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Measurement of the electron affinity of thulium

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The electron affinity of thulium has been measured using laser photodetachment electron spectroscopy. The electron affinity of Tm($^2F_{7/2}$) was determined to be 1.029 ± 0.022 eV. The data also show that Tm^- has at least one bound excited state with a binding energy of 0.979 ± 0.017 eV relative to the ground state of the thulium atom. The present experimental measurements are compared to a recent calculation of the electronic structure of Tm^- and a recent experimental investigation of Tm^-.

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Experimentally determined parameters are crucial to the understanding of the electron-electron interactions responsible for the existence of most negative ions. Several recent reviews of negative ion research [1–3] have pointed out the computational complexity encountered by theoretical investigations of lanthanide negative ions and the paucity of experimentally derived information for these ions. The experimental verification of the existence of the predicted negative-ion structure is therefore key in assessing the validity of theoretical approximations. In particular, since knowledge of the electron affinities of rare-earth atoms is limited, there is keen interest in experimental data concerning the electron affinities of the lanthanides [1].

Semiempirical estimates of the electron affinities of certain lanthanides have been made in the past [4–6]. A more recent theoretical calculation was made by Chevary and Vosko [7]. Their calculation yielded an estimate of the electron affinity of Tm to be in the range of 1–5 millihartrees (mH) (0.0272–0.136 eV) with a ground-state configuration not of $[\mathrm{Xe}](4f^{14}6s^2)$ (the ground state of Yb), but instead, a configuration of $[\mathrm{Xe}](4f^{13}6s^26p)$ [7]. That is, Chevary and Vosko predicted the formation of a stable Tm negative ion by the attachment of a $6p$ electron rather than a $4f$ electron, due to stronger correlation effects between the $4f$ electrons, which have relatively smaller orbital radii than their outer neighbors [7]. Since relativistic effects are important in this system, the calculation was based on a Dirac-Hartree-Fock density-functional theory. For heavy systems, spin-orbit interactions become comparable or stronger than electrostatic interactions between electrons (LS coupling), and are best described by jj-coupling schemes represented by the notation $(j_1,j_2)_{J_{\mathrm{TOT}}}$ [8]. In this case, the ground state of neutral Tm ($j=7/2$) may couple with the additional $6p$ electron ($j=1/2$), forming the $(7/2,1/2)_{J=3,4}$ doublet for Tm^-. Chevary and Vosko predict this splitting to be in the range 0.2–0.3 mH (5–8 meV) [7]. It is important to note, as the authors themselves do, that their results are based, in part, on a solution that does not converge for $Z<69.1$, and that the given electron affinity (EA) of Tm is an estimation [7].

Previous experimental investigators have reported production of stable lanthanide negative ions (including thulium) using accelerator mass spectrometry techniques [9,10]. Nadeau *et al.* have reported measurements of the electron affinities of Tm, Yb, and Dy using an electric-field dissociation technique [11], although some of these results are disputed [12]. Using this technique, Nadeau *et al.* have reported a value of 32 ± 7 meV for the binding energy of Tm^- [10].

The present experimental study of Tm^- was performed using the laser photodetachment electron spectroscopy technique. A detailed description of the experimental apparatus has been given elsewhere [13], so only a brief description is presented here. The experimental apparatus consisted of a commercial cesium-sputter negative-ion source, an accelerator, and an interaction chamber in which photoelectrons were produced and analyzed. The source of the negative ions was a target pellet consisting of a mixture of copper powder, thulium powder, and sodium carbonate. The negative ions produced were accelerated by a 10 kV potential, mass selected by a 90° bending magnet, then focused and steered into the interaction chamber. Once inside the chamber, the ion beam intersected a photon beam at an intersection angle of 90°. The photon beam was produced by a continuous Nd:YAG laser operating in single line mode at 1064 nm and typically delivering between 6–8 W to the interaction chamber. Copper dimer anions ($^A\mathrm{Cu}_2^-$, $A=126$) produced from sputtering of the copper powder were used as mass markers to identify the $^{169}Tm^-$ beam.

Electrons photodetached in the interaction region were energy analyzed using a spherical-sector, 160° electrostatic kinetic-energy analyzer which operated in a fixed pass-energy mode. The electron spectrometer was positioned below the plane, which contained the laser and ion beams at a 45° declination angle. Electrons with the correct energy for transmission through the spherical-sector analyzer were detected with a channel electron multiplier. Analog outputs from the ion-beam current and the laser power meters were converted to frequencies by a voltage-to-frequency converter, and logged with counters for normalization of electron counts.

A typical photoelectron kinetic-energy spectrum for Tm^- is shown in Fig. 1. Fourteen Tm^- photoelectron spectra were recorded. The energy scale for all of the Tm^- photoelectron kinetic-energy spectra taken was determined using the pho-

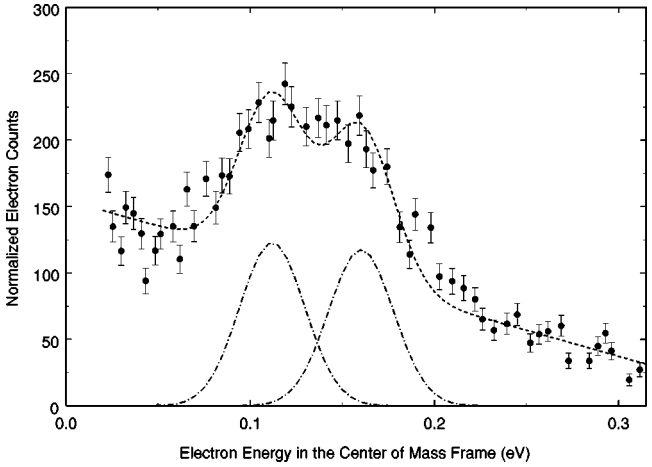

FIG. 1. Typical photoelectron kinetic-energy spectrum for photodetaching Tm^- using a Nd-YAG laser (1064 nm). The laser output power was 6.5 W. The kinetic energy of the Tm^- ions in the beam was 10 keV, and the ion current, measured in the interaction chamber, was 40 pA. The data accumulation time for each data point was 90 sec. and the spectrum took approximately 1.5 h to complete. The two Gaussian photopeaks are superimposed on an exponential background of low-energy electrons created by collisional detachment of Tm^- ions. No other features were observed in the spectrum throughout the entire energy range of the laser.

toelectron energy spectra of Na^- produced by the sputtering of the sodium carbonate and the known EA of Na [1]. Electron energy spectra were taken for the photodetachment of Na^- either before or after each Tm^- photoelectron spectrum was accumulated.

The energy scale for the Tm^- photoelectron spectra in the laboratory frame was then transformed into the ion rest frame using the Na^- photoelectron spectra as a reference. The energy separation of the photoelectron peaks correspond to the initial and final states for the process $h\nu + Tm^- \rightarrow Tm + e^-$, where Tm and Tm^- can be in excited states. Conservation of energy requires that the kinetic energy of the photoelectron E_c is given by

$$E_c = E_\gamma - E_e^a - E_a + E_e^n, \tag{1}$$

where E_γ is the photon energy, E_e^a is the excitation energy of the final state of the atom, E_a is the electron affinity, and E_e^n is the excitation energy of the initial negative ion state.

The photoelectron peaks in Fig. 1 were fit to Gaussian functions using a weighted least-squares technique to determine the energy centroid of each peak. The width of each Gaussian peak was fixed to match the width of each fine-structure resolved Na^- reference scan. Decomposition of the photopeak reveals two transitions of energies 1.029 ± 0.022 eV. and 0.979 ± 0.017 eV relative to the $^2F_{7/2}$ ground state of the thulium atom. This bound excited state of Tm^- must be long lived since the flight time to the interaction region for an ion in the beam was approximately 56 μs. The observed increase in electron counts near 0 eV was due to low-energy electrons created by collisional detachment of Tm^- ions in the beam by background gas and ion-aperture scattering. No other features were observed in the electron spectra throughout the entire energy range accesable by the Nd:YAG laser. The first excited state of neutral Tm is 1.0875 eV above the ground state [14], hence, any transitions from the negative ion to the first excited state of the neutral could not be accessed by the laser used in this study.

The reported uncertainty in the measurements represents one standard deviation of the mean. The uncertainties include statistical and systematic contributions due to the photoelectron count rates for Tm^- and the fitting of the data to Gaussian functions for the Tm^- and Na^- photoelectron energy spectra, the uncertainty in the EA of Na, and the determination of the ion-beam kinetic energy. The reported uncertainty was dominated by the variance in the energy centroids resulting from fitting the data to Gaussian function for peaks in the Tm^- photoelectron spectra. This variance was due to the relatively low photoelectron count rates in the Tm^- photoelectron spectra.

In summary, the electron affinity of thulium has been measured using laser photoelectron energy spectroscopy. The electron affinity of Tm($^2F_{7/2}$) was determined to be 1.029 ± 0.022 eV. The present measurements indicate that the electron affinity of thulium is greater than that predicted by Chevary and Vosko [7], who predicted the electron affinity of Tm to be in the range 1–5 mH (0.0272–0.136 eV). We observe no evidence of photopeaks in the Tm^- spectra that would support that prediction. There was also no evidence in our Tm^- photodetachment spectra of a Tm^- state bound by 32 meV as previously reported [10]. However, the results do support the prediction by Chevary and Vosko of the formation of Tm^- by the attachment of a $6p$ electron and the splitting of the ensuing $(7/2,1/2)_{J=3,4}$ doublet, although the measured splitting of the Tm^- doublet (50 meV) is greater than the estimate of the splitting made by Chevary and Vosko of 5–8 meV [7].

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