

An X-Ray Photoelectron Study of Nonstoichiometric Lutetium Monosulfides*

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X-Ray photoelectron spectra of the nonstoichiometric lutetium monosulfides Lu_3S_4 and Lu_2S_3 were investigated. Binding energies for the S $2p$, Lu $4d$, and Lu $4f$ levels were measured. It is shown that the bonding in the monosulfide compositions and Lu_3S_4 is predominantly covalent, while that in Lu_2S_3 is relatively more ionic. Binding energies for lutetium in the pure metal and Lu_2O_3 are also reported.

Introduction

Among the lanthanide monosulfides lutetium sulfide is unique in that the nonstoichiometric composition extends from $\text{LuS}_{0.75}$ on the metal-rich side to $\text{LuS}_{1.25}$ on the sulfur-rich side while maintaining the fcc rock-salt structure (1–4). This extended homogeneity range apparently results from the presence of vacancies in the sulfur and metal sublattices, respectively, on either side of the true monosulfide composition. In addition, lutetium forms the sesquisulfide, Lu_2S_3 , which has the $\alpha\text{-Al}_2\text{O}_3$ structure. During the course of a high-temperature investigation of the Lu–S system a new intermediate phase, Lu_3S_4 , with a structure closely related to the defect Sc_2S_3 type (5), was also established (6) between the sulfur-rich end of the monosulfide homogeneity range and Lu_2S_3 .

Lutetium is typically trivalent in the metal with its filled and localized $4f^{14}$ electrons, and

a valence-conduction band originating from the $5d\ 6s^2$ atomic states. To the extent that this description is valid lutetium may be considered at a transition metal. In particular, because of the lanthanide contraction and a corresponding increase in the electronegativity, the crystal chemistry of lutetium compounds tends to be similar to that of $3d\ 4s^2$ scandium. In the chalcogenides lutetium enters almost exclusively into regular octahedral coordination.

As part of a continuing study of the structure and bonding in metal-rich chalcogenides (7, 8) by X-ray photoelectron spectroscopy, the lutetium–sulfur system with its extended homogeneity of the monosulfide region was of interest. This paper summarizes the results of XPS measurements in lutetium sulfides, along with those of Lu metal and Lu_2O_3 .

Experimental

Lutetium sulfide compositions in the range of $\text{LuS}_{0.82}$ to $\text{LuS}_{1.5}$ were synthesized by the direct combination of the elements at high temperatures. High-purity Lu metal rolled into 8-mil sheets and Ventron 99.9995% S were

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initially allowed to react in outgassed, evacuated, sealed quartz tubes at 870°C. The as-reacted materials were individually homogenized at 1500°C under high vacuum with the samples contained in tungsten crucibles. Although the lutetium sulfides were not reactive in ordinary laboratory air, samples were normally stored in evacuated vials. X-Ray diffraction patterns of the polycrystalline samples were taken with a Hagg-type Guinier camera ($\text{CuK}\alpha_1$ radiation; silicon internal standard). Sample compositions, crystal structures, and lattice parameters are given in Table I.

The XPS measurements were made in an AEI ES-200 B spectrometer equipped with $\text{AlK}\alpha$ radiation (1486.6 eV) and coupled to a Nicolet computer. Powdered samples of $\text{LuS}_{0.82}$ to $\text{LuS}_{1.34}$ were mounted on indium sheets over a silver metal strip in a recirculating helium drybox (<0.5 vpm of H_2O and O_2) attached to the spectrometer. Although these lutetium sulfides are presumably electronic conductors, the Fermi edge could not be located accurately in their photoelectron spectra, and hence Ag was utilized as an internal calibrant ($\text{Ag } 3d_{5/2}$ 368.0 \pm 0.2 eV (9)) to the energy scale. Spectra were recorded for the $\text{S } 2p$ and $\text{Lu } 4d$ levels of the as-mounted samples. The latter initially showed relatively small peaks from the 1s levels of oxygen and carbon impurities. The samples were then argon ion etched (~ 10 μA at 5 kV for >2 hr)

to remove the surface contamination, and the $\text{S } 2p$, $\text{Lu } 4d$, and $\text{Lu } 4f$ levels were scanned. Resolution of the $\text{Lu } 4f$ levels required use of the monochromatized X rays. The binding energies of the pertinent levels in the unetched and etched samples were within the experimental uncertainty of ± 0.2 eV. The spectrometer vacuum chamber was $<5 \times 10^{-9}$ Torr during all measurements. Spectra were recorded by the signal-averaging procedure.

The $4d$ and $4f$ spectra of Lu metal were obtained from a sheet of high-purity (O, 220; C, 24; Gd, 50; Tm, 10 ppm; all other impurities including rare earths, <1 ppm) electropolished sample, which was surface abraded and argon ion etched before scanning the spectrum. The Fermi edge of the metal could be located sharply at a kinetic energy consistent with the known instrumental work function.

Samples of Lu_2S_3 and high-purity Lu_2O_3 were mounted directly on a sintered stainless-steel strip. After an initial argon ion etch a thin deposit of gold was vaporized onto the samples to serve as an internal calibrant ($\text{Au } 4f_{7/2}$ 84.0 \pm 0.2 eV (9)) to compensate for anticipated charging effects in these non-conducting samples. The $\text{S } 2p$, $\text{Lu } 4d$, and $\text{Lu } 4f$ spectra in Lu_2S_3 and $\text{O } 1s$, $\text{Lu } 4d$, and $\text{Lu } 4f$ spectra in Lu_2O_3 were recorded. The absence of differential charging shifts in the case of the Lu_2O_3 sample with the Au deposit was checked by use of an electron flood gun. The $\text{Au } 4f$ and $\text{Lu } 4d$ spectra both shifted identically by 1 eV to lower relative binding energies when the flood gun was turned on.

TABLE I
LUTETIUM SULFIDES

Composition	Crystal structure	Lattice parameters (Å)
$\text{LuS}_{0.82}$	Cubic, $Fm\bar{3}m$	$a_0 = 5.323(1)$
$\text{LuS}_{1.03}$	Cubic, $Fm\bar{3}m$	$a_0 = 5.356(1)$
$\text{LuS}_{1.21}$	Cubic, $Fm\bar{3}m$	$a_0 = 5.359(1)$
Lu_3S_4	Orthorhombic, $Fddd$	$a = 10.836(12)$ $b = 7.708(9)$ $c = 22.870(39)$
Lu_2S_3	Rhombohedral, $R\bar{3}c$	$a_h = 6.722(2)$ $c_h = 18.141(7)$

Results and Discussion

The binding energies of the pertinent levels in Lu metal and Lu sulfides, relative to the appropriate calibrant binding energy as given above, are reported in Table II. The $4f$ spectra of Lu metal, obtained with monochromatic X rays, were sharp with a FWHM of ~ 0.6 eV, which corresponds to the instrumental FWHM of the $\text{Ag } 3d_{5/2}$ level recorded

TABLE II
S 2*p*, Lu 4*d*, AND Lu 4*f* BINDING ENERGIES (eV ± 0.2 eV) IN LUTETIUM
SULFIDES

Compound	S 2 <i>p</i>	Lu 4 <i>d</i> _{5/2}	Lu 4 <i>d</i> _{3/2}	Lu 4 <i>f</i> _{7/2}	Lu 4 <i>f</i> _{5/2}
Lu	—	196.0	205.8	7.2	8.7
LuS _{0.82}	162.9	196.8	206.6	7.4	8.9
LuS _{1.03}	162.6	196.7	206.6	7.5	8.9
LuS _{1.21}	162.5	196.7	206.5	7.6	8.9
LuS _{1.34}	162.6	196.7	206.5	7.4	8.7
LuS _{1.5}	161.8	197.1	206.9		8.8

similarly. The 4*d* peaks, taken with the standard X-ray optics, however, were broad with FWHM of ~3.1 eV. The spin-orbit splittings of the two *J* values of the 4*f* and 4*d* levels are 1.5 and 9.8 eV, respectively, and compare very well with those reported previously (10–12).

It is generally assumed that the 4*f* levels in Lu do not participate to any significant extent in chemical bonding, and their binding energies in the sulfides are within 0.2 to 0.3 eV of the values for pure Lu metal. However, the intensity of the Lu 4*f*_{7/2} peak drops systematically with increasing sulfur content of the samples. The intensity ratio, Lu 4*f*_{7/2}/Lu 4*f*_{5/2}, measured with respect to the low-energy flank, was 1.01 in Lu; this reduces to 0.88 in LuS_{0.82} and 0.73 in LuS_{1.34}. Although the 4*f* peaks in Lu₂S₃ were not resolved in the spectrum taken with a surface deposit of Au, it could be resolved (interpolated binding energies: 7.6 and 8.8 eV) on a sample without Au, and where the intensity ratio was only 0.62.

The core 4*d* levels show a significant shift of 0.7 eV with reference to Lu metal in both the 4*d*_{5/2} and 4*d*_{3/2} spin-orbit peaks from the sulfides LuS_{0.82} to LuS_{1.34}. The corresponding shift in Lu₂S₃ is 1.1 eV.

The most significant information about the cation-anion interaction in lutetium sulfides is obtained from the S 2*p* binding energies. The value of 162.9 eV in LuS_{0.82} is very close to the binding energies in neutral S, and those

observed in typically metallic sulfides (8). In LuS_{1.03} through LuS_{1.34}, the S 2*p* binding energy is 162.6 eV, which is very near the value in the most metal-rich composition of LuS_{0.82}. However, in Lu₂S₃ the S 2*p* level is significantly shifted to 161.8 eV. The latter value is typical of ionic sulfides (8). LuS_{0.82} has a rock-salt structure with vacancies in the sulfur sublattice, and one would expect appreciable metal-metal bonding in the solid with this composition. The binding energy for S in LuS_{0.82} indicates very low charge transfer from the metal to sulfur or, alternatively, appreciable back bonding from the anions to the metal. This effect is maintained in the structurally similar compositions of LuS_{1.03}, LuS_{1.21}, and Lu₃S₄, although the vacancies are in the metal sublattice. Lu₃S₄ has a structure derived from the parent fcc lattice (6). The anion lattice is completely filled, and vacancies occur in the cation sublattice sites (ordered in the case of Sc₂S₃ structure type, but partly occupied in Lu₃S₄). Thus a marked covalency is indicated in the nonstoichiometric lutetium monosulfide compositions and in the intermediate Lu₃S₄ phase. The significant shift of S 2*p* binding energy in Lu₂S₃ is indicative of the fact that in this composition conventional ionic bonding is important.

The X-ray photoelectron spectra intensities in the valence band region in the lutetium sulfides are very weak compared to the Lu 4*f* signals. Ultraviolet photoelectron spectroscopy was used to obtain the spectrum in the

valence band region. Only a broad peak at a binding energy of 4.6 eV with respect to the clearly discernible Fermi edge in $\text{LuS}_{1.03}$, $\text{LuS}_{1.21}$, and $\text{LuS}_{1.34}$ was observed. This peak may be predominantly ascribed to the S 3*p* level, with broadening due to hybridization with the outer *dsp* Lu orbitals. The constancy of the binding energy, and its near correspondence to the values observed in typically metallic sulfides (7, 8) lends support to the conclusion that appreciable mixing of the sulfur and lutetium orbitals is involved in these lutetium sulfides. As was also observed by previous workers (13), it was found that the Lu 4*f* levels did not contribute observable spectral features to the uv photoelectron spectra, just as the S 3*p* levels did not contribute to the X-ray spectra, indicating a substantial difference in the transition probabilities for the two levels at the two excitation energies.

For Lu_2O_3 , an O 1*s* peak at 529.9 eV, two Lu 4*d* peaks at 196.3 eV and 206.2 eV, and an unresolved Lu 4*f* peak at 8.4 eV were obtained. Although the O 1*s* and Lu 4*d*_{5/2} binding energies correspond to previously observed values (14) in Lu_2O_3 , the shift of only 0.3 eV in the Lu 4*d*_{5/2} level with respect to the pure metal in this predominantly ionic oxide is out of line when compared to the shifts observed in lutetium sulfides. A reasonable interpretation of the relatively small binding energy shift in Lu_2O_3 is that the intraatomic shift arising from the effect of chemical bonding on the atomic electron distribution is compensated by the interatomic (lattice site potential) effect. The lattice site potential shift calculated for the Lu sites in the *Ia3* structure of the oxide and assuming Lu^{3+} and O^{2-} point charges is -31.5 ± 0.1 eV per unit of electronic charge.¹ The observed 0.3-eV binding energy shift then corresponds to a

chemical shift effect of 31.8 eV. Assuming that this intraatomic value when divided by 3 yields a chemical shift per electronic unit charge, and using the observed shift of 1.1 eV for Lu 4*d*_{5/2} in Lu_2S_3 and the calculated lattice site potential¹ yields a Lu charge of only 0.6 unit in this relatively ionic sulfide. Thus the evidence obtained from such a simplified calculation is consistent with the generally accepted electronegativity difference between oxygen and sulfur. The general conclusion that Lu_2S_3 is substantially less ionic than Lu_2O_3 is independent of the initial assumption of a +3 charge for Lu (i.e., the site charges need not have this assumed value, and it still follows that the effective site charges in Lu_2S_3 are significantly reduced relative to Lu_2O_3). The calculated lattice site potential for the Lu sites, assuming Lu^{3+} and S^{2-} point charges, is 26 eV per unit electronic charge, and is 5.2 eV if the Lu charge is taken to be 0.6 electronic charge unit.

Thus the indications of the photoelectron spectral data are that Lu_2O_3 is substantially more ionic than Lu_2S_3 , presumably because of the inherent electronegativity difference between oxygen and sulfur, and that Lu_2S_3 is more ionic than the conducting nonstoichiometric monosulfides of lutetium. The reduction in ionic character in the latter can be viewed as arising from back-bonding interactions of the sulfur *p* orbitals with the metallic *d* band. The significant reduction of ionic character, it is proposed, makes the interpretation of the shifts in the metallic compounds as purely chemical shifts appropriate.

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¹The lattice site potentials were calculated by the Ewald method using a computer program PALS (potentials at lattice sites) written locally by J. Merrick.

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