Experimental Proof for Coordination-Dependent Valence of Tm Metal

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Photoemission measurements of Tm metal films ($\simeq 1000$ Å thick) grown on a copper substrate at 13 K reveal a partial surface valence transition to the divalent $4f^{13}$ state. At room temperature, Tm films deposited on smooth substrates remain purely trivalent, whereas deposition on rough substrates yields small divalent components in the photoemission spectrum. This phenomenon is shown to occur for particularly low-coordinated atoms on rough surfaces, in quantitative agreement with thermochemical predictions.

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Across the series of rare-earth (RE) elements, a repetition of certain physical properties is observed in the second half of the $4f$ shell from Gd to Yb as compared to the first half from La to Eu. This systematic behavior is reflected, e.g., in the melting and boiling points, which exhibit maxima for La and Gd and minima for the divalent metals Eu and Yb. It is based on increasing $4f \rightarrow 5d$ promotional energies from La to Eu and from Gd to Yb, respectively, which cause a decrease in the stability of the trivalent RE configurations. In the gas phase, nearly all RE atoms—with the exception of La and Gd—are known to exist in a divalent $[\mathrm{Xe}]4f^n5d^06s^2$ ground state. In the condensed metallic phase, the $4f \rightarrow 5d$ promotional energy is compensated by a gain in cohesive energy in the trivalent $[\mathrm{Xe}]4f^{n-1}5d^16s^2$ configuration. Therefore, most RE metals are trivalent, with the exception of Eu and Yb; in these two cases with half-filled or completed $4f$ shells, the promotional energies are too large to be compensated by gains in cohesive energy.[1,2]

At the surface, the cohesive energy is generally lowered by a reduction in coordination, causing the well-known phenomenon of surface core-level shifts.[3] For trivalent RE systems with the empty divalent $4f$ level not far above the Fermi edge, such as Sm and Tm metal, this decrease in cohesive energy can be sufficiently large to stabilize the divalent configuration at the surface.[1,2] In fact, such a surface valence transition was first observed for Sm metal,[4] whereas the corresponding heavy RE element Tm was subsequently found to remain trivalent at the surface.[5,6] These observations are in accordance with theoretical calculations based on a broken-bond model,[7] which resulted in an energy difference of -0.28 eV ($+0.15$ eV) between trivalent Sm (Tm) metal with a divalent top layer and the completely trivalent metal. These calculations, however, were performed for close-packed smooth surfaces only. If the surface is rough and contains edges and corners, the cohesive energy will be reduced further at such sites.[2] This may lead to a surface valence transition even for Tm metal and possibly for other RE elements.

Photoemission is an ideal tool for the investigation of surface valence transitions in rare-earth materials as a result of the characteristic final-state multiplets, separated by large Coulomb correlation energies. Furthermore, photoemission with $h\nu \leq 100$ eV is highly surface sensitive because of the small mean free path of the photoelectrons, and the coordination dependence of surface core-level shifts provides direct insight into the surface microstructure. This has been proven for various Ir and Au single-crystal faces, where the $4f$ core-level shifts show a clear dependence on the packing density at the surface.[8,9] For rare-earth metals, a recent photoemission study of thin Yb metal films grown on cold substrates revealed an increase in the surface core-level shift with decreasing substrate temperature, i.e., with surface roughness.[10]

In this paper, we report on the first observation of valence change at a rough surface of Tm metal, which was grown by vacuum deposition onto either a copper substrate cooled to liquid-helium temperatures or a heavily sputtered Tm substrate at room temperature. The surface valence transition, observed by $4f$ photoemission (PE), is found to be incomplete, since—by the use of surface core-level shifts—trivalent Tm atoms are also identified at the surface in addition to the completely trivalent bulk. Deposition of a Tm film onto a smooth substrate at room temperature leads to a completely trivalent surface, which remains stable upon subsequent cooling to liquid-helium temperatures. These facts clearly show that the surface valence transition observed for Tm metal is characteristic of the microstructure of the film. The known coordination dependence of $4f$ surface core-level shifts for cryodeposited Yb metal films[10] allows us to assign the divalent Tm atoms to low-coordinated surface sites.

The PE measurements were performed at the SX-700 monochromator beam line at the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY), using a cylindrical-mirror electron-energy analyzer. The total system resolution was $\simeq 0.3$ eV (FWHM) at $h\nu = 70$ eV. About 1000 Å of Tm metal of 99.9% purity was evaporated from a current-heated tungsten coil onto a copper substrate which could be cooled to low temperatures by a Heli-Tran cryostat. The base pressure in the experimental chamber was 1×10^{-10} Torr. During evaporation, the pressure rose briefly to $\simeq 10^{-8}$ Torr (mainly due to hydrogen), just before the Tm flash started, and fell back to the 10^{-10}-Torr range within a few seconds after the flash. PE spectra were taken at a photon energy of 70 eV, where both the $4f$ cross section and the surface sensitivity are known to be high.[11]

A typical PE spectrum of Tm metal grown on the copper substrate at $\simeq 13$ K is presented in Fig. 1(a). It is dominated by the multiplet of the $4f^{11}$ final state of trivalent Tm at binding energies between 4 and 11 eV,[5,6] which contains both a surface and a bulk part (see below). An additional triplet of peaks is observed at lower binding energies, where the $4f^{12}$ final-state multiplet of divalent Tm is expected, as known, e.g., from the PE spectra of Tm chalcogenides containing divalent Tm.[12,13] This divalent-Tm feature has not been observed previously in the PE spectra of Tm metal films deposited onto smooth substrates at room temperature.[5,6] It is also missing in spectra obtained in this work from Tm metal deposited onto a smooth substrate at 270 K with subsequent cooling within 5 min to liquid-helium temperatures, as shown in Fig. 1(b). Since emission from Tm^{2+} atoms, however, is observed for cryodeposited Tm metal films, this valence transition clearly depends on the preparation technique and cannot be explained in terms of a possible bulk crystallographic phase transition at low temperatures.[14]

Cryodeposited metal films exhibit porous surface structures, as recently proved in a direct way by vacuum tunneling microscopy.[15] In the specific case of Tm metal, a minimum in the electrical resistivity versus temperature has previously been observed for cryodeposited films, pointing also to a highly distorted metal lattice.[16] In the present experiment, the observed increase in the PE scattering background for cryodeposited films (see Fig. 1) is in good agreement with this interpretation, since the scattering probability is expected to increase with the degree of disorder. In addition, the divalent-Tm feature was found to vanish within half an hour after deposition, whereas the O-$2p$ PE signal at 6–7 eV binding energy was not yet detectable. This highly reactive behavior confirms the given picture that the divalent Tm atoms exist only at surface sites with particularly low coordination; such sites are known to be extremely sensitive to contamination.[17]

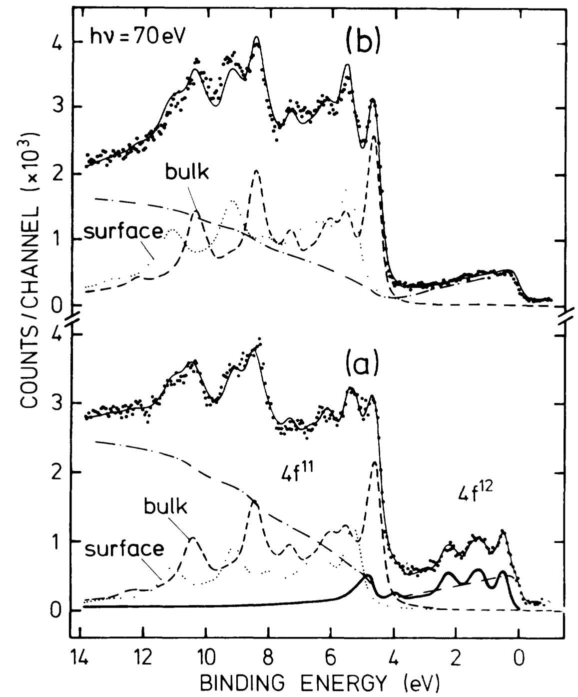

FIG. 1. Photoemission spectra taken at 13 K of an $\simeq$ 1000-Å-thick Tm metal film grown on a copper substrate at two different temperatures: (a) 13 K and (b) 270 K. The thin solid line through the data points represents the results of a least-squares–fit analysis (see text). Also shown are the subspectra for trivalent bulk (dashed), trivalent surface (dotted), and divalent surface (thick solid) Tm atoms, including the Tm $5d$ band, and the integral background of inelastically scattered electrons (dash-dotted).

In order to gain further support for this interpretation, we have carefully studied Tm metal films after Ar-ion sputtering at room temperature and after controlled deposition of Tm at room temperature on heavily sputtered Tm metal substrates. We find that the films evaporated on smooth substrates at room temperature do not contain any divalent Tm atoms even after Ar-ion sputtering under various conditions. Weak divalent-Tm PE signals [with about one third of the $4f^{12}$-multiplet intensity of Fig. 1(a)] are observed, however, for Tm surfaces prepared by deposition of Tm at room temperature on top of a heavily sputtered Tm metal substrate, if suitable evaporation rates are employed (about 10 Å/sec). The divalent features in those spectra (not shown here) exhibit the same sensitivity to contamination as observed for cryodeposited films and are characterized by a similarly high background of inelastically scattered electrons. Subsequent Ar-ion sputtering of these surfaces leads to a decrease of both the Tm^{2+} intensity and the inelastic scattering background. We may therefore conclude that evaporation of Tm onto a distorted surface results in disordered or porous structure with low-coordinated surface atoms; these rough surfaces may be annealed by sputtering at room temperature.

In order to substantiate this conjecture by comparison with theoretical predictions of surface-induced valence changes,[7] quantitative information on the energy positions of the $4f$ multiplets is needed. Therefore, a least-squares fit was performed with Doniach-Sunjic line shapes, convoluted with a Gaussian spectrometer function. The background was described by a triangular-shaped Tm $5d$ band plus an integral background of inelastically scattered $4f$-derived photoelectrons, the later taken only for the bulk $4f^{11}$ multiplet. The relative intensities of the individual multiplet components were taken from the intermediate-coupling calculations of Gerken[18] with the following modifications: (i) The $4f^{11}$-multiplet splitting was enlarged by about 10%; (ii) the phenomenon of delayed onset of the PE cross section above threshold[19] was taken into account by an exponential decrease in the intensities of the $4f^{11}$-multiplet components towards higher binding energies; and (iii) variations of the relative intensities of the individual multiplet components up to 15% were allowed in the binding-energy region from 5.5 to 7.5 eV.

The trivalent $4f^{11}$-multiplet spectra of Fig. 1 can be fitted in a satisfactory way only if separate $4f^{11}$ multiplets for bulk and surface emission are assumed. Surface and bulk subspectra were allowed to differ only in the total intensities and linewidths of the multiplet components. The derived surface core-level shift of 0.7 eV agrees well with the results of former measurements.[19] Only small differences are found for the Tm^{3+} subspectra of Tm metal films grown at different substrate temperatures. The additional features at low binding energies observed at $T_{\mathrm{sub}} = 13$ K [Fig. 1(a)] can be excellently described by the $4f^{12}$ final-state multiplet of divalent Tm, with the lowest multiplet component at a binding energy of 0.5 eV. The linewidth of the components of this multiplet is nearly the same as that of bulk Tm^{3+}; this indicates that the divalent-Tm signal originates from atoms with one specific coordination. On the other hand, broader multiplet lines are obtained for the trivalent $4f^{11}$ surface part, which suggest that the Tm^{3+} atoms reside in several surface sites with different coordinations.

Coordination-dependent surface core-level shifts have previously been observed for Yb metal, evaporated onto substrates at different temperatures.[10] Since both Tm and Yb metal have similar crystallographic structures (hcp or fcc), we may analyze the Tm results in an analogous way as done for Yb. In particular, we adopt the $4f$ energy shift found for Yb metal between coordination-9 and coordination-7 atoms (0.35 eV).[10] From the position of the empty Tm^{2+} $4f$ level on a close-packed surface (0.15 eV above the Fermi level),[7] we thus expect a $4f$ binding energy of 0.2 eV for coordination-7 atoms: Hence these atoms should become divalent. The difference from the measured binding energy of 0.5 eV may be explained by the final-state relaxation energy (impurity term), which is given by the heat of solution of the final-state ion in the matrix of the unperturbed atoms. This quantity has been calculated to be about 0.5 eV for the series of rare-earth metals in the bulk;[2] for close-packed surface atoms, it is expected to decrease by a factor of 0.7,[3, 11] and further for atoms with even lower coordination. Assuming a value of 0.3 eV for coordination-7 atoms, we arrive at an expected binding energy of 0.5 eV, which is in excellent agreement with the present experimental result. We thus can assign the observed $4f^{12}$ final-state multiplet structure to the presence of low-coordinated divalent atoms at the rough surface of a Tm metal film formed by deposition onto either a substrate at liquid-helium temperatures or a heavily sputtered substrate at room temperature.

For the cryodeposited films, the amount of surface atoms in the divalent state is found to be $(15 \pm 3)\%$. This is much less than observed for Yb metal films grown at 10 K, where about 60% of the surface atoms were found to be due to sites with coordination 7.[10] This difference is most likely due to the difference in kinetic energies of the impinging Tm and Yb atoms: In order to obtain comparable vapor pressures for both elements, the temperature of Tm had to be raised by about 500 K above that of Yb during the evaporation process.

In summary, we have found that low-coordinated surface atoms are responsible for the partial valence change at the surface of Tm metal films. This surface valence change is expected to influence strongly the physical and chemical properties of Tm metal in all situations where a surface roughening may occur, e.g., in sputtering processes, chemical reactions, and phase transitions. In fact, among the trivalent rare-earth metals, the boiling points of both Sm and Tm metals are exceptionally low, and also the melting points are slightly lower than expected. On the basis of the present work, it should be very instructive to search for anomalies in the reactivity of the trivalent rare-earth metals. The observations and conclusions of the present work are of considerable interest for an improved understanding of phenomena where rough surface structures are expected to play an essential role, e.g., for surface-enhanced Raman spectroscopy and, quite generally, for the field of catalysis.

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