pounds, but have thereby provided the first observation of CDW's in other than one-dimensional (1D) metals. Since their electron concentration can be varied by doping, and since different band structures are provided by the different polytypes, these layer systems offer greater latitude for study than do the 1D metals like $K_2Pt(CN)_4 \cdot Br_{0.30} \cdot 3H_2O$.[10] The 1D metals have point Fermi "surfaces" and just the one spanning vector. We have now found a CDW occurring in a case where there are several possible perhaps competing spanning vectors.

The existence of a CDW/PSD in 2*H*-$TaSe_2$, etc. brings property changes that appear very similar to those occurring in *A*15's like Nb_3Sn, at and below the Batterman-Barrett transition. For both groups of materials there results an intriguing interplay with the superconducting properties.

A much fuller account of the electron diffraction studies on many of these layered compounds has been submitted elsewhere. Studies of the transport, magnetic, and superconducting properties, and of the effects of intercalation are also to be published.

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Spontaneous Interconfiguration Fluctuations in the Tm Monochalcogenides

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Spontaneous interconfiguration fluctuations have been detected in TmTe and TmSe by x-ray photoemission. The resulting instantaneous picture of the Tm ions fluctuating between the divalent and trivalent state within the same environment allows a direct measurement of the magnitude of the Coulomb correlation energy, U_{eff}. Spontaneous interconfiguration fluctuations are shown also to affect the binding energies of core levels within the same rare-earth ion, resulting in a chemical shift of 3.5 ± 0.1 eV for the Tm(5*p*) core levels.

Temporal valence fluctuations between two distinct configurations of a rare-earth (RE) 4*f* shell have been recently interpreted to be the source of the demagnetization of RE ions in dilute and concentrated alloy systems.[1,2] According to this concept, nonmagnetic behavior of a strongly localized 4*f* shell is related to a nonintegral, time-averaged occupation of that shell. Generally speaking, the phenomenon of spontaneous interconfiguration fluctuations (ICF), introduced by Hirst,[1] and based on a modification of the Friedel-Anderson model of local-moment formation,[3] seems successfully to connect the experimental fact of nonmagnetic behavior in the collapsed phase of, for example, SmS or SmB_6 with spontaneous valence fluctuations in the 4*f* shell.

The purpose of this Letter is to present direct experimental evidence for the existence of such fluctuations, based on high-resolution x-ray photoemission spectroscopy (XPS). Since photoexcitation takes place in a time short compared to that assumed for the fluctuations (up to 10^6–10^7 times shorter) it should be possible to observe the instantaneous picture of the ions in the two valence states. The same measurement then also allows a direct measurement of the intra-atomic Coulomb correlation energy, $U_{\rm eff}$, i.e., the difference in energy between a $4f^n$ and a $4f^{n-1}$ configuration within the same environment (same screening conditions and work function).

We discuss here results obtained with the Tm chalcogenides TmTe and TmSe and with TmSb. These compounds are especially suitable for this type of investigation for the following reasons:

(1) Since the relative intensity of the signal in high-energy photoemission from f shells increases in going from Ce to Yb,[4] it is easier to obtain reliable data with ions lying at the end of the RE series, e.g., Tm^{3+} ($4f^{12}$), Tm^{2+} ($4f^{13}$).

(2) Calculations[5] of the probabilities of occupying highly excited final states of the $4f$ multiplets which are well separated in energy (more than 0.5 eV apart) show that these coefficients are significantly different from 0, especially in nearly filled shells. In this case it should also be possible to determine unambiguously whether the structure observed in the photoemission spectrum is due to divalent or trivalent ions, even though the energy resolution in the experiment is only 0.5 eV.

(3) The physical properties of TmSb, a singlet-ground-state system,[6] can be well understood assuming that the Tm ion is strictly *trivalent* (lattice constant $a_0 = 6.067$ Å). TmSe, on the other hand, is one of the simplest compounds showing evidence of an intermediate-valence state.[7] From susceptibility measurements on TmSe and TmTe ($a_0 = 5.71$ and 6.35 Å, respectively, for our samples) one obtained effective moments of $6.32\mu_B$ and $4.96\mu_B$, i.e., different from the expected effective Bohr-magneton numbers, $p_{\rm eff} = g[J(J+1)]^{1/2}$, of $4.5\mu_B$ for the f^{13} or $7.57\mu_B$ for the f^{12} configuration. The low-temperature behavior of the magnetization[8] and the specific heat[7] of the Tm chalcogenides is also peculiar. Moreover, neutron diffraction measurements on TmSe down to 1°K detected neither magnetic long-range order nor crystal-field splittings.[9]

(4) Large single crystals of the Tm pnictides and Tm chalcogenides can be grown, and optically flat surfaces can be obtained by cleaving *in situ* under ultrahigh-vacuum conditions because they have the simple NaCl structure.

Single crystals of 5×4 mm^2 were cleaved[10] in a vacuum of 5×10^{-9} Torr in the sample preparation chamber of the Hewlett-Packard 5950A spectrometer. The data were taken in a vacuum better than 10^{-9} Torr with monochromatized Al $K\alpha$ radiation (spectrometer resolution 0.5 eV). Freshly cleaved optically flat surfaces turned out to be oxygen and carbon free, as evidence by the absence of O(1s) and C(1s) signals immediately after cleaving. At the end of a run, typically of 6 to 8 h duration, the ratio intensity of the O(1s) to the Sb($3d_{5/2}$) signal was 1:48. The C(1s) signal was approximately $\frac{1}{2}$ as large. A smooth background has been subtracted from the data.[11]

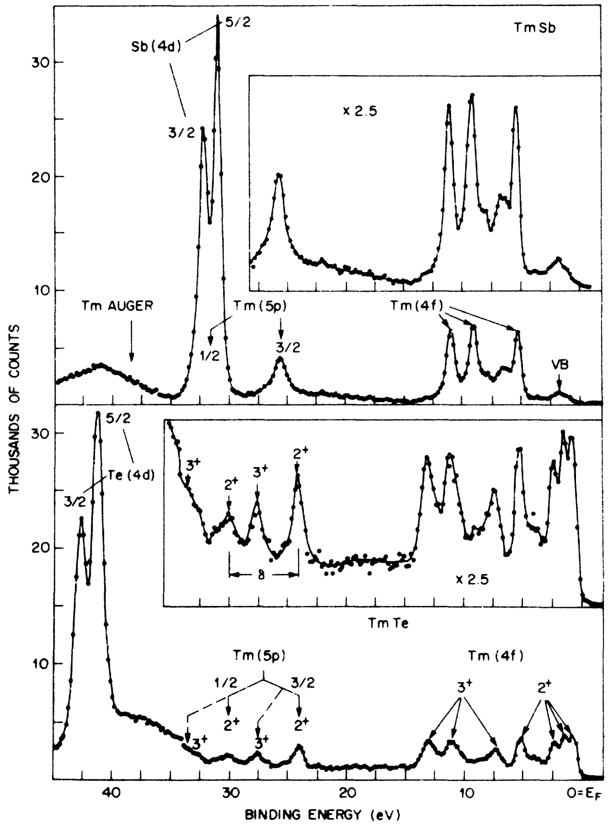

FIG. 1. Overview of the occupied energy levels in the binding-energy range 0–45 eV for TmSb and TmTe.

In Fig. 1 we show an overview of the occupied energy levels of TmSb and TmTe lying in the range 0–45 eV. The zero of the energy scale is the Fermi level E_F. In the spectrum of TmSb we can identify the valence band [mainly due to Sb($5s$, $5p$) wave functions], and a sharp $4f$ final-state multiplet structure extending from 5 to 13 eV. The Tm($5p_{3/2}$) level appears at a binding energy of 25.5 eV. The position of the Tm($5p_{1/2}$) level coincides with the Sb($4d$) levels. The shoulder starting at ~ 36 eV is mainly due to Tm $M_{\rm V}N_{\rm VI,\,VII}N_{\rm VI,\,VII}$ Auger transitions.

The data of TmTe in Fig. 1 (and Fig. 2) show a surprising feature which we believe to be indicative of *spontaneous ICF* in a RE ion. We can,

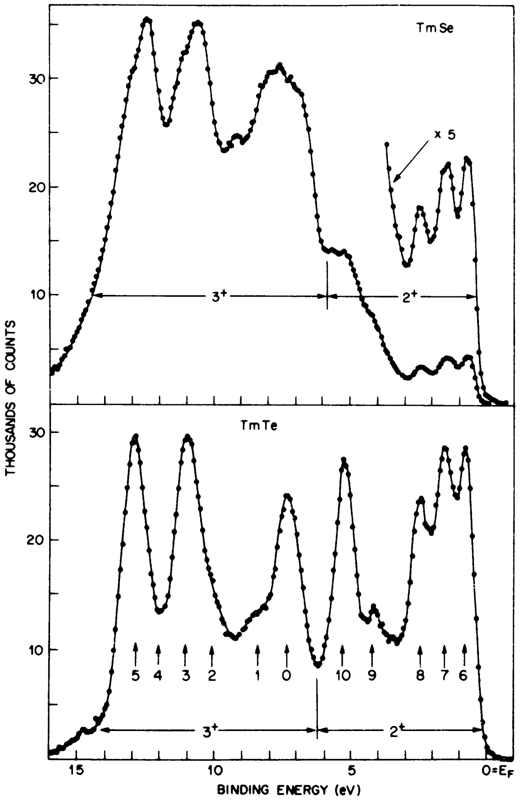

FIG. 2. X-ray photoelectron spectra of the $4f$ electrons in TmSe and TmTe.

in fact, identify the additional structure appearing in the energy range $E_F - 6.4$ eV as due to Tm ions in the 2+ valence state, while the structure between 6.4 and 14 eV is due to Tm ions in the 3+ valence state. Further unambiguous confirmation of this fact is the appearance of two sets of peaks corresponding to the Tm($5p$) levels. (The fourth peak appears as a shoulder at 33.5 ± 0.10 eV.) The data of TmTe in Fig. 1 allow us directly to detect the effect of spontaneous ICF on the $5p$ levels of Tm; the $5p$ levels are shifted by 3.5 ± 0.1 eV towards lower binding energy in going from Tm^{3+} to Tm^{2+}. To our knowledge this is the first direct measurement of a chemical shift for two states of an ion within the same environment.

In Fig. 2 we present the results for the valence-band and $4f$-multiplet structure TmSe and TmTe. The structure between 6.4 and 14 eV is the one expected for Tm ions initially in the $^3H_6$ ground state. The spectrum of the Tm^{4+} ion produced by photoemission corresponds to that of Er^{3+},[12,13] as is shown in Table I. The peaks, like in the RE-Sb,[14] have a slightly greater energy separation (10%) than the multiplet structure of the trivalent ion with next lower Z. The data for TmTe corresponding to the Tm^{2+} excitations, on the other hand, show close agreement with the optical data of Tm^{3+}. This demonstrates that the

TABLE I. Identification of the multiplet structure in the x-ray photoemission $4f$ spectra of trivalent and divalent Tm.

No. of the Structure	0	1	2	3	4	5	6	7	8	9	10
Term: Er^{3+}	$^4I_{15/2}$	$^4I_{13/2}$ $^4I_{11/2}$ $^4I_{9/2}$	$^2H_{11/2}$ ^4F	^4G $^2K_{15/2}$	^4D	$^2L_{11/2}$					
Relative Peak Position in the Er^{3+}-Spectra [eV], Ref. 13	0	0.8 to 1.5	2.4 2.5	3.7 3.4	4.9 to 6.1	5.2					
Relative Position in TmSb [eV]	0	1.2	2.7	3.8	-	5.7					
Term: Tm^{3+}							$^3H_6$	$^3F_4$	$^3H_4$ $^3F_3$	$^1D_2$	$^1I_6$ ^3P
Relative Peak Position in the Tm^{3+}-Spectra [eV]							0	0.7	1.6	3.4	4.3 4.6
Relative Position in TmTe [eV]							0	0.7	1.6	3.4	4.3

final state of the ion corresponds not to a Koopmans state but to a relaxed final state.[5]

We believe that the data in Figs. 1 and 2 and in Table I clearly demonstrate that TmTe and TmSe are in the state of spontaneous ICF at room temperature and atmospheric pressure. Under these conditions $E_{\text{exc}}^- = [E(4f^n)] - [E(f^{n-1}) + E(e^-)]$, i.e., the energy necessary for making an ICF excitation through the emission of one f electron into the conduction band, must be 0. The signal corresponding to the Tm^{2+} ground state $^2F_{7/2}$ is much smaller in TmSe than in TmTe, where the 3+ and 2+ spectra are comparable in intensity. This is in agreement with the susceptibility measurements showing $\mu_{\text{eff}} = 6.32\mu_B$ for TmSe and $\mu_{\text{eff}} = 4.96\mu_B$ for TmTe.

From Fig. 2 we can calculate the correlation energy U_{eff} between two electrons with opposite spin in the same $4f$ orbital in TmTe. We calculate U_{eff} as the difference between the centroids of the 3+ and 2+ spectra. Numerical integration yields $U_{\text{eff}} \cong 10.3 - 2.9$ eV $= 7.4$ eV. The same value of U_{eff} is obtained from the energy separation between $^4I_{15/2}$ and $^3H_6$, i.e., the peaks labeled 0 and 6 in Fig. 2. This value of U_{eff} is in good agreement with the estimate of $U_{\text{eff}} \cong 6.5$ eV for Tm metal by Herbst, Lowy, and Watson on the basis of the renormalized-atom scheme.[15] The experimental U_{eff} should be quite accurate since it is not based on data taken on different samples with different work functions and screening conditions.

The photoholes corresponding to the excitations from the 2+ and 3+ initial states are most probably subject to only slightly different intra-atomic (and extra-atomic) relaxations. If we assume that during the spontaneous ICF the electron excited in the conduction band is creating a finite local density of states, then we expect the *relaxation energy* E_{rel} to be slightly larger in the case of (3+)-state photoexcitation. U_{eff} as estimated in this experiment is therefore a lower bound for the "true" U_{eff}.

Although the spectra for TmSe do not show a well-defined separation between 2+ and 3+ contributions, like that in TmTe, we have carried out the numerical integration with the same criteria used for TmTe, yielding $U_{\text{eff}} \cong 10.1 - 3.5$ eV $= 6.6$ eV. This value is less reliable because we have not considered the contribution of the $4p$, $4s$ valence bands to the spectrum.

A number of important conclusions can be drawn from the data we have presented: (i) Spontaneous ICF are present in the Tm chalcogenides at room temperature and atmospheric pressure and can be clearly detected with the XPS technique. (ii) The Friedel-Anderson model as modified by Hirst to describe the configuration crossover in the Sm chalcogenides seems to be applicable to these substances as well. (iii) From (ii) we deduce that the Falicov-Kimball model,[16] which does *not* permit a spontaneous ICF to be thermodynamically stable over a finite range of pressures and predicts transitions from pure $4f^n$ to pure $4f^{n-1}$ configurations, is inadequate for describing the metal-insulator transitions observed in a number of RE compounds. (iv) High-resolution XPS is shown to be able to directly detect the magnitude of the correlation energy U_{eff} in concentrated alloys showing spontaneous ICF. In the Tm chalcogenides we estimate U_{eff} to be 6.5 to 7.5 eV, in good agreement with recent calculations by Herbst, Lowy, and Watson,[15] and experimental estimates by Hüfner and Wertheim.[17] (v) Because of the inherent characteristic of being able to detect the instantaneous picture of an ion emitting and absorbing "conduction" electrons, high-resolution XPS is shown to be an ideal technique for investigating the physics of a configuration crossover and of the spontaneous ICF.[18] A thorough investigation is in progress.

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Do the 3^- Octupole States in the Even Cd Isotopes Exist?

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In high-resolution $(n,n'\gamma)$ studies the previously assigned 3^- octupole states in ^{114}Cd and ^{116}Cd have not been observed.

The presence of 3^- states in nuclear level schemes at approximately 2 to 3 MeV excitation is taken as a justification for the collective model. Consequently their existence or lack thereof, while not decisive for the collective approach, is of importance.

Using small enriched samples of ^{114}Cd (98.5%) and ^{116}Cd (94.3%) in the close neutron source-to-scatterer geometry and data-analysis techniques described previously,[1,2] we have studied the $(n, n'\gamma)$ reaction on these nuclei for neutron energies from $E_n = 1.1$ to 3.2 MeV. These nuclei have been studied by many authors,[3-22] some of whom have reported[13,16-18,20,21] a 3^- state in the neighborhood of 1900 keV.

Figure 1 shows a part of the γ-ray spectrum of ^{116}Cd obtained in this work with a Ge(Li) detector for $E_n = 3.2$ MeV. We know of no other Ge(Li)-detector studies of the γ rays above 1300 keV for this nucleus. It can be seen from Fig. 1 that the previously observed[21] 1412-keV γ ray is probably one member or more of a triplet whose energies are 1404, 1409, and 1416 keV. These γ rays (Fig. 2) have been assigned to levels at 1917, 1923, and 1930 keV from consideration of their thresholds of production. All these proposed levels decay to the first excited state at 513 keV only. No ground-state transitions were observed for these levels and no branches to the states at 1213 (2^+), 1220 (4^+), 1283 (0^+), or 1381 (0^+) were found.

Comparing the excitation functions for these levels (Fig. 2) with theoretical cross sections calculated as described previously,[2] we found none of sufficient strength to be assigned a $J^\pi = 3^-$ state. For comparison, Fig. 3 shows that using the previously assigned spins and parities in the theoretical calculations produces agreement with the data for the first three levels of ^{114}Cd. The observed cross sections for the other levels in ^{114}Cd below 1.9-MeV excitation are also in agreement with the theoretical calculations. The situation in ^{116}Cd is similar. In all the calculations, the Rosen optical model parameters[23]

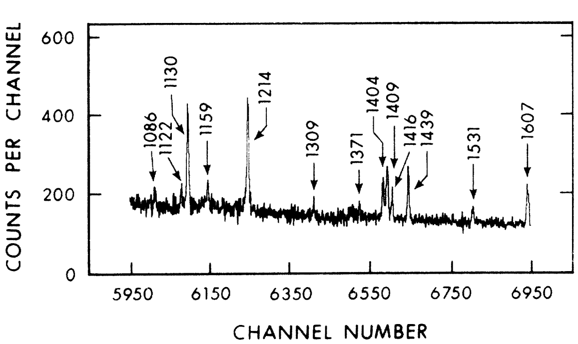

FIG. 1. A part of the (scatterer-in) − (scatterer-out) γ-ray spectrum of ^{116}Cd for $E_n = 3.2$ MeV.