

Correlation between the atomic and bulk chemical potentials of low work
function metals

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Abstract

An attempt is made to identify preferred values for the work functions of the rare earth elements by correlating the atomic chemical potential with the work function of the bulk elements. Trends in the alkali and alkali earth metal are evaluated in the same context. Strong linear correlation between the two quantities is observed within the IA, IIA, and IIIB (Sc, Y, La) groups. Within the lanthanide series the nature of the correlation between the metallic radius and the work function suggests a dependence on the total angular momentum.

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Text

In 1977 H. B. Michaelson published a compilation of the work functions of 44 elements.¹ The data presented for polycrystalline samples is frequently used as a measure of the bulk chemical potential of the metal or as an average over several low index crystallographic faces which may differ by more than 0.6 eV in their work function. No values are given for the elements Pr, Pm, Dy, Ho, Er, Tm, or Yb. Investigations of the work functions of each of these elements except Pm can be found in the literature and are evaluated with the intent of identifying an appropriate "polycrystalline" value. Pm has no stable isotopes nature and no experimental values for the work function of this element appear to exist. The references cited below represent all of the very few known reports for the lanthanide work functions which might be considered as candidates for polycrystalline work functions. A recent review of the work functions of the rare earth elements obtained from crystallographic faces of single crystal samples has been given by Fomenko.²

To identify chemical trends in the low work functions elements the correlation between the bulk work function and the atomic chemical potentials of the elements was tested for the alkali metals (group IA), alkaline earth metals (group IIA) and the group IIIB (Sc, Y, and La) metals which have no *f* electrons. Based on their chemical properties the group IIIB metals are identified as rare earth elements rather than transition metals.³ The atomic chemical potentials, μ_{α} , are derived from measured values of atomic polarizability, α .⁴ In Figure 1 the work functions, ϕ , of these elements are plotted as a function of $\mu_{\alpha}/2$. The close correlation of the values of ϕ and $\mu_{\alpha}/2$

is coincidental. The factor of 2 reduction in the atomic chemical potential accounts in a very crude way for electron-electron repulsion in the solid. Only the overall trends should be considered as significant.

In the figure a straight line fit to the group IIA (diamonds) elements has a slope of approximately 0.91. This line is translated to the group IA (circles) and IIIB (triangles) elements. The three open squares represent values from Michaelson which have been replaced. The new values for Sr (2.64 eV) and Ba (2.3 eV) were specifically determined for polycrystalline thin films of those elements by Gaudart et al.⁵ In the Michaelson compilation an earlier report by Gaudart is cited for Ca. Gaudart's value for Sr is close to that reported by Michaelson while that for Ba represents a substantial correction. The value for La (2.91 eV) is the preferred value discussed later in the text. The lowest experimental value is $\phi(\text{La}) \sim 3.0$ eV obtained from thermionic emission in the temperature range 1200-1500 K. The correlation for the group IA and IIA elements is excellent with only Rb exhibiting a notable deviation of ~ 0.1 eV. In the group IIIB series all elements are within 0.1 eV of the line.

A tabulation of the experimental work function and atomic chemical potential data for the rare earth elements are given in Table I with high temperature values for La and Nd in parentheses. Much of the data is taken from Michaelson. Data for Sr and Ba are measured by photoemission from polycrystalline thin films.⁵ Values for La, Pr, and Nd are from the thermionic emission data of Schumacher and Harris as evaluated by Haas.^{6,7} The value for Pm was estimated in this work. Values for Dy, Ho, Er, and Tm are identified with those associated with a few monolayers of metal deposited on a W(111) surface evaluated by field emission microscopy.⁸ The value for Yb was derived from the angle resolved ultraviolet photoemission

spectroscopy of Yb evaporated on a Ta substrate.⁹ Neither the thickness or structure of the Yb film was specified.

In selecting these sources it was noted that there are several reports of work function data for crystalline surfaces and for thin metallic films deposited on the close packed (110) face of W or Mo.^{10,11} In the latter cases the variation in work function $\Delta\phi$ is measured for a few monolayers of metal deposition. Typically the variation in $\Delta\phi$ decreases with the deposition of electropositive elements, demonstrates a minimum, a maximum and then slowly decreases again. The maximum is attributed a smooth single monolayer coverage. A constant saturated value of $\Delta\phi$ is often not achieved for coverages investigated. In this work, values of ϕ cited for Dy, Ho, Er, and Tm were obtained from $\Delta\phi$ measurements of these metals deposited on W(111). In those measurements $\Delta\phi$ first went through a lower minimum than on W(110) and subsequently came up to a constant saturated maximum. The immediate saturation of $\Delta\phi$ at the maximum and the resulting magnitude of the rare earth work functions suggest that this is a reasonable valuation of the desired quantity. Additionally, it may be noted that quasi saturated values of $\Delta\phi$ for low work function elements on W or Mo (110) typically imply work function values 0.3-0.5 eV greater than the preferred polycrystalline values. This is exemplified in a study of Sr and La deposited on both W and Mo (110) and is in agreement with the difference seen between the final $\Delta\phi$ observed for the heavy lanthanides deposited on W(110) as compared to W(111).¹² Similar results have been obtained for the deposition of Sm, Yb, and Er on Si(111) or Si(100).¹³⁻¹⁵

The work functions of the lanthanide elements and Ba are shown as a function of atomic number in Figure 2 as solid circles. The open circles are the theoretical work functions of the elements calculated for the most close

packed surface of the crystal structure appropriate to each element.¹⁶ The lowest work function elements Ba [Xe,6s²], Eu [Xe,4f⁷,5d⁰,6s²], and Yb [Xe,4f¹⁴,5d⁰,6s²] are all divalent. The remaining lanthanide elements are trivalent with the exception of Ce which has a valence in excess of three and is predicted to have a work function greater than the general trend for the purely trivalent metals.¹⁷ The experimental values for the trivalent lanthanide work functions are bounded above by the theoretical values but do not show a monotone increase. The straight line fit to Ba, Eu, and Yb has been shifted upward to suggest the existence of four subgroups within the lanthanide series: (Ba, Eu, Yb), (Pr, Sm, Dy, Tm), (Ce, Nd, Pm, Tb, Ho, Er), and (La, Gd, Lu). These subgroup may be classified according to the total angular momentum, L , of the elements in each group; for (La, Gd, Lu) $L = 0$, for (Ce, Eu, Tb, Yb) $L = 3$, for (Pr, Sm, Dy, Tm) $L = 5$, and for (Nd, Pm, Ho, Er) $L = 6$. It has been recognized that many properties of the lanthanides for distinguished groups according to the L values of the elements.¹⁷ For the trivalent atoms there are three groups corresponding to $L = 0$, $L = 3$ or 6 , and $L = 5$. Eu and Yb are exceptional in being divalent rather than trivalent.

To emphasize the systematic variation the heavy lanthanides are connected by a solid line. This pattern is translated (dashed line) so that endpoint of the pattern at Lu coincides with Gd. The experimental values for La and Nd were determined by thermionic emission at high temperatures (above 1150 K) and a decrease of less than 0.2 eV to put them exactly on the dashed line is very reasonable. The values predicted by the dashed line will be adopted as the preferred room temperature work functions for these elements. In support of this assignment the thermionic emission data for Pr, determined in the same work as for La and Nd, was sufficiently precise as to allow the extraction of the temperature dependence of the work function.

The plotted value is the extrapolated room temperature value. The value for Ce, cited by Michaelson remains to only point not falling on the dashed curve. This is attributed to its valency being greater than three in agreement with theory.

In Figure 3 the work functions, ϕ (solid circles), are compared with the atomic chemical potentials, $\mu_a/2$ (open circles). The values for La and Nd are the room temperature values predicted by the dashed line in Figure 2. In the absence of experimental data the value for Pm was also taken from the dashed line prediction of Figure 2. With the exceptions of Ce and Pr the differentiation of the $L = 0$ elements from the $L > 0$ elements may be noted. The agreement between ϕ and $\mu_a/2$ for Ce may be fortuitous because the high experimental value for ϕ is justified on the basis of valency effects which are not apparent for Yb and has the same fcc crystal structure. Additionally, the adjacent value for Pr is anomalously high. The low work functions of Eu, and Yb are clearly not captured by trends in $\mu_a/2$. In the solid the stability of the filled or half filled f shell prevents the d electron from participating in bonding and the solids are divalent. In the atom the small energy difference between the d and f energy levels allows the d electron to resonate between the two levels which contributes to the relatively large atomic chemical potential as derived from the atomic polarizability.

To unify the picture the preferred work functions of all of the rare earth elements are plotted as a function of the metallic radius (coordination number, CN = 12). In this plot the $L = 0$ trivalent and $L = 3$ divalent atoms fall on a single straight line. All of these elements have either filled or exactly half filled f shells and have large metallic radii as compared to lanthanide metals with partially filled f shells.¹⁷ Ce has an anomalously small radius which is largely offset in the plot by its large work function. The remaining

"unique" element is Sm with the rhombohedral crystal structure. Expressed in a hexagonal basis it has a mixed hexagonal close packed (hcp)/face centered cubic (fcc) sequencing in the (111) direction corresponding to a 33% cubic structure. In no case does the crystal structure appear to have a first order impact on the variation of the work function.

In summary, preferred values of the "polycrystalline" work functions of barium and the rare earth elements have been tabulated. The choice of preferred values is determined by comparison with experimental atomic chemical potentials, metallic radius and with theory. A high degree of internal consistency is found and a previously unexpected dependence upon the total angular momentum of the lanthanide series is demonstrated. This implies that crystal field effects must be important in determining the work function. Such effects would not be captured either by the atomic chemical potential or the theoretical estimation of ϕ which used only an *spd* basis in a tight binding - linear muffin tin orbital model within the local density approximation. The specific rationale for the distinct behavior of the $L = 5$ elements is not known. The deviation in ϕ from the $L = 3, 6$ metals is about 0.2 eV which is the combined uncertainty limit for the precision of many of the experimental values. However, the values of the $L = 5$ elements are taken from three different sources and determined by three separate techniques. Against this fact is the lack of a supporting theory and the stark paucity of data. Further experimental work is required to definitively settle the issue.

Acknowledgements

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element	ϕ (eV)	$\mu_{\alpha}/2$ (eV)	structure	source
Ba	2.3	2.660	bcc	reference 5
La	2.91 (3.0)	2.885	dhcp	reference 7
Ce	2.9	2.930	fcc	reference 1
Pr	2.62	2.980	dhcp	reference 7
Nd	2.93 (2.95)	2.875	dhcp	reference 7
Pm	2.89	2.915	dhcp	estimated
Sm	2.7	2.960	rhomb	reference 1
Eu	2.5	3.000	bcc	reference 1
Gd	3.1	3.165	hcp	reference 1
Tb	3.0	3.080	hcp	reference 1
Dy	2.78	3.125	hcp	reference 8
Ho	3.03	3.160	hcp	reference 8
Er	3.09	3.205	hcp	reference 8
Tm	2.94	3.245	hcp	reference 8
Yb	2.7	3.290	fcc	reference 9
Lu	3.3	3.240	hcp	reference 1
Sc	3.5	1.6406	hcp	reference 1
Y	3.1	1.8012	hcp	reference 1

Table I Given are the preferred room temperature experimental values of the work functions (ϕ) of barium and the rare earth elements. Values of ϕ given in parentheses are high temperature values. Also given are the scaled atomic chemical potentials ($\mu_{\alpha}/2$) and the sources for the experimental data. Crystal structures: hcp - hexagonal close packed, dhcp - double c hcp, bcc - body centered cubic, fcc - face centered cubic, rhomb - rhombohedral.

Figure Captions

Figure 1) Work functions of the alkali (IA: solid circles), alkali earth (IIA: solid diamonds), and rare earth (IIIB: solid triangles) metals plotted as a function of the scaled atomic chemical potential $\mu_a/2$. Values of ϕ are taken from the compilation of Michaelson except for Sr, Ba, and La. The open squares represent values cited by Michaelson which have been revised as discussed in the text.

Figure 2) Work functions of Ba and the lanthanide elements are shown a function of their atomic number. Solid circles are experimental values. Open circles are theoretical values. The straight solid lines group the trivalent elements according to total angular momentum, L. The divalent elements form a distinct group.

Figure 3) Experimental work functions (solid circles) and the scaled atomic chemical potential, $\mu_a/2$ (open circles), are plotted as a function of atomic number. A strong correlation for most of the trivalent elements is observed including the excess valent element Ce. The atomic chemical potential does not capture the behavior of the divalent atoms (Ba, Eu, Yb) or the atoms with $L = 5$ (Pr, Sm, Dy, Tm).

Figure 4) Experimental work functions plotted as a function of the metallic radius (CN = 12). Elements with a filled or exactly half filled f shell form a well defined group. The $L = 5$ and $L = 3, 6$ lanthanides with partially filled f shells form separate groups with a slope which is distinct from that first group.

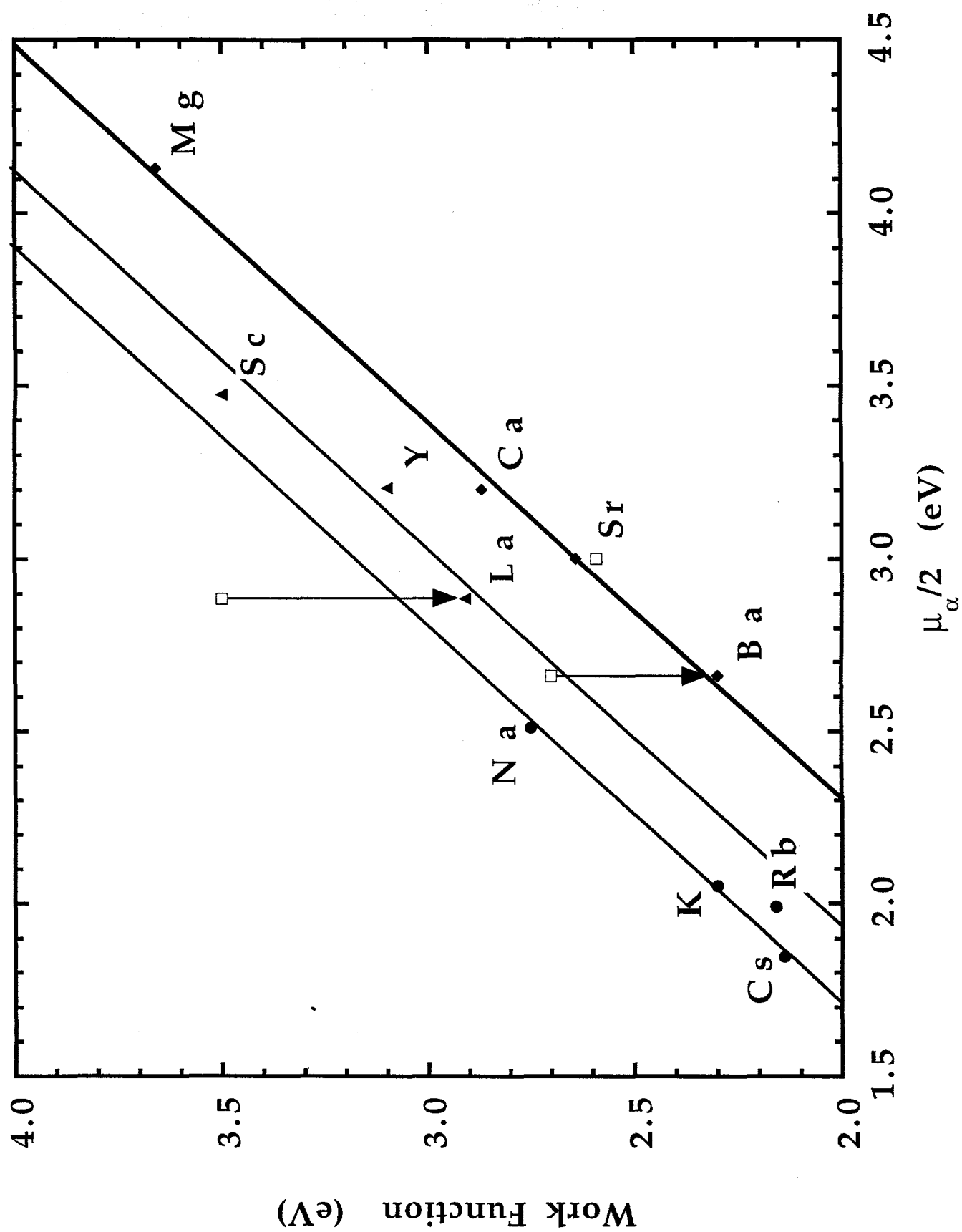


Figure 1

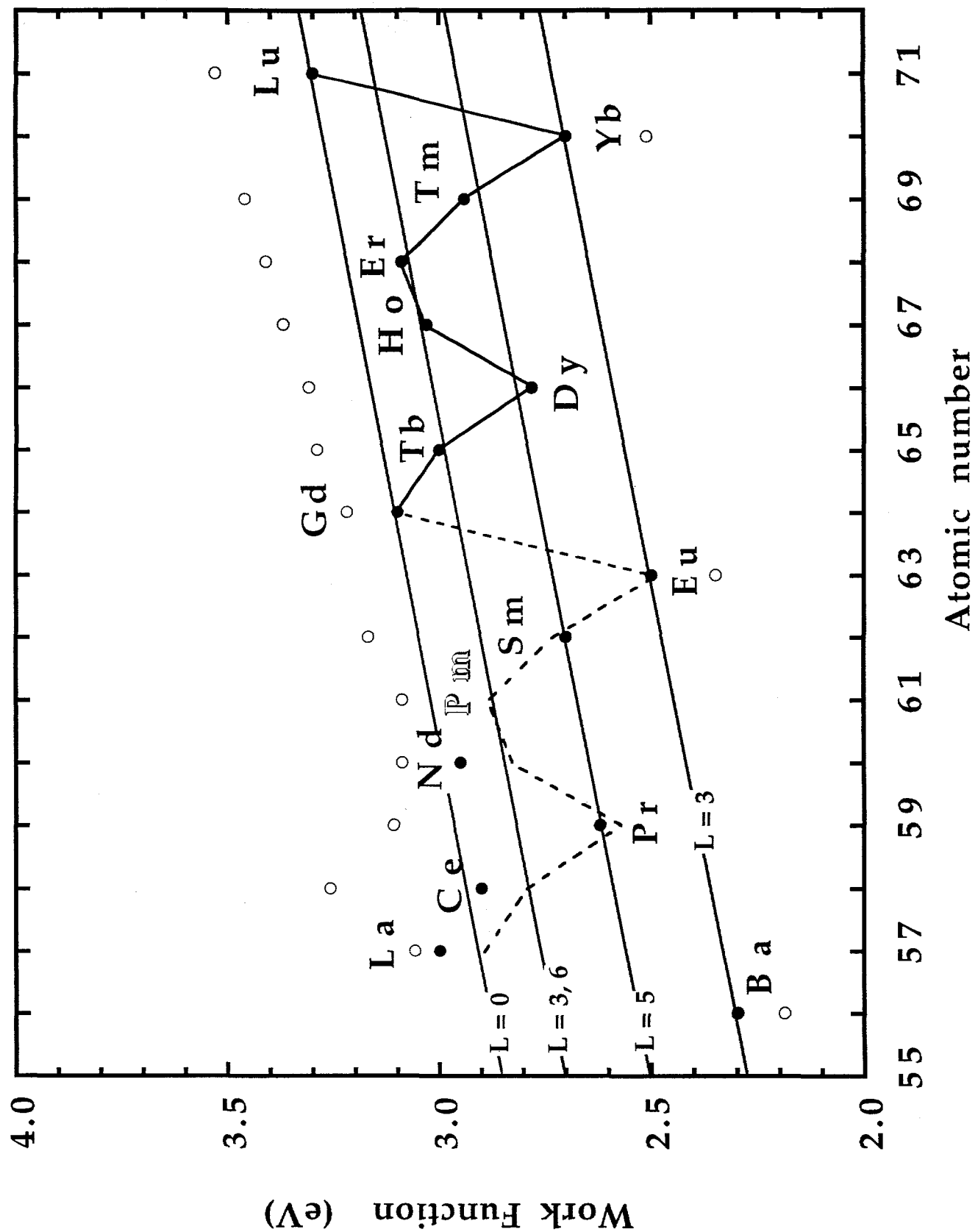


Figure 2

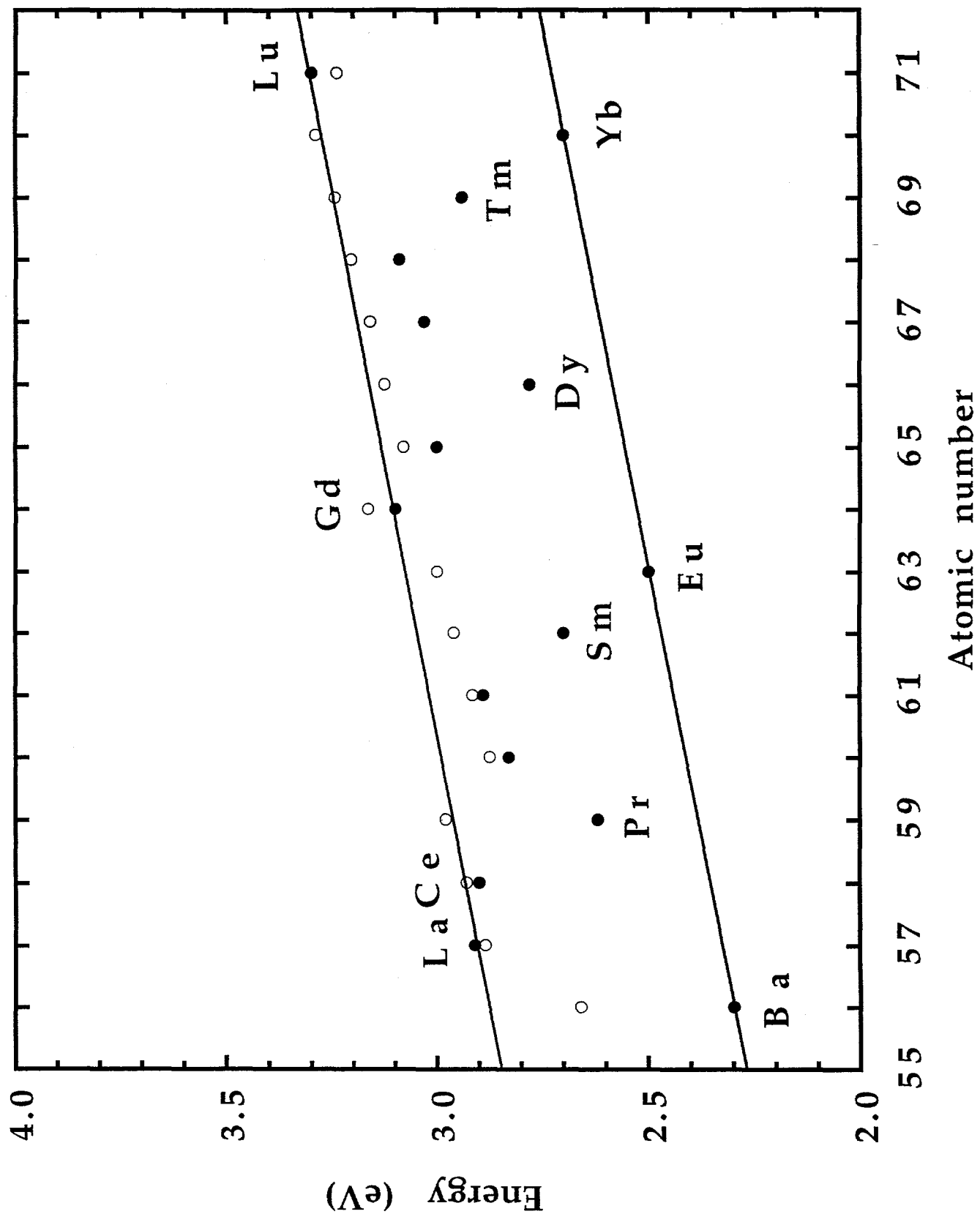


Figure 3

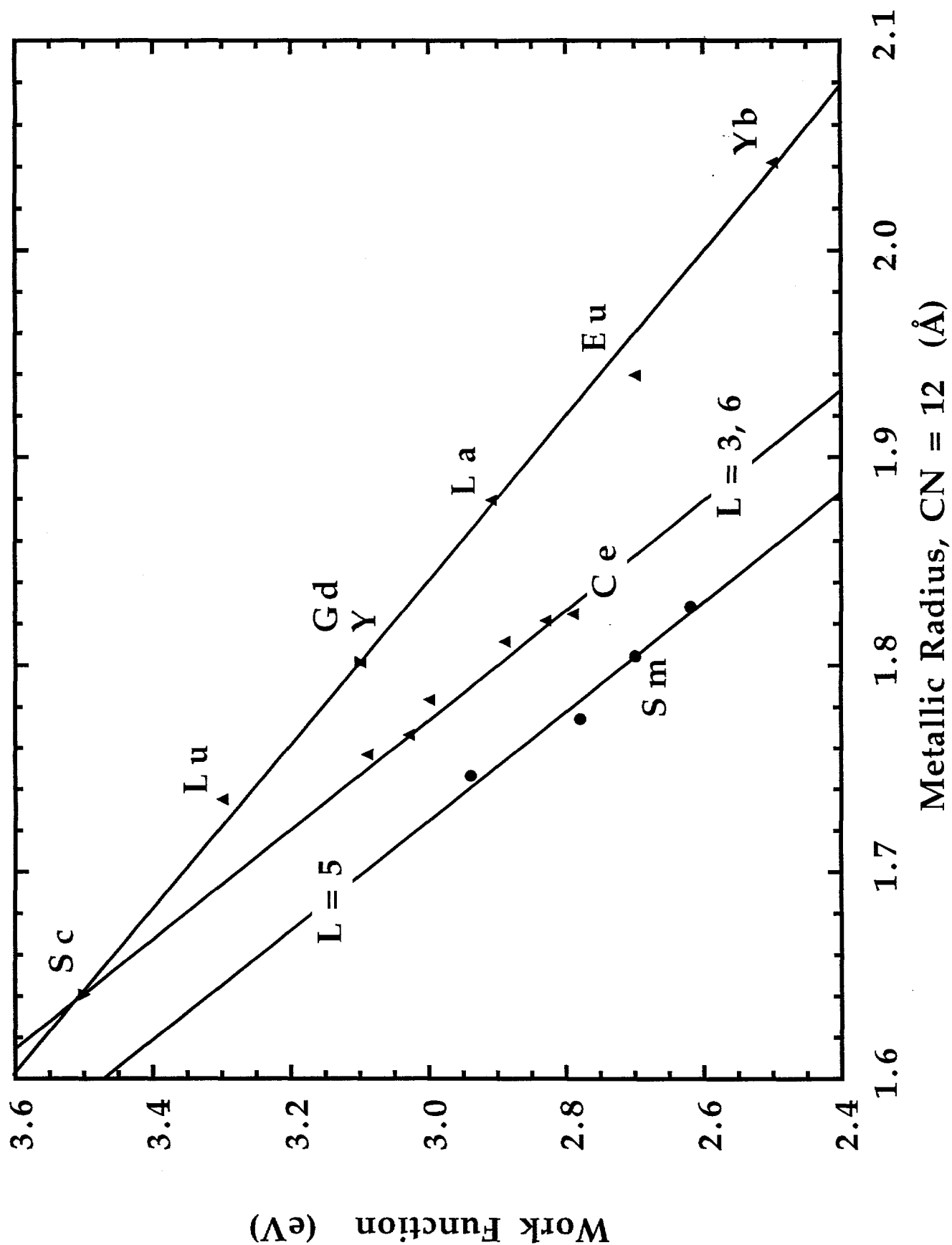


Figure 4