Thermodynamics of the Semiconductor–Metal Transition in the Lanthanide Monosulphides *

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A simple principle of lanthanide thermochemistry is used to estimate the standard free energy change for the semiconductor–metal transition in the lanthanide monosulphides at 298.15 K. The results are in satisfactory agreement with the distribution of semiconducting and metallic monosulphides within the lanthanide series, and with the observed transition pressure regions in SmS, EuS, and YbS. In cases where experimental values of the standard enthalpies of formation are currently unavailable, estimated values for both semiconducting and metallic monosulphides are also obtained.

Some thermodynamic properties of the lanthanide elements vary nearly smoothly with atomic number; others show marked irregularities. There is a principle which helps us to distinguish these two types of property: the energies of reactions in which the $4f$ electrons are conserved vary nearly smoothly with atomic number, but those of reactions in which the number of $4f$ electrons changes vary irregularly.[1,2] When the number of $4f$ electrons decreases by one, the irregular energy variation is very similar to that in the ionization energy of the M^{2+} ions in the configuration $[Xe]4f^{n+1}$.†

These principles can be tested with a reaction which has recently aroused great interest. This is the insulator-metal transition in the lanthanide monosulphides.[1,4–6] With the exception of the samarium, europium, and ytterbium compounds which are semiconductors, all of the lanthanide monosulphides are metallic at normal pressures. Magnetic measurements [7] show that in the semiconductors, the lanthanide site carries the same number of $4f$ electrons as the $[Xe]4f^{n+1}$ configuration of the M^{2+} ion. By contrast, in the metallic monosulphides, the lanthanide site has the same $4f$ population as the $[Xe]4f^{n}$ configuration of the M^{3+} ion. Following the terminology of earlier papers,[1,2] we therefore classify the semiconducting sulphides as di-f compounds, and the metallic sulphides as tri-f compounds. The semiconductors can be given the ionic formulation $M^{2+}S^{2-}$; the metals are often written $M^{3+}(e^-)S^{2-}$, with the odd electron taken to be in a conduction band composed of the $5d$ and/or $6s$ orbitals of the lanthanide atom. It follows that the semiconductor–metal transition is a reaction in which the number of $4f$

$$\mathrm{MS\ (s,\ di\text{-}}f) \rightarrow \mathrm{MS\ (s,\ tri\text{-}}f) \qquad (1)$$

electrons decreases by one. We therefore expect the variation in an energy of reaction (1), such as $\Delta G_m^\ominus(1)$ or $\Delta H_m^\ominus(1)$, to correspond closely to that in $I(M^{2+}, g, \text{di-}f)$, the ionization energy of dipositive gaseous ions in the configuration $[Xe]4f^{n+1}$.

Other expectations are concerned with the sign of $\Delta G_m^\ominus(1)$. The compound SmS is a black semiconductor in which the bulk phase seems to be di-f; if any tri-f samarium sites are present they seem to occur at the surface.[8,9] However, if the pressure is increased to only 6—7 kbar, the molar volume and resistivity drop sharply and a first-order transition occurs to a golden yellow compound in an intermediate valence state. The sample now contains *ca.* 70% tri-f samarium, and 30% di-f samarium in a state of interconfigurational fluctuation.[6] A further rise in pressure increases the proportion of tri-f samarium, but the exact pressure at which the fully tri-f metallic phase is realised seems to be uncertain. Studies of the resistivity variation with pressure at low temperatures suggest that the sample is close to being fully metallic above 20 kbar,[10,11] but there also exist claims [12] that this state is not realised below 100 kbar (10^{10} Pa).

In the case of YbS, the semiconductor–metal transition occurs in the pressure range 150—200 kbar. With EuS, the analogous change has not been observed because the compound undergoes a first-order transition to the CsCl structure at 215 kbar.[13] This suggests that the transition pressure for the conversion of EuS to the fully metallic phase with retention of the NaCl structure lies above 215 kbar.

It follows that a theory which predicts values of $\Delta G_m^\ominus(1)$ at 298.15 K and 1 atm pressure should have the following characteristics. First, the variation in $\Delta G_m^\ominus(1)$ should correspond closely to that in $I(M^{2+}, g, \text{di-}f)$. Secondly, because the properties of SmS suggest that it lies close to the semiconductor–metal phase boundary at normal temperatures and pressures, $\Delta G_m^\ominus(1)$ should lie close to zero in this case, and thirdly, $\Delta G_m^\ominus(1)$ should be positive for EuS and YbS and negative for the sulphides of the elements La→Nd and Gd→Tm inclusive. Finally, the positive values of $\Delta G_m^\ominus(1)$ for YbS and EuS should be consistent with transition pressures of 150—200 kbar and >215 kbar respectively.

In this paper we show how the principle outlined at the beginning of this paper can be used to estimate values of $\Delta G_m^\ominus(1)$ which meet these requirements. The calculations also provide estimates of $\Delta H_f^\ominus(\text{MS, s, di-}f)$ and $\Delta H_f^\ominus(\text{MS, s, tri-}f)$ for the elements La→Yb in cases where these quantities are not available from experiment.

The calculation proceeds in steps dictated by equation (2).

$$\Delta G_m^\ominus(1) = \Delta H_f^\ominus(\text{MS, s, tri-}f) - \Delta H_f^\ominus(\text{MS, s, di-}f) - T\Delta S_m^\ominus(1) \qquad (2)$$

In separate operations, we estimate values for the standard enthalpies of formation of the metallic and semiconductor phases for each element, and for the standard entropy change for reaction (1).

Results

Standard Enthalpies of Formation of the Metallic Monosulphides.—The metallic monosulphides are tri-f systems, and with the exception of europium and ytterbium, the elemental

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* *Non-S.I. units employed:* 1 atm = 101 325 Pa; 1 cal = 4.184 J.

† Here and throughout the paper, n is the number of $4f$ electrons carried by the tripositive ion in its ground state. Thus for lanthanum, $n = 0$, for gadolinium, $n = 7$, and for lutetium, $n = 14$. $[Xe]4f^{n+1}$ is the ground state configuration for all gaseous dipositive ions except $La^{2+}(g)$ and $Gd^{2+}(g)$.[3]

Table 1. Thermodynamic data for the tri-*f* monosulphides, and for the semiconductor-metal transition at 298.15 K

Element	$\Delta H_f^\ominus$(MS, s, tri-*f*)[a] kcal mol^{-1}	a_0(MS, s, tri-*f*)[b] pm	$\Delta H_m^\ominus$(1)[c] kcal mol^{-1}	$\Delta S_m^\ominus$(1)[d] cal K^{-1} mol^{-1}	$\Delta G_m^\ominus$(1)[e] kcal mol^{-1}
La	−108 ± 4[f]	585.0	−100 ± 8	−5 ± 4	−99 ± 9
Ce	−109 ± 1[f]	577.5	−66 ± 6	−3 ± 4	−65 ± 6
Pr	−106 ± 5[f]	573.6	−35 ± 8	−2 ± 4	−34 ± 9
Nd	−108 ± 6	569.4	−31 ± 8	−2 ± 4	−30 ± 9
Pm	−108 ± 6	565.4[d]	−29 ± 8	−1 ± 4	−29 ± 9
Sm	−108 ± 6	562.0[d]	−1 ± 8	−1 ± 4	−1 ± 9
Eu	−89 ± 6	559.0[d]	20 ± 7	−4 ± 4	21 ± 9
Gd	−111 ± 4[f]	556.6[g]	−85 ± 7	−3 ± 4	−84 ± 8
Tb	−108 ± 6	551.7	−49 ± 8	−2 ± 4	−48 ± 9
Dy	−107 ± 6	548.8	−26 ± 8	−2 ± 4	−25 ± 9
Ho	−106 ± 6	546.1	−28 ± 8	−2 ± 4	−27 ± 9
Er	−105 ± 6	543.1	−32 ± 8	−2 ± 4	−31 ± 9
Tm	−104 ± 6	541.2	−10 ± 8	−1 ± 4	−10 ± 9
Yb	−95 ± 6	537.0[d]	15 ± 8	2 ± 4	14 ± 9
Lu	−100 ± 3[h]	535.2[i]			

[a] Estimated by the method described in the text unless otherwise stated. [b] a_0 = Lattice pameter. Ref. *i* of Table 2 unless otherwise stated. [c] Calculated from the figures in column five of Table 2, and column two of Table 1. [d] Estimated by the method described in the text. [e] Calculated from equation (2). [f] Ref. 15. [g] Reference *b* averaged with the value of ref. 15. [h] Ref. 16. [i] Ref. *b* averaged with the value of ref. 16.

metals fall in the same category.[14] Thus for all of the elements La→Lu except europium and ytterbium, the process in equation (3) is one in which the 4*f* electrons are conserved.

$$\mathrm{M(s)} + \mathrm{S(s)} \longrightarrow \mathrm{MS(s,\ metallic)} \qquad (3)$$

For these elements therefore, we expect the values of $\Delta H_f^\ominus$(MS, s, metallic) to vary nearly smoothly with atomic number.

Experimental values of $\Delta H_f^\ominus$(MS, s, metallic) for LaS, CeS, PrS, and GdS have been determined or reviewed by Fries and Cater.[15] Their figures are recorded in column two of Table 1, together with the experimental value for LuS obtained by Franzen and Hariharan.[16] The five values lie in the narrow range −105 ± 6 kcal mol^{-1}, and support the supposition of a smooth variation with atomic number. The five values were therefore weighted as their uncertainties and fitted to a smooth four-parameter curve. Estimates of $\Delta H_f^\ominus$(MS, s, tri-*f*) for NdS, PmS, SmS, TbS, DyS, HoS, ErS, and TmS were then directly read off from the curve. These are also recorded in column two of Table 1.

In the case of europium and ytterbium, the figures read off the curve are estimates of $\Delta H_m^\ominus$ for the reaction (4). However,

$$\mathrm{M(s,\ tri\text{-}}f) + \mathrm{S(s)} \longrightarrow \mathrm{MS(s,\ tri\text{-}}f) \qquad (4)$$

the figures can be converted to $\Delta H_f^\ominus$(EuS, metallic) and $\Delta H_f^\ominus$(YbS, metallic) if for these two elements the values of $\Delta H_m^\ominus$ for reaction (5) are known. Then, for europium and

$$\mathrm{M(s,\ di\text{-}}f) \longrightarrow \mathrm{M(s,\ tri\text{-}}f) \qquad (5)$$

ytterbium, equation (6) applies. The required values of

$$\Delta H_f^\ominus(\mathrm{MS,\ tri\text{-}}f) = \Delta H_m^\ominus(4) + \Delta H_m^\ominus(5) \qquad (6)$$

$\Delta H_m^\ominus$(5) can be obtained by plotting $\Delta H_f^\ominus$(MCl_3, s) and $\frac{1}{2}\Delta H_f^\ominus$($M_2O_3$, s) against atomic number for the elements La→Lu. The values lie on a smooth curve, except at europium and ytterbium where there are displacements which yield estimates of $\Delta H_m^\ominus$(5).[17–19] Using the data given by Morss,[20] and averaging the two figures for each element, we obtain values of $\Delta H_m^\ominus$(5) equal to 19.4 kcal mol^{-1} for europium and 7.5 kcal mol^{-1} for ytterbium. Equation (6) was then used to obtain the values of $\Delta H_f^\ominus$(EuS, tri-*f*) and $\Delta H_f^\ominus$(YbS, tri-*f*) which are in column two of Table 1.

Standard Enthalpies of Formation of the Semiconducting Monosulphides.—The estimation method used in the last section is a general one. We can estimate the standard enthalpies of formation of lanthanide compounds by choosing a reaction of the compounds in which the 4*f* electrons are conserved. If some experimental values for the standard enthalpy of the process are known, then we plot them against atomic number, and obtain unknown values by interpolation.

For example, values of $\Delta H_f^\ominus$(MS, s, di-*f*) could be obtained from $\Delta H_m^\ominus$ values for the process shown by equation (7). The

$$\mathrm{MS(s,\ di\text{-}}f) \longrightarrow \mathrm{M(g,\ di\text{-}}f) + \mathrm{S(g)} \qquad (7)$$

ground state configuration of the gaseous atom is M(g, di-*f*) except at lanthanum, cerium, and gadolinium, where corrections must be made by using the atomic spectra of the elements. However, in this case the experimental data are very limited: for the elements Ba→Yb, experimental values of $\Delta H_m^\ominus$(7) are available only at barium and europium. It is therefore better to choose a reaction where the smoothness of the energy variation has a more developed theoretical basis. A suitable reaction is shown by equation (8) whose standard

$$\mathrm{MS(s,\ di\text{-}}f) \longrightarrow \mathrm{M^{2+}(g,\ di\text{-}}f) + \mathrm{S^{2-}(g)} \qquad (8)$$

internal energy change is equal to the lattice energy of the semiconducting monosulphide. Lattice energies of this kind can be generally treated by an ionic model, and alongside the barium and europium values, we can include experimental data on CaS and SrS. This strengthens the empirical base of the estimation method.

From the Born-Haber cycle for MS(s, di-*f*) at 298.15 K,

$$\Delta H_f^\ominus(\mathrm{MS,\ s,\ di\text{-}}f) = \Delta H_f^\ominus(\mathrm{M^{2+},\ g,\ di\text{-}}f) + \Delta H_f^\ominus(\mathrm{S^{2-},\ g}) - \Delta U_m^\ominus(8) - 2\boldsymbol{R}T \qquad (9)$$

$\Delta U_m^\ominus$(8) is the standard internal energy change of reaction (8), the lattice energy of the semiconducting sulphide at 298.15 K.

Because reaction (8) is one in which the 4*f* electrons are conserved, we expect $\Delta U_m^\ominus$(8) to vary smoothly across the series Ba→Yb. The same conclusion can be reached through classical ionic models for the calculation of lattice energies, provided the internuclear distances in the semiconductor phases follow a smooth lanthanide contraction analogous to that observed in the ionic radii of the tripositive ions.

Table 2. Thermodynamic data for di-*f* lanthanide monosulphides at 298.15 K

Element	$\Delta H_f^\ominus$(M, g)[a] kcal mol^{-1}	$\Delta H_f^\ominus$(M^{2+}, g, di-*f*)[b] kcal mol^{-1}	r_e(MS, s, di-*f*)[c] pm	$\Delta H_f^\ominus$(MS, s, di-*f*)[c] kcal mol^{-1}	$\Delta U_m^\ominus(8)$[c] kcal mol^{-1}
Ba	43.5 ± 2	397.3 ± 2[d]	319.4[e]	−110 ± 3[f]	658[g]
La	103.0 ± 1	510.2 ± 2	312	−8 ± 6	669
Ce	100.4 ± 1[h]	480 ± 3	310	−43 ± 6	674
Pr	85.3 ± 0.5[h]	457 ± 3	307	−71 ± 6	679
Nd	78.1 ± 0.5[h]	455 ± 3	304	−78 ± 6	684
Pm	76 ± 6[h]	458 ± 7	302	−79 ± 6	688
Sm	49.4 ± 0.5	437 ± 3	298.5[i]	−107 ± 6	695
Eu	42.4 ± 0.3[h]	435.2 ± 0.5	298.4[j]	−109 ± 3[k]	695[g]
Gd	95.0 ± 1	525 ± 3	295	−26 ± 6	702
Tb	92.9 ± 1	497 ± 3	293	−59 ± 6	706
Dy	69.4 ± 1	478 ± 3	291	−82 ± 6	711
Ho	71.8 ± 0.3[h]	485.7 ± 2	289	−78 ± 6	715
Er	75.6 ± 0.5[h]	494.4 ± 2	287	−74 ± 6	719
Tm	55.5 ± 1	479 ± 3	285	−94 ± 6	724
Yb	37.2 ± 0.5[h]	465.3 ± 0.6	284.3[i]	−109 ± 6	725
Sr	39.3 ± 2[f]	427.9 ± 2[d]	301.0[e]	−108 ± 4[k]	687[g]
Ca	42.6 ± 0.4	460.3 ± 0.5[d]	284.5[e]	−115.3 ± 2[f]	726[g]

[a] From R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, K. K. Kelley, and D. D. Wagman, ' Selected Values of the Thermodynamic Properties of the Elements,' American Society for Metals, Metals Park, Ohio, 1973, unless otherwise stated. [b] Calculated from the expression $\Delta H_f^\ominus(\mathrm{M, g}) + I_1 + I_2' + 5RT$ where I_1 is the first ionization potential, and I_2' is the second ionization potential the prime indicating that the dipositive ion is in the lowest level of the [Xe]$4f^{n+1}$ configuration. Population of excited states in the Sm case has no significant effect because, as ref. 28 reveals, the pattern of accessible energy levels is very similar in the gaseous atom and ion. Unless otherwise stated, the values of I_1 and I_2' are those recommended by ref. 3. I_2' is the same as I_2 except at La and Gd where the corrections given by ref. 30 were used. [c] Estimated by the method described in the text unless otherwise stated. [d] As footnote *b*, but the values of I_1 and I_2 are from C. E. Moore, ' Ionization Potentials and Ionization Limits Derived from the Analyses of Atomic Spectra,' NSRDS-NBS 34, U.S. Govt. Printing Office, Washington, D.C., 1970. [e] R. W. G. Wyckoff, ' Crystal Structures,' 2nd edn., vol. 1, Interscience, New York, 1963. [f] V. B. Parker, D. D. Wagman, and W. H. Evans, U.S. National Bureau of Standards Technical Note 270–6, U.S. Govt. Printing Office, Washington D.C., 1971. [g] Calculated from the Born-Haber cycle as described in the text. [h] Ref. 20. [i] J. Flahaut and P. Laruelle, *Prog. Sci. Technol. Rare Earths*, 1968, **3**, 149. [j] O. D. McMasters, K. A. Gschneidner, E. Kaldis, and G. Sampietro, *J. Chem. Thermodyn.*, 1974, **6**, 845. [k] Ref. 15.

To establish the smooth variation in $\Delta U_m^\ominus(8)$, we substitute the experimental values of $\Delta H_f^\ominus$(MS, s) for BaS, SrS, EuS, and CaS in equation (9). The corresponding values of $\Delta U_m^\ominus(8)$ are calculated and fitted to a Kapustinskii expression [21] in the form of equation (10), where $B = 34.5$ pm and r_e is the known

$$\Delta U_m^\ominus(8) = \frac{A}{r_e}\left(1 - \frac{B}{r_e}\right) \qquad (10)$$

internuclear distance. The average value of A was $(2.347 \pm 0.008) \times 10^5$ kcal mol^{-1} pm, and this was used in the subsequent calculations.

Values of $\Delta U_m^\ominus(8)$ for the elements La→Sm and Gd→Yb were then calculated from the internuclear distances in the semiconducting sulphides. In most cases, these distances were not experimentally available, so they were estimated from a linear plot of the experimental r_e values for BaS, SmS, EuS, and YbS against the six-co-ordinate ionic radii,[22,23] for the tripositive ions with the same number of 4*f* electrons *i.e.* La^{3+}, Eu^{3+}, Gd^{3+}, and Lu^{3+} respectively. The resulting values of $\Delta U_m^\ominus(8)$ were then substituted into equation (9), thereby providing estimates for those values of $\Delta H_f^\ominus$(MS, s, di-*f*) which are not experimentally available.

The calculations and data are summarized in Table 2. What value of $\Delta H_f^\ominus(S^{2-}, g)$ is used is largely immaterial, because the values of $\Delta U_m^\ominus(8)$ which are obtained by using it are interpolated. Errors introduced by the uncertainty in $\Delta H_f^\ominus(S^{2-}, g)$ must be almost entirely eliminated when the quantity is re-used in the reverse operation to generate unknown $\Delta H_f^\ominus$(MS, s, di-*f*) values from the interpolated lattice energies. Here we use the value, $\Delta H_f^\ominus(S^{2-}, g) = 152$ kcal mol^{-1} proposed by Waddington.[24]

Values of $\Delta S_m^\ominus(1)$.—Although the entropy of the transition will be small, its estimation is difficult because of the absence of reliable experimental entropies for the individual sulphides. This is especially the case for the tri-*f* sulphides, where literature values [25] for CeS and NdS involve the extrapolation of heat capacity data to 0 K from temperatures of 50 K or more. Such extrapolations have probably missed a significant proportion of the magnetic entropy.

The entropies of a series of lanthanide solids can often be broken down into a nearly smoothly varying term and the magnetic entropy. The magnetic entropy is close to $R\ln(2J + 1)$ where $(2J + 1)$ is the degeneracy of the lowest level arising from the splitting of the $4f^n$ ground term by spin-orbit coupling. This breakdown seems to apply, for example, to the solid metals,[26] and the trichlorides.[27]

Values of $\Delta S_m^\ominus(1)$ were estimated by assuming that the entropies of the two series of monosulphides vary in a similar way. The baseline term for $\Delta S_m^\ominus(1)$ was set equal to a constant given by the average value of $\{S^\ominus(\mathrm{M, s, tri}\text{-}f) - S^\ominus(\mathrm{M', s, di}\text{-}f)\}$, where M and M′ have the same number of 4*f* electrons at the metal atom site. The value obtained from the molar entropies [20] of the pairs La/Ba, Gd/Eu, and Lu/Yb is −1.9 cal K^{-1} mol^{-1}. This value was then supplemented by the difference in the magnetic entropies of the tri-*f* and di-*f* monosulphides. This completed the estimate for all cases except SmS and EuS. Here the values were decreased by 2.8 cal K^{-1} mol^{-1} and increased by 2.2 cal K^{-1} mol^{-1} respectively to allow for the population of excited states of the ^7F multiplet in SmS(s, di-*f*) and EuS(s, tri-*f*) at 298.15 K. These increments were calculated from the electronic partition function using the energy levels of Sm^{2+} and Eu^{3+} given by Dupont [28] and by Carnall *et al.*[29] The complete set of estimates for $\Delta S_m^\ominus(1)$ are recorded in column five in Table 1.

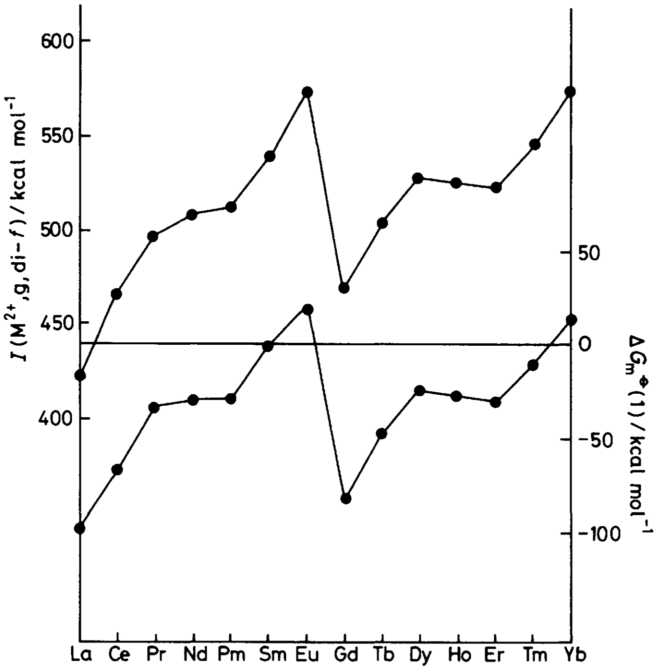

Figure. The ionization energy of dipositive lanthanide ions in the [Xe]$4f^{n+1}$ configuration (upper plot, left hand axis) and the standard free energy change of reaction (1) (lower plot, right hand axis)

Discussion

We can now calculate values of $\Delta G_m^{\ominus}(1)$ from equation (2), and these results are given in column six of Table 1. They are plotted in the Figure along with the values of $I(M^{2+}, g, di\text{-}f)$. The latter were obtained from the third ionization energies of the elements,[3] corrected at lanthanum and gadolinium to the [Xe]$4f^{n+1}$ configuration of the dipositive ions by using the data given by Sugar and Reader.[30] The expected parallelism between the two plots is observed.

Next we note that, in agreement with the experimental details given earlier, $\Delta G_m^{\ominus}(1)$ is very close to zero for SmS, clearly positive for EuS and YbS, and negative in the remaining cases. We predict that PmS will be metallic.

Finally we must consider the transition pressures of EuS and YbS. Knowing the value of $\Delta G_m^{\ominus}$ we can estimate the corresponding value of a *first-order* transition pressure at 298.15 K from equation (11), where, P_1 = 1 atm (virtually

$$\Delta G_m = \Delta G_m^{\ominus} + \int_{P_1}^{P_2} \Delta V_m \mathrm{d}P \qquad (11)$$

zero) and P_2 is the first-order transition pressure when $\Delta G_m = 0$. We first calculate the standard molar volumes ($V_m^{\ominus}$) for the semiconducting and metallic phases of EuS and YbS. For the semiconductors, we use the experimental internuclear distances given in Table 2. For the metallic phases we estimate unit cell parameters from the straight line generated by plotting the experimental cell sides of the 10 fully metallic monosulphides (LaS$\rightarrow$NdS, GdS$\rightarrow$ErS, and LuS) against the ionic radii [22,23] of the tripositive ions. These estimates, and the auxiliary data, are given in column three of Table 1. The resulting $V_m^{\ominus}$ values for the semiconducting and metallic phases of EuS and YbS are recorded in Table 3.

When applying equation (11) to a reaction, it is often assumed that ΔV_m does not vary with pressure. With 1 kcal $\equiv$41.84 kbar cm^3, and our estimated values of $\Delta G_m^{\ominus}(1)$, this approximation gives first-order transition pressures of 154 and 134 kbar for EuS and YbS respectively. These figures are too low, most obviously for EuS where there is no sign of a transition below 215 kbar. Low values might have been expected because the di-*f* phase is more compressible than the tri-*f*, and ΔV_m is not constant; it decreases with pressure.

Table 3. Estimated and experimental data used in the application of equation (12) (see text)

Solid phase	$V_m^{\ominus}$/cm^3	a/kbar^{-1}	b/kbar^{-2}
EuS(s, di-*f*)	32.00	-1.64×10^{-3}	3.08×10^{-6}
YbS(s, di-*f*)	27.68	-1.39×10^{-3}	2.16×10^{-6}
EuS(s, tri-*f*)	26.30	-8.33×10^{-4}	1.17×10^{-6}
YbS(s, tri-*f*)	23.31	-8.33×10^{-4}	1.17×10^{-6}

The accuracy of the estimates can be improved by a crude attempt to express ΔV_m as a function of pressure in the pressure range of interest. For the semiconductor and metallic phases of EuS and YbS equation (12) holds. In each case we

$$V_m = V_m^{\ominus}(1 + ap + bp^2) \qquad (12)$$

ignore the tiny difference between $V_m^{\ominus}$ and V_m extrapolated to zero pressure. For the semiconductor phases, the value of a is then fixed by the bulk moduli of EuS and YbS given by Jayaraman *et al.*[13] Data in the same paper suggest that for EuS, $V_m/V_m^{\ominus} = 0.79$ at 215 kbar, and that for YbS, $V_m/V_m^{\ominus} = 0.84$ at 150 kbar. This fixes the two values of b. For fully metallic phases, data are sparse. For both EuS and YbS, we use the bulk modulus of 1 200 kbar quoted for GdS.[31] We then assume that in the 250—300 kbar range, YbS is fully metallic. By correcting the corresponding $V_m/V_m^{\ominus}$ data to our estimated value of $V_m^{\ominus}$(YbS, s, tri-*f*), we can obtain a value of b which we use for both EuS and YbS in the metallic state. The final values of $V_m^{\ominus}$, a, and b for each phase are given in Table 3. Application of equation (11) then leads to first-order transition pressures of 274 and 203 kbar for EuS and YbS respectively.

As first-order transitions from a fully di-*f* to a fully tri-*f* phase have not been observed experimentally, a direct comparison of our estimated transition pressures with experiment is not possible. As we have seen, the first-order transition in SmS occurs to a compound of intermediate valence, and in general, it seems likely that the di-*f* to tri-*f* transition occurs over a pressure range *via* an intermediate valence compound in a state of interconfigurational fluctuation. Nevertheless, if with increasing pressure, we can experimentally identify the point at which purely di-*f* behaviour ceases, and the point at which purely tri-*f* behaviour begins, then provided thermodynamic equilibrium exists, the first-order transition pressure must lie somewhere within this pressure range. For YbS, the range seems to be roughly 150—200 kbar,[13] so our estimated first-order transition pressure of 203 kbar is very reasonable: our value of $\Delta G_m(1)$ in the middle of the pressure range at 175 kbar is only about 1 kcal mol^{-1}.

The estimated first-order transition pressure for EuS is also satisfactory in that it lies above 215 kbar where the di-*f* phase is converted to the CsCl structure. It is worth pointing out that the estimate of 274 kbar for EuS is somewhat higher than the first-order transition pressure of 193 kbar calculated by Nolting [32] using very different methods; his value is well within the range of uncertainty of our calculation: the value of $\Delta G_m(1)$ at 193 kbar, calculated from equation (11), is only *ca.* 4 kcal mol^{-1}. Nevertheless our higher figure is marginally unfavourable to his suggestion that, with increasing pressure, the semiconductor-metal transformation in EuS might occur before the CsCl transition below the Curie temperature.

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References

1 D. A. Johnson, *Adv. Inorg. Chem. Radiochem.*, 1977, **20**, 1.
2 D. A. Johnson, *J. Chem. Educ.*, 1980, **57**, 475.
3 W. C. Martin, L. Hagan, J. Reader, and J. Sugar, *J. Phys. Phys. Chem. Ref. Data*, 1974, **3**, 771.
4 J. H. Jefferson and K. W. H. Stevens, *J. Phys. C*, 1978, **11**, 3919.
5 R. D. Parks, 'Valence Instabilities and Related Narrow-Band Phenomena,' Plenum Press, New York, 1977.
6 A. Jayaraman, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 587.
7 J. W. McClure, *J. Phys. Chem. Solids*, 1963, **24**, 871.
8 J. E. Rowe, M. Campagna, S. B. Christman, and E. Bucher, *Phys. Rev. Lett.*, 1976, **36**, 148.
9 W. Gudat, M. Campagna, R. Rosei, J. H. Weaver, W. Ekbrhardt, F. Hulliger, and E. Kaldis, *J. Appl. Phys.*, 1981, **52**, 2123.
10 M. Konczykowski, J. Morillo, and J. P. Senateur, *Solid State Commun.*, 1981, **40**, 517.
11 F. Holtzberg and J. Wittig, *Solid State Commun.*, 1981, **40**, 315.
12 R. Keller, G. Guntherodt, W. B. Holzapfel, M. Dietrich, and F. Holtzberg, *Solid State Commun.*, 1979, **29**, 753.
13 A. Jayaraman, A. K. Singh, A. Chatterjee, and S. Usha Devi, *Phys. Rev. B*, 1974, **9**, 2513.
14 K. G. Gschneidner, 'Rare Earth Alloys,' Van-Nostrand-Reinford, Princeton, New Jersey, 1961.
15 J. A. Fries and E. D. Cater, *J. Chem. Phys.*, 1978, **68**, 3978.
16 H. F. Franzen and A. V. Hariharan, *J. Chem. Phys.*, 1979, **70**, 4907.
17 K. A. Gschneidner, *J. Less-Common Met.*, 1969, **17**, 13.
18 D. A. Johnson, *J. Chem. Soc. A*, 1969, 1525.
19 D. A. Johnson, 'Some Thermodynamic Aspects of Inorganic Chemistry,' 2nd edn., Cambridge University Press, 1982, ch. 6.
20 L. R. Morss, *Chem. Rev.*, 1976, **76**, 827.
21 A. F. Kapustinskii, *Q. Rev. Chem. Soc.*, 1956, 283.
22 R. D. Shannon and C. T. Prewitt, *Acta Crystallogr. Sect. B*, 1969, **25**, 925.
23 R. D. Shannon and C. T. Prewitt, *Acta Crystallogr. Sect. B*, 1970, **26**, 1046.
24 T. C. Waddington, *Adv. Inorg. Chem. Radiochem.*, 1959, **1**, 157.
25 K. C. Mills, 'Thermodynamic Data for Inorganic Sulphides, Selenides and Tellurides,' Butterworths, London, 1974.
26 R. E. Skochdopole, M. Griffel, and F. H. Spedding, *J. Chem. Phys.*, 1955, **23**, 2258.
27 J. A. Sommers and E. F. Westrum, *J. Chem. Thermodyn.*, 1977, **9**, 1.
28 A. Dupont, *J. Opt. Soc. Am.*, 1967, **57**, 867.
29 W. T. Carnall, D. M. Gruen, and R. L. McBeth, *J. Phys. Chem.*, 1962, **66**, 2159.
30 J. Sugar and J. Reader, *J. Chem. Phys.*, 1973, **59**, 2083.
31 A. Jayaraman, P. D. Dernier, and L. Longinotti, *High Temperatures High Pressures*, 1975, **7**, 1.
32 W. Nolting, *J. Phys. C*, 1982, **15**, 733.

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