. The contributions from the anion valence band were generally considered to be sufficiently small to be ignored. Comparisons with theoretical final-state spectra were usually limited to bar diagrams based on energies obtained from optical spectroscopy and the fractional parentage intensities calculated by Cox.⁶ It would clearly be advantageous to use this information explicitly in the data analysis to improve the reliability of the final-state spectral intensities.

TmSe, which figured prominently in the original work, has become an even more attractive materi-

al for further investigations because of our increased understanding of its properties. Most important is the recognition that the average valence can be varied by controlling the stoichiometry.^{7,8} The valence can be estimated from the lattice constant, as well as from the susceptibility.⁹ This makes possible a systematic study of the photoemission properties in a series of well characterized materials.

For this work we have prepared a series of TmSe crystals using techniques previously described.¹⁰ Samples, typically $2 \times 3 \times 3$ mm,³ were cemented with conducting epoxy into a gold-plated copper sample holder. These samples were introduced into a preparation chamber attached to a Hewlett-Packard 5950A ESCA spectrometer which was then baked at a temperature of 175 °C for at least 24 h. Upon cool-down the samples were cleaved in a vacuum in the 10^{-8} -Pa range and introduced into the main spectrometer chamber which has a comparable vacuum. Satisfactory $4f$ spectra could be obtained in one hour. (All the data shown in this paper were taken during the first hour after cleaving.) Degradation of the sample surface was monitored by recording O 1s spectra, as well as by taking sequential $4f$ spectra. After about 10 h oxygen buildup was clearly detected. At the same time the $4f$ spectra showed a decrease in the intensity of the mixed-valence components and as the growth of a new trivalent component. The latter was broader and shifted to greater binding energy than the original trivalent spectrum. It presumably represents a stable surface oxide which can also be seen in some of the early data.¹

With the exception of the Se $4d$ emission, no ef-

fort was made to study core-electron spectra. The main reason lies in the rich Auger spectra of both Tm and Se which blanket the most interesting part of the kinetic-energy region accessible with Al $K\alpha$ radiation.

The data obtained are summarized in Fig. 1. The z coordinate is proportional to the lattice constant. The systematic variation of the intensity of the divalent components between 0 and 5 eV is apparent. In an initial step in data analysis we decided to test the hypothesis that the rising background is due to plasmon losses. This was done using an iterative process. We assume that associated with each line element is a plasmon loss having the known plasmon energy. A first estimate of the loss spectrum is obtained by convolution of the data with the plasmon-loss function. This result is subtracted from the data to yield a first estimate of the loss-free spectrum. After a few iterations, this process converges to give a good approximation of the loss-free spectrum. A unique solution is obtained provided the strength of the plasmon per unit line element is known. Using the plasmon loss associated with the Se $4d$ line as a guide, only a very small plasmon correction is obtained. If this constraint is ignored in order to bring the left-hand end of the spectrum to the baseline, almost one-half of the total area of the valence band can be assigned to plasmon losses. The resulting loss-free spectrum was, however, found to be incompatible with the known properties of the final state multiplets, giving proof that such a subtraction is not physical. Since the properly constrained plasmon background was found to be very small and not accurately determined, this step in data reduction was eliminated.

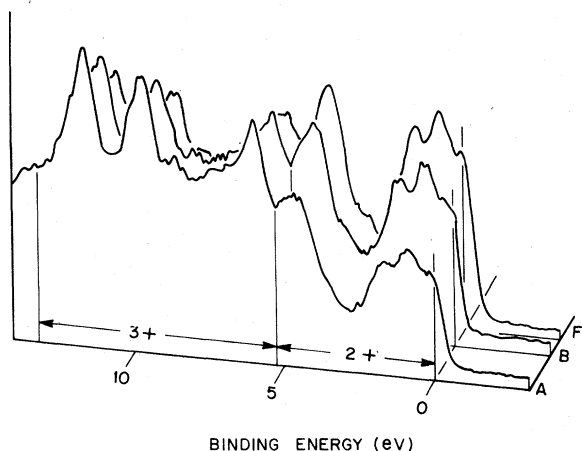


FIG. 1. Comparison of x-ray photoemission data for three samples of TmSe with different stoichiometry. The data have been normalized to have the same area. The position along the z axis is proportioned to the lattice constant.

In order to assure reliability of the data analysis we decided to check the compatibility of the spectra with the optical energies and fractional parentage intensities. To facilitate this procedure we first isolated the divalent part of the spectrum by taking a linear combination of two data sets (with widely different average valences) with intensities chosen so as to cancel the trivalent spectrum. The result is shown in Fig. 2(a). The *divalent* spectrum corresponds to a $4f^{12}$ final-state configuration and should therefore be well represented by the optical excited states of *trivalent* Tm. Using the optical data of Dieke¹¹ in conjunction with the relativistic intensities recently provided by Beatham *et al.*¹² a satisfactory fit was readily obtained. See Fig. 2(a). The calculated line contains the optical energies and multiplet intensities as fixed-input parameters. The instrumental resolution function was also included as a known quantity. The only adjustable parameters were the lifetime width and singularity index of the $4f$ hole state. The latter was determined largely by its effect on the relative peak in-

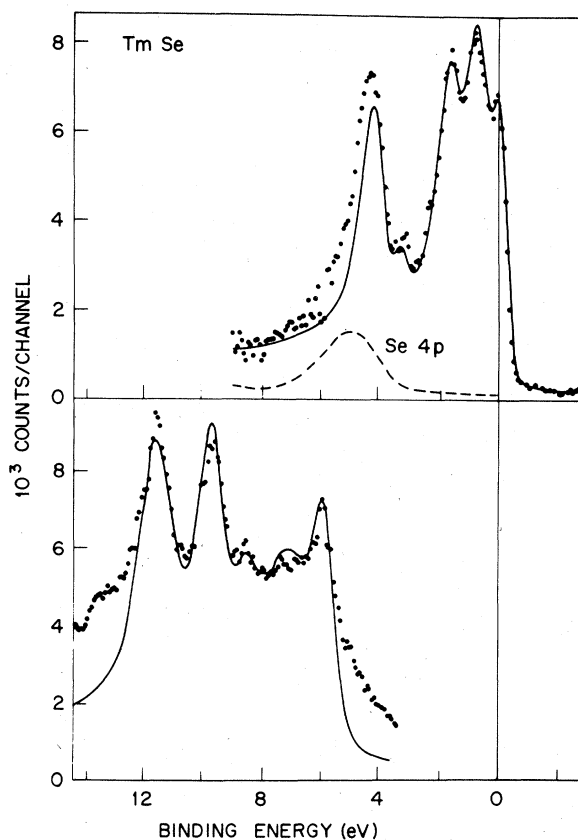


FIG. 2. Divalent and trivalent parts of the final-state valence-band spectrum of TmSe, separated as described in the text. The solid lines are obtained using optical multiplet energies and fractional parentage intensities (see text).

tensities. It is responsible for the long tail associated with the calculated spectrum. The major misfit occurs in the region of the second group of multiplets near 3 eV, where the experimental spectrum has considerable excess intensity. By comparison with the uv spectra of TmSe this has been identified as due to emission from the Se 4p valence band.¹³ A broad peak near 13 eV is similarly associated with the Se 4s emission.

A similar treatment of the *trivalent* final-state spectrum is shown in Fig. 2(b). In this case there are other complications. There is an additional free parameter because it is necessary to use optical data for *trivalent* Er. This requires an expansion of the energy scale of the multiplets in order to compensate for the unit increase in the core charge in going from Er to Tm. The required expansion was found to be 15%. The value of the lifetime width was found to be much greater for the trivalent spectrum, as was previously noted in the case of SmB₆.^{2,14} Since there are no relativistic calculations for this configuration, we have used the results of an empirical adjustment¹⁵ of the fractional parentage coefficients due to Cox⁶ made on the basis of a fit to TmSb data. Table I shows the final-state energies and intensities used in our fits.

Analysis of the data was then done as follows. First the theoretical divalent spectrum was fitted to the data with major emphasis on matching the intensities of the lowest energy group of lines. The area, $A(2+)$, associated with the theoretical spectrum was used as a measure of the divalent intensity because it excludes the Se 4p valence-electron emission. The fitted spectrum was then subtracted

from the data to obtain a representation of the trivalent part. It in turn was fitted with the corresponding theoretical spectrum using the singularity index determined from the fit to the divalent part, and the resulting area noted. The average valence is then calculated from

$$V_{\text{XPS}} = 2 + [1 + 12A(2+)/13A(3+)]^{-1}. \quad (1)$$

Figure 3 shows the fits to the original data obtained by this process. Note that the positions and intensities of the two spectral groups are the only parameters which are ultimately adjustable in this analysis.

RESULTS AND DISCUSSION

In the virtual bound-state model of the mixed-valence state a 4f level is pinned at the Fermi energy.¹⁶ It is somewhat misleading to identify this level with a particular 4f configuration since the level actually marks the boundary between the stability of two different valences, i.e., the upward passage of the Fermi level through this level results in the localization of one additional electron on the rare-earth ion. It has been previously pointed out¹⁷ that this level is formally equivalent to the ground state of the lower-valence multiplet seen by x-ray photoelectron spectroscopy in mixed-valence systems. As a result we have a simple way to distinguish between systems in which ions with two different stable valences coexist at inequivalent lattice sites, e.g., Eu₃O₄ or Tb₃O₄, and those in which individual ions fluctuate between two

TABLE I. Final-state energies and intensities.

Thulium 2+			Thulium 3+		
Final state	Energy (eV)	Intensity	Final state	Energy (eV)	Intensity
³ H ₆	0.017	3.107	⁴ I _{15/2}	0.012	2.536
³ H ₄	0.717	2.208	⁴ I _{13/2}	0.814	0.914
³ H ₅	1.032	1.375	⁴ I _{11/2}	1.257	0.700 ^a
³ F ₄	1.571	0.950	⁴ I _{9/2}	1.525	0.250 ^a
³ F ₃	1.799	0.875	⁴ F _{9/2}	1.885	0.486
³ F ₂	1.874	0.778	² H _{11/2}	2.368	0.909
¹ G ₄	2.642	0.217	⁴ F _{7/2}	2.528	0.151
¹ D ₂	3.473	0.739	⁴ G _{11/2}	3.267	1.157
¹ I ₆	4.321	1.768	² G _{9/2}	3.389	0.359
³ P ₀	4.419	0.164	² K _{15/2}	3.421	1.288
³ P ₁	4.500	0.375	⁴ G _{7/2}	4.195	0.106
³ P ₂	4.733	0.358	⁴ G _{9/2}	4.506	0.419
¹ S ₀	9.884	0.087	² D _{5/12}	4.758	0.296
			⁴ D _{7/2}	4.839	0.687 ^a
			² L _{17/2}	5.137	1.500
			⁴ I _{13/2}	5.394	0.242

^a Adjusted.

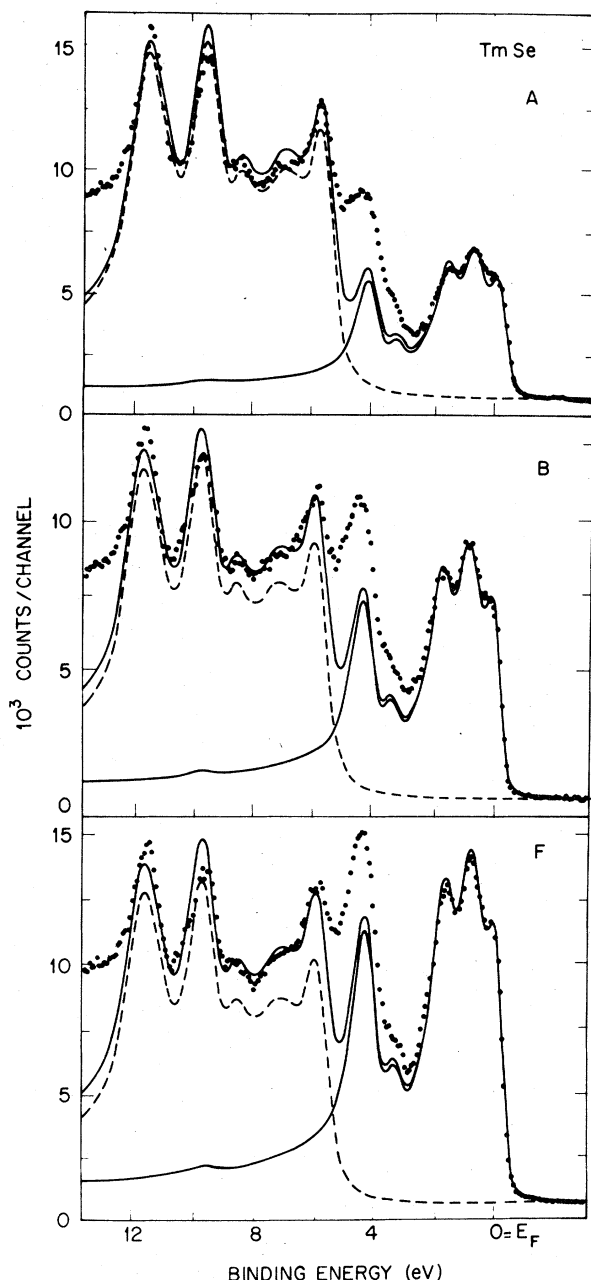


FIG. 3. Analysis of the TmSe spectra shown in Fig. 1.

valences. In the former none of the multiplets will appear at E_F , in the latter the lowest-energy multiplet *must* appear there. In most of the earlier work no attempt was made to check this requirement. (In the HP spectrometer the zero of energy depends on the elevation of the sample and must be explicitly determined.)

In the present experiments the location of the Fermi energy was determined for each cleaved surface by measuring the Fermi cutoff in the con-

duction band of an evaporated Au layer deposited on the sample at the end of the measurements. Since TmSe is itself a metallic conductor of the coincidence of the Fermi energies is assured. The results of these determinations are illustrated in Fig. 4, which shows an expansion of the region in the vicinity of E_F . It is worth noting that the Fermi level falls near the first peak, not in the initial rise, because the data represent narrow multiplet lines. The metallic character resides in the underlying $5d6s$ conduction band whose photoemission intensity is too small to be detected in these spectra. In view of the well-established mixed-valence character of TmSe,^{7,8,9} these results give a clear confirmation of the validity of the identification of the lowest-energy multiplet with the $4f$ virtual bound state. This also proves that it is possible to distinguish between homogeneous and inhomogeneous mixed valency by x-ray photoemission spectroscopy (XPS).

Since the ground state of the *divalent* multiplets lies at the Fermi energy, the binding energy of the ground state of the *trivalent* multiplets directly corresponds to the Coulomb correlation energy, U . The data for all three samples yield $U = 6.04 \pm 0.08$ eV. The value obtained in the earlier investigation (6.6 eV) was larger because it was based on the centroid of the multiplets, and was consequently sensitive to the presence of trivalent surface oxide. The new experimental value remains in satisfactory agreement with that calculated by Herbst, Watson, and Wilkins¹⁸ (6.4 eV).

The other major question which we seek to answer is whether the intensity of the final-state multiplets directly reflects the initial-state valence. In order to answer this question we require an independent measure of the properties of the samples. The one property which has been most useful in identifying and characterizing mixed-valence systems, and can be obtained without additional assumptions, is the lattice constant. These were measured for the actual cleaved surfaces and are used as the independent variable in the comparisons shown in Table II. The average valences obtained from the spectra are consistently smaller by ~ 0.16 than those calculated from the lattice constant under the assumption that the lattice constant of purely trivalent TmSe is 5.615 Å and that of the hypothetical purely divalent compound 5.950 Å. The former corresponds to the composition Tm/Se = 0.83 having the Tm_5Se_6 superstructure. The latter is obtained from an interpolation based on the lattice constants of the other divalent rare-earth monoselenides. It is interesting to note that even samples close to the limiting composition show a significant Tm^{2+} intensity in XPS. The crystal investigated had a lattice constant of 5.635 Å and a

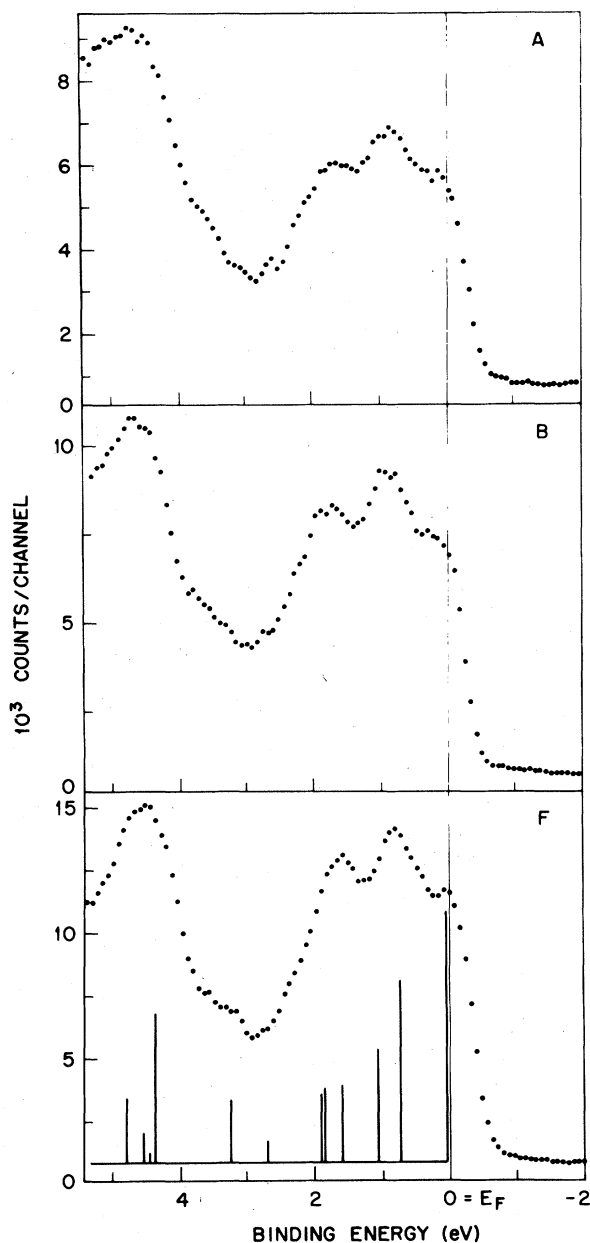


FIG. 4. Expanded view of the divalent part of the spectra of Fig. 3 to show the location of the first multiplet relative to the Fermi level.

Tm/Se atomic ratio of 0.86. This lies close to the phase boundary of nonstoichiometric TmSe at 0.85 ± 0.01 determined in a systematic investigation¹⁹ of 40 single crystals in which the lattice constant, chemical composition, density, and microhardness were measured.

The difference between the average valence obtained from the lattice constant and from the XPS data calls for an analysis of the reliability of the XPS technique. The major uncertainty in the aver-

TABLE II. Comparison of valence obtained from XPS intensities with those obtained from lattice constant.

TmSe	a (Å)	V_a^a	V_{XPS}	ΔV
A	5.635	2.97	2.85	0.12
B	5.645	2.94	2.77	0.17
F	5.687	2.81	2.65	0.16
	5.705	2.75	2.56	0.19

^a Calculated for $a(3^+) = 5.625$ and $a(2^+) = 5.950$ Å.

age valence determined from XPS spectra arises from the surface sensitivity of that technique. Because of the small mean free path of the photoelectrons, the first atomic layer contributes ~20% of the signal. A surface-valence change to a divalent state could therefore account for the observed lowering of the average valence. We have investigated this possibility by taking spectra at a large (75°) take-off angle to increase the surface contribution. (The standard take-off angle is 52° .) Since the effective escape depth at the two angles are in the ratio of $\cos 75^\circ / \cos 52^\circ = 0.42$, a significant enhancement of the surface signal is expected. The spectra obtained did not show any change in valence ratio outside of experimental uncertainties, suggesting that the surface volume does not differ significantly from that of the bulk. It must be borne in mind, however, that such experiments are reliable only when a step-free surface is obtained. This ideal was not realized in the present experiments, preventing a firm conclusion regarding the reality of a surface valence change.

In order to further investigate the question of the valence of TmSe we compare in Fig. 5 the average valence of TmSe deduced from three types of measurement. Also shown in the valence expected on the basis of the lattice constant itself. One should not be overwhelmed by the apparent agreement between three of the determinations because each one is subject to criticism. The valence deduced from the lattice constant is also subject to challenge because of the presence of vacancies in the nonstoichiometric compounds.

The following observations provide a fixed point for the interpretation of all the data. We note that $\text{Tm}_{0.86}\text{Se}$ with $a = 5.63$ Å, which corresponds to the composition of the limiting Se-rich phase, gives evidence of being fully trivalent in three types of measurement: (1) by the *absence* of an anomalous increase in resistivity at low temperature, (2) by the *lack* of deviation of the inverse susceptibility from the Curie-Weiss law, and (3) by the *absence* of an anomalous thermal coefficient of expansion. Positive results would be considered a clear indication of noninteger valence. Consequently one is

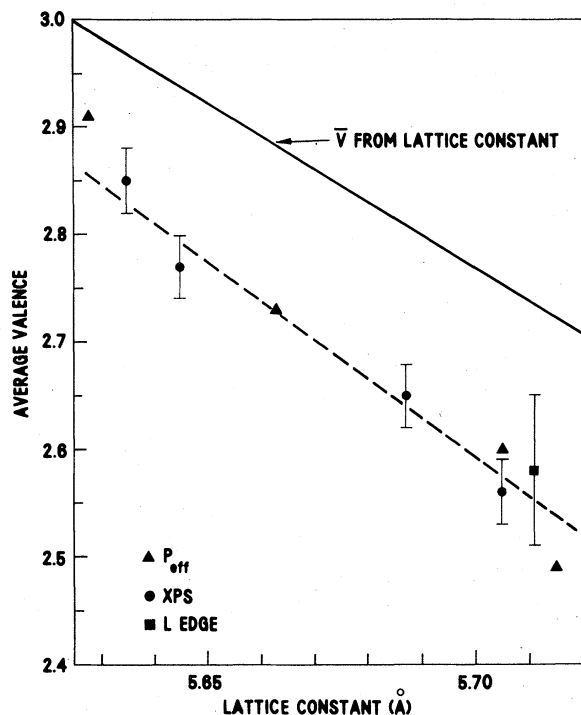


FIG. 5. Comparison of average valence of Tm_xSe obtained by four different techniques. The p_{eff} values from data in Ref. 8; the L -edge value from Ref. 20. The dashed line is the best linear fit to the XPS data.

inclined to believe that at this composition other measurements should confirm the trivalent character of the material.

The extrapolation of the valence from this composition on the basis of the lattice constant encounters some difficulties because it is based on ionic radii obtained from compounds which are not fully ionic and because of lattice defects present in Se-rich TmSe. The concentration of vacancies is about 7% for $\text{Tm}_{0.86}\text{Se}$, 2% for TmSe, but only 1% for $\text{Tm}_{1.05}\text{Se}$. Beyond the equiatomic composition the effect of vacancies on the estimate of valence should therefore be relatively small. The line relating valence to lattice constant is consequently determined with high confidence by the points at $a = 5.63 \text{ \AA}$ and reasonably well by values near $a = 5.71 \text{ \AA}$.

We now consider the interpretation of the other measurements shown in Fig. 5. The valence from the effective magnetic moment is based on the free-ion values of $7.56\mu_B$ for Tm^{3+} and $4.54\mu_B$ for Tm^{2+} . These are not necessarily applicable in a solid with a high concentration of free carriers be-

cause of the Ruderman-Kittel-Kasuya-Yosida interaction which can significantly lower the effective magnetic moment.^{21,22} This could lead to an erroneous indication of the presence of Tm^{2+} in the compound with the limiting composition. In the mixed-valence state, interpretation based on a simple linear combination of ionic susceptibilities is theoretically not defensible, especially in the presence of strong $4f$ - $5d$ hybridization. One must recognize that there is as yet no adequate theoretical basis for deriving an average valence from an effective magnetic moment in a mixed-valence system.

The valence obtained from the L -absorption edge²⁰ is also subject to uncertainty, arising largely from final-state effects produced by the deep core hole. In some of the rare-earth metals it has been shown that such a core hole pulls the empty f state below the Fermi energy causing localization of an additional f electron.²³ This seems particularly applicable to mixed-valence compounds in which the f level is already at the Fermi energy. This phenomenon would result in a false indication of a valence lower than that in the initial state. In insulators or compounds with stable valence this effect may be suppressed or entirely absent, depending on the relative positions of the valence-band edge and empty $4f$ level. (This phenomenon is not encountered in photoemission from the $4f$ state itself, as in the present experiments.)

One is consequently left with the conclusion that the "agreement" between the measurements shown in Fig. 5 is likely to be an accident, resulting from the lowering of the valence from its true value by the variety of mechanisms outlined above. The determination of the valence of a mixed-valence compound by XPS then depends critically upon the ability to correct for surface effects. In the present measurements a fully divalent surface monolayer would suffice to bring the XPS bulk valence into coincidence with the valence estimated from the lattice constant. An investigation of the defect structure of Tm_5Se_6 is expected to lead to a more definitive conclusion regarding the role of the surface in XPS studies of these materials.

ACKNOWLEDGMENTS

The authors are indebted to B. Batlogg, B. Fritzer, and P. Wachter for enlightening discussions, to A. Wisard for growing the crystals, and to Mrs. A. Jilek and Miss B. Steineman for their characterization.

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