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Extension of the "Inclined W" Concept to the d-Transition Elements and Ions

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The Inclined W systematization, i.e., *the linearization of the properties of the atoms and ions with respect to their free ion L (orbital angular quantum number) values, has been extended to include the atoms and ions in the d-series. Examples are taken from the spectroscopic parameters, B, C, ζ, the lattice and hydration energies of the 3d ions and the ionization potentials of the 3d, 4d and 5d elements to illustrate the linearization systematics. The Inclined W parameters for these systems have been calculated.*

Introduction

It has been recently shown that various properties of the f-ions (lanthanides and actinides) could be systematized in terms of the orbital angular quantum numbers (L) of the free ions [1, 2]. Usually, four straight lines within the four tetrads, f^0–f^3, f^4–f^6, f^6–f^9 and f^{10}–f^{14}, are obtained for the plots of the properties vs. the values of the orbital angular quantum numbers (L) of the originating ions. A quantitative application of the Inclined W systematics has been

$$P_i = w_i L + k_i \tag{1}$$

demonstrated by Sinha [3] in calculating the sixth through seventeenth ionization potentials for the whole lanthanide series.

If this linearization hypothesis is of general validity, it could be extended to the d-transition elements and their ions in different oxidation states. While the L-values of the f-series [S(0), F(3), H(5), I(6)] oscillates as

$$L = 6 - 0.5(\Delta L) - 0.5(\Delta L)^2 \tag{2}$$

those of the d-transition ions [S(0), D(2), F(3)] follow

$$L = 3 - 0.5(\Delta L) - 0.5(\Delta L)^2 \tag{3}$$

relation, and repeat themselves in the same fashion as in the f-ion case. It is of no use to consider the p-elements, as one is always able to draw a straight line through two points for the plots of the properties of the p-ions *vs.* their L quantum numbers, *e.g.,* S(0), and P(1). Here we wish to present several examples showing that the Inclined W systematization could be equally useful for the d-elements.

Results and Discussion

The nonlinear variation of the properties of the d-transition ions with their atomic numbers(Z) is well known. However, the effective nuclear charge (Z*) [4] seen by the d-electrons does not vary linearly with their atomic numbers (Z) within the series (Fig. 1). But plots based on Z* as a parameter for the

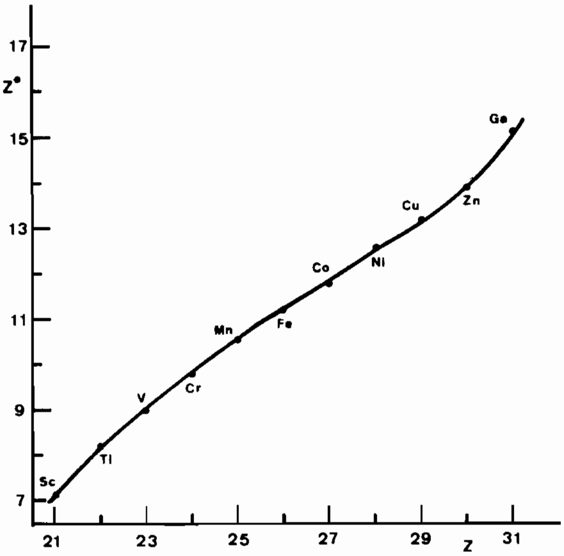

Figure 1. Variation of the effective nuclear charge (Z*) with the atomic number (Z) of the 3d elements.

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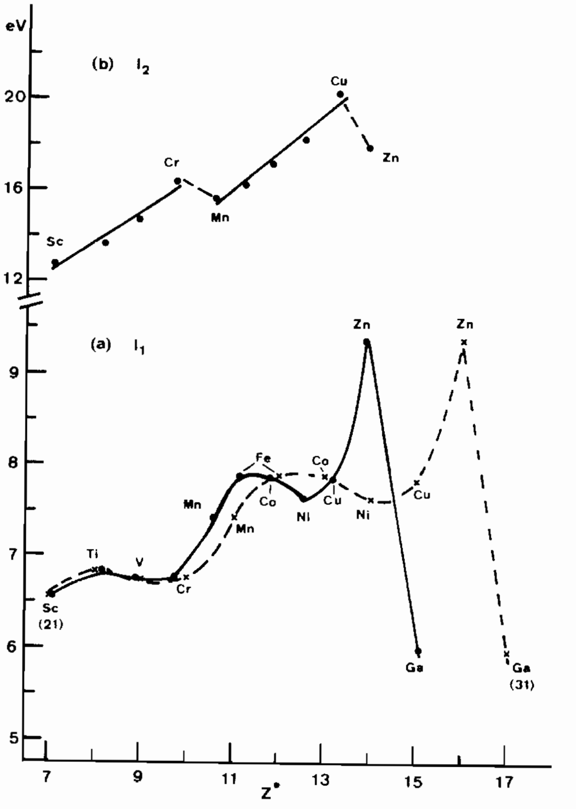


Figure 2. (a) Variation of the first ionization potentials (I_1) with Z and Z* for the 3d transition elements. (b) Variation of the second ionization potentials (I_2) with Z* for the 3d ions.

abscissa are not common. We have compared the first and the second ionization potentials (I_1, I_2) [5] for the 3d series by plotting these values against Z and Z* in Fig. 2. Although the Z *vs.* Z* plot for the 3d elements produces a sigmoid curve (Fig. 1), the I_1 *vs.* Z* plot resembles in profile that of the I_1 *vs.* Z curve (Fig. 2). The I_2 data [5] for Sc through Cr, and from Mn through Cu could, however, be expressed in terms of two least squares straight lines in Z*:

for (Sc–Cr) $I_2 = 1.37Z^* + 2.76$

for (Mn–Cu) $I_2 = 1.69Z^* - 2.57$

The Ionization Potentials

In contrast to these plots (Fig. 2), if one chooses to express the ionization potentials I_2, I_3, I_4 for the 3d elements in terms of the values of the L quantum numbers of the respective free ions, the linear variation of the ionization potentials within the tetrads becomes at once apparent (Fig. 3). In the case of the second ionization potentials (I_2), where a complete plot could be made, the general profile of the plot resembles that of the inclined W, as in the case of the f-ions.

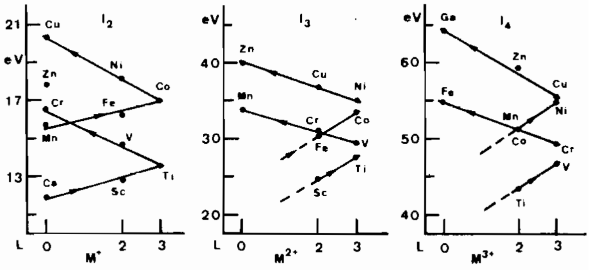


Figure 3. Variation of the ionization potentials (I_2, I_3, I_4) of the 3d ions with their L values showing excellent "Inclined W" plots.

Notice that the ionization process $M^+ \rightarrow M^{2+}$ for the ions Ca, Sc and Ti involves removal of a 4s electron from cores consisting of d^0, d^1, and d^2 respectively. In the case of I_3 and I_4 only the second and the fourth tetrad could be drawn within the confidence limit. We are left with two points (Fig. 3) in the first tetrad, because of the absence of a suitable d^0 ion, and in the third tetrad because of the break in the middle of the series. This is the drawback in the case of the d-ions, where a maximum of only three points are available for correlation. For the f-ions, even when the break occurs in or near the half-filled shell, we are still left with three points [2]. The following w_i and k_i parameters (eq. 1) satisfy the least squares straight lines for I_2, I_3 and I_4 of the 3d series.

The 3d-ions

For I_2: First tetrad(Ca–Ti) $w_1 = 0.555$, $k_1 = 11.83$; Second tetrad (Ti–Cr) $w_2 = -0.966$, $k_2 = 16.52$; Third tetrad(Mn–Co) $w_3 = 0.444$, $k_3 = 15.55$; Fourth tetrad(Co-Cu) $w_4 = -1.075$, $k_4 = 20.30$.

For I_3: Second tetrad (V–Mn) $w_2 = -1.438$, $k_2 = 33.71$; Fourth tetrad (Ni–Zn) $w_4 = -1.507$, $k_4 = 39.75$.

For I_4: Second tetrad (Cr–Fe) $w_2 = -1.886$, $k_2 = 54.84$; Fourth tetrad (Cu–Ga) $w_4 = -2.843$, $k_4 = 64.27$.

We have also investigated the fifth ionization potentials (I_5) for the 3d ions. Here, most of the data [5] are estimated ones and are less complete. But still the second tetrad (Mn–Co) is satisfied with $w_2 = -2.35$ and $k_2 = 79.55$. In the fourth tetrad (Zn, Ga, Ge) we have no values for $Ga^{4+}(d^9) \rightarrow Ga^{5+}(d^8)$. This limits us to draw a least squares straight line. But looking at the trend, a value for I_5 of Ga could be predicted to be about 86.2 eV.

The analysis of the limited amount of the available data [5] for the 4d and 5d series are presented in Fig. 4 and Fig. 5 respectively. Here also the linear variations with L of the free ions are apparent.

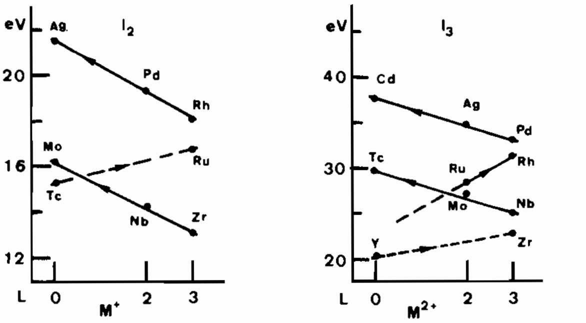


Figure 4. Variation of the ionization potentials I_2 and I_3 of the 4d ions with their L values.

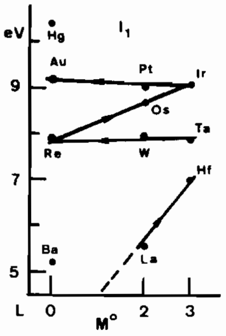


Figure 5. Plot of I_1 of the 5d elements against the atomic L values.

The 4d-ions

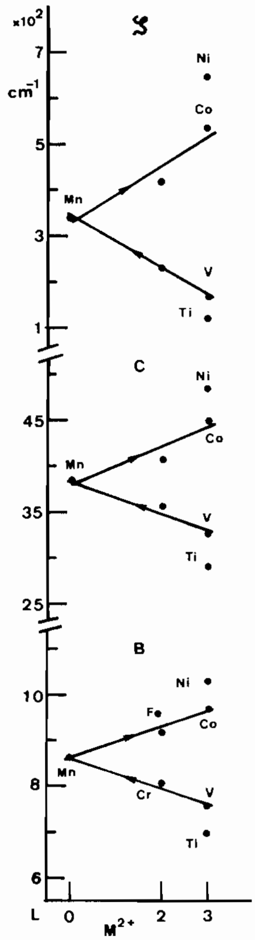
For I_2: First tetrad (Zr–Mo) $w_1 = -0.994$, $k_1 = 16.189$; Third tetrad (Rh–Ag) $w_3 = -1.121$, $k_3 = 21.54$.

For I_3: Second tetrad (Nb–Tc) $w_2 = -1.456$, $k_2 = 29.67$; Fourth tetrad (Pd–Cd) $w_4 = -1.489$, $k_4 = 37.56$.

The first ionization potentials for the 5d elements show good correlation with L of the free atoms within the second through fourth tetrads (Fig. 5). The scattering within the first tetrad is probably due to the change of the electronic configurations of the monovalent ions: Ba($6s^2$, S) → Ba^+(6s, S), La($5d6s^2$, D) → La^+($5d^2$, F), and Hf($5d^26s^2$, F) → Hf^+ ($5d6s^2$, D). The Re and Ir points seemed to be common points for the second/third and third/fourth tetrads. The least squares treatment generated these two points within reasonable accuracy, when either of the tetrads is taken into consideration. The following values of the Inclined W parameters are obtained.

The 5d-elements

For I_1: Second tetrad (Ta–Re) $w_1 = 0.01$, $k_1 = 7.9$; Third tetrad (Re–Ir) $w_3 = 0.0407$, $k_3 = 7.88$; Fourth tetrad (Ir–Au) $w_4 = -0.0518$, $k_4 = 9.195$. However, if one considers the scattering and calculates the best least squares straight line through the Ba, La, and Hf points with $w_1 = 0.54$ and $k_1 = 5.03$, one is not too far off the experimental values, in the worst case the calculated value for La being 0.53 eV higher and that for Hf being only 0.35 eV lower.



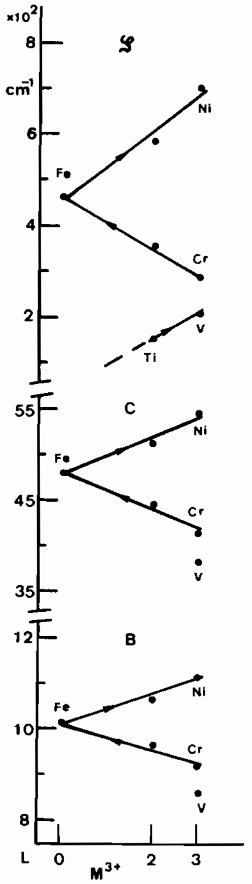


Figure 6. Plots of the spectroscopic B, C, and ζ parameters of the free divalent 3d ions against their L values.

Figure 7. Plots of the spectroscopic B, C, and ζ parameters of the free trivalent 3d ions against their L values.

The Racah Parameters and the Spin–Orbit Coupling Parameter

Other spectroscopic parameters like the Racah interelectronic repulsion parameters (B, C) and the one electron spin–orbit coupling parameter ζ [6] for the divalent and the trivalent 3d ions were considered and when these parameters are plotted against the L values of the originating free ions, good linear relationships are obtained (Fig. 6 and Fig. 7).

Divalent 3d-ions

B(M^{2+}): (V–Mn) tetrad, $w_1 = -33.57$, $k_1 = 864.29$; (Mn–Co) tetrad, $w_2 = 35.79$, $k_2 = 856.36$.

C(M^{2+}): (V–Mn) tetrad, $w_1 = -189.79$, $k_1 = 3873.6$; (Mn–Co) tetrad, $w_2 = 198.43$, $k_2 = 3798$.

$\zeta(M^{2+})$: (V–Mn) tetrad, $w_1 = -59.79$, $k_1 = 347.64$; (Mn–Co) tetrad, $w_2 = 57.64$, $k_2 = 333.93$.

Trivalent 3d-ions

$B(M^{3+})$: (Cr–Fe) tetrad, $w_1 = -31.29$, $k_1 = 1018.14$; (Fe–Ni) tetrad, $w_2 = 32.14$, $k_2 = 1011$.

$C(M^{3+})$: (Cr–Fe) tetrad, $w_1 = -215.6$, $k_1 = 4820.3$; (Fe–Ni) tetrad, $w_2 = 208.6$, $k_2 = 4775.7$.

$\zeta(M^{3+})$: (Cr–Fe) tetrad, $w_1 = -61.14$, $k_1 = 463.6$; (Fe–Ni) tetrad, $w_2 = 78.6$, $k_2 = 450.7$.

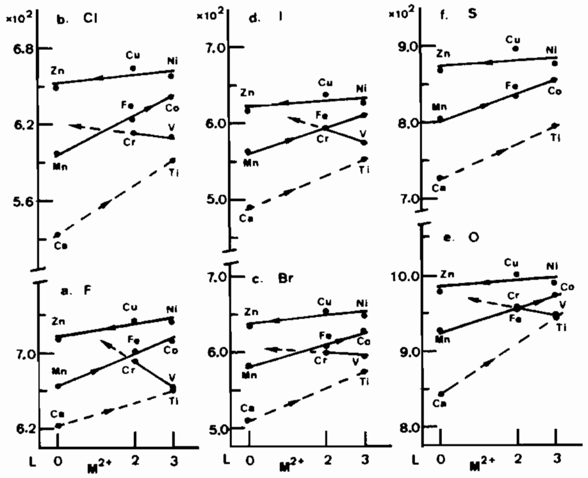


Figure 8. Linear variation of the lattice energies (kcal/mol) of the halides and chalconides of the divalent 3d ions with their L values.

The Lattice Energies

George and McClure [7] have calculated the lattice energies for various halides and chalconides of the divalent and trivalent 3d-ions. It was of interest to investigate the variation of these lattice energies as a function of the L values of the free divalent and trivalent 3d ions. The results for the 3d series are shown in Fig. 8 and Fig. 9. It should be remarked here that many properties, other than the spectroscopic ones, for the lanthanides showed [2] linear L dependence. Beside the unavoidable limitation in the first tetrad (Ca, Sc, Ti), where no divalent Sc compound could be obtained, and in the second tetrad where only two points are available, the third (Mn, Fe, Co) and the fourth (Ni, Cu, Zn) tetrads present very good linear correlation for the divalent ions.

Divalent fluorides

(Mn–Co) tetrad, $w_3 = 16.12$, $k_3 = 665.36$; (Ni–Zn) tetrad, $w_4 = 6.74$, $k_4 = 715.23$.

Divalent chlorides

(Mn–Co) tetrad, $w_3 = 14.59$, $k_3 = 597.16$; (Ni–Zn) tetrad, $w_4 = 4.21$, $k_4 = 650.02$.

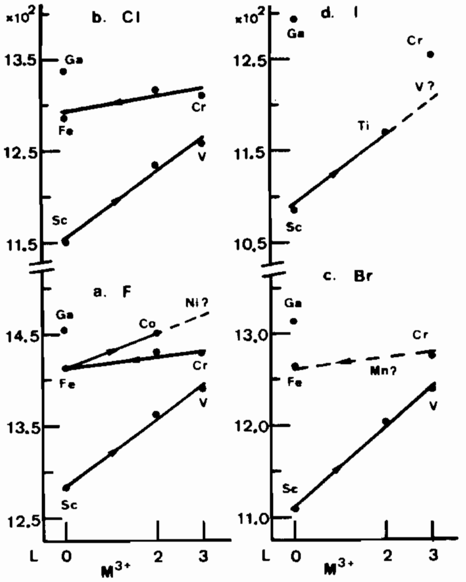


Figure 9. Linear variation of the lattice energies (kcal/mol) of the halides of the trivalent 3d ions with their L values.

Divalent bromides

(Mn–Co) tetrad, $w_3 = 13.55$, $k_3 = 581.55$; (Ni–Zn) tetrad, $w_4 = 5.24$, $k_4 = 635.33$.

Divalent iodides

(Mn–Co) tetrad, $w_3 = 14.76$, $k_3 = 563.49$; (Ni–Zn) tetrad, $w_4 = 3.96$, $k_4 = 620.1$.

Divalent oxides

(Mn–Co) tetrad, $w_3 = 14.86$, $k_3 = 924.37$; (Ni–Zn) tetrad, $w_4 = 4.68$, $k_4 = 981.94$.

Divalent sulphides

(Mn–Co) tetrad, $w_3 = 16.79$, $k_3 = 803.36$; (Ni–Zn) tetrad, $w_4 = 5.14$, $k_4 = 871.23$.

In the case of the trivalent 3d halides, the following Inclined W parameters (eq. 1) are found to satisfy the least squares lines in Fig. 9.

Trivalent fluorides

(Sc–V) tetrad, $w_1 = 36.6$, $k_1 = 1283.4$; (Cr–Fe) tetrad, $w_2 = 5.93$, $k_2 = 1411.69$.

Trivalent chlorides

(Sc–V) tetrad, $w_1 = 36.73$, $k_1 = 1153.39$; (Cr–Fe) tetrad, $w_2 = 9.11$, $k_2 = 1289.22$.

Trivalent bromides

(Sc–V) tetrad, $w_1 = 40.25$, $k_1 = 1119.75$.

These plots (Figs. 8, 9) may be compared to those made by George and McClure (Figs. 2, 3 and 5 of ref. [7]) by plotting the lattice energies against the atomic numbers of the 3d elements. These authors described the variation of the lattice energies with Z, as "a steady increase in lattice energy with two humps superimposed on it" [7]. They further tried to draw a straight line between points for Ca^{2+} ($3p^6$, $^1S_0$, $L = 0$), and Zn^{2+}($3d^{10}$, $^1S_0$, $L = 0$) and found that it passed below the point for Mn^{2+}($3d^5$, $^6S_{5/2}$, $L = 0$). The common feature of these three points is that they all have nondegenerate ground states (S, $L = 0$) and no crystal field stabilization could be expected for these ions. The deviations of other ions from the straight lines joining d^0 and d^5, and d^5 and d^{10} are assumed to be due to the contribution of the crystal field to the lattice energies [7].

The Hydration Energies

Similar approach was also made for the hydration energies [7] for the divalent and the trivalent 3d ions, and the irregularities were attributed to the crystal field effect. However, when the data for the hydration energies were plotted against the L values of the divalent and the trivalent 3d ions, an extremely good linear relationship was obtained (Fig. 10).

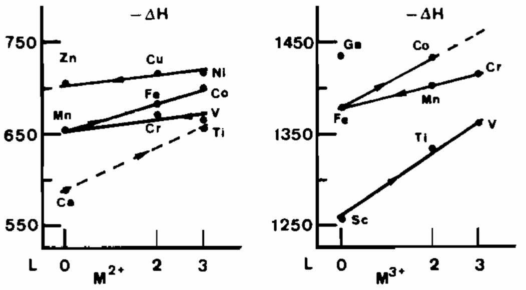


Figure 10. Variation of the hydration energies (kcal/mol) of the di-, and the tri-valent 3d ions with the L values of the respective ions.

Hydration energies: divalent 3d-ions

Second tetrad (V–Mn), $w_2 = 3.86$, $k_2 = 655.57$; Third tetrad (Mn–Co), $w_3 = 14.14$, $k_3 = 653.4$; Fourth tetrad (Ni–Zn), $w_4 = 5.39$, $k_4 = 702.36$.

In this plot (Fig. 10) Mn(d^5) behaves as a common point for the second and the third tetrad, and the calculated hydration energy for Mn is reproduced within 0.2% of the reported value [7].

Less complete data for the trivalent 3d ions also exhibited good linear L dependence (Fig. 10).

Hydration energies: trivalent 3d-ions

First tetrad (Sc–V), $w_1 = 36.0$, $k_1 = 1256$; Second tetrad (Cr–Fe), $w_2 = 12.0$, $k_2 = 1378$.

It has been recently argued [3] that the success of the Inclined W theory lies in the fact that the complexes preserve the high spin character in the case of the f-ions, with ligands perturbing the f-wavefunctions of the lanthanides nominally in the complexes. In the case of the d-ions both high and low spin complexes of the 3d-ions are obtained. We looked for data for both high and low spin complexes of the 3d-ions, where such character prevailed through the series. Recently, Shannon and Prewitt [8] reported the effective ionic radii for both high spin and low spin 3d ions, after considering a wide variety of high and low spin complexes of the divalent and the trivalent 3d ions. These effective ionic radii for coordination number six are plotted against the free ion L values of the divalent and trivalent 3d ions, and the general validity of the Inclined W concept is verified (Fig. 11).

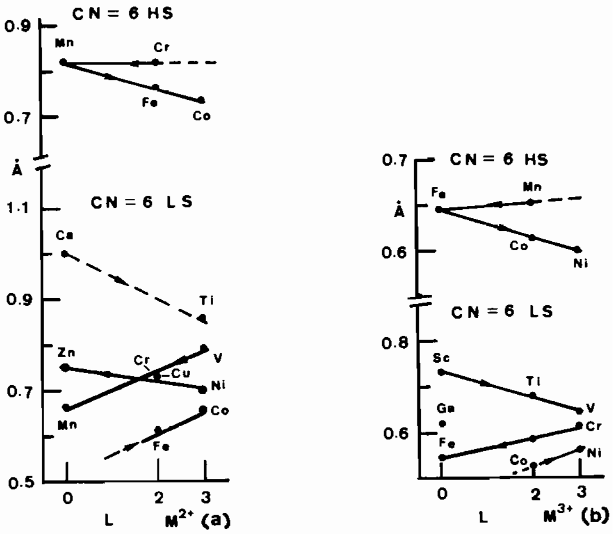


Figure 11. "Inclined W" plots of the effective ionic radii of the (a) divalent and (b) trivalent 3d ions for both high spin (HS) and low spin (LS) cases with CN = 6.

It would be difficult to find organic ligands which would produce either high spin or low spin complexes through the whole series. As the spin character often changes in the complexes within the d-series, it would be rather unjustified to plot the stability constants against the L values of the free d-ions and expect linear correlation within the tetrads.

The properties (P_i) of the d and f ions are complex function of q, the number of electrons in the partly filled shell

$$P_i = F(q) \tag{4}$$

F(q) could be approximated to a polynomial of nth degree.

We illustrate this by taking the fourth ionization potential (I_4) of the lanthanides as an example. The plot of I_4 values [3] for the first half of the lanthanide series, *i.e.*, from Ce to Gd, results in a sigmoid curve (Fig. 12a), and the quadratic expressions for the first two tetrads in terms of q are:

First tetrad (Ce–Nd):

$$I_4 = -0.395q^2 + 3.405q + 33.75 \tag{5}$$

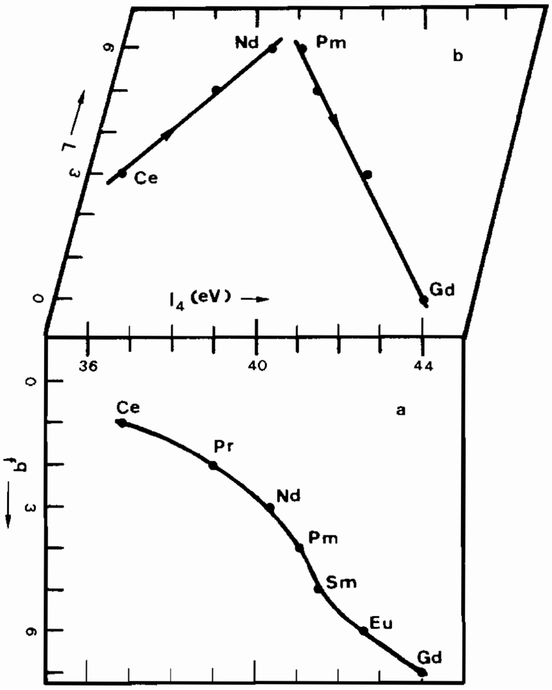


Figure 12. A two way classification of the fourth ionization potentials (I_4) for the first half of the lanthanide series (Ce–Gd): (a) nonlinear variation with f^q (b) linear variation with L.

Second tetrad (Pm–Gd):

$$I_4 = 0.27q^2 - 2.15q + 45.37 \qquad (6)$$

In comparison to Fig. 12a, when the I_4 values are plotted against the free ion L values of the lanthanides in question, two distinct tetrads are obtained (Fig. 12b) having I_4 varying linearly with L. Using the Inclined W parameters (eq. 1) for these tetrads from ref. 9 we have

First tetrad (Ce–Nd):

$$I_4 = 1.202L + 33.11 \qquad (7)$$

Second tetrad (Pm–Gd):

$$I_4 = -0.504L + 44.04 \qquad (8)$$

Equating eq. (5) and eq. (7), and eq. (6) and eq. (8) it is easily shown that the ionization potentials I_4 (*i.e.*, a property of the lanthanides) while varying nonlinearly with q, present a linear variation with L. In fact, the ground state L values of the d and f ions could be expressed in terms of the number of electrons (q) in the partly filled shell by the following quadratic equations:

For d-ions:

with $(0 \leqslant q \leqslant 5)$

$$L = -0.5q^2 + 2.5q = -0.5q(q - 5) \qquad (9)$$

with $(6 \leqslant q \leqslant 10)$

$$L = -0.5q^2 + 7.5q - 25 = -0.5(q - 5)(q - 10) \qquad (10)$$

For f-ions:

with $(0 \leqslant q \leqslant 7)$

$$L = -0.5q^2 + 3.5q = -0.5q(q-7) \qquad (11)$$

with $(8 \leqslant q \leqslant 14)$

$$L = -0.5q^2 + 10.5q - 49 = -0.5(q - 7)(q - 14) \qquad (12)$$

References

1 S. P. Sinha, *Helv. Chim. Acta, 58,* 1978 (1975).
2 S. P. Sinha, *Struct. Bonding, 30,* 1 (1976).
3 S. P. Sinha, *Inorg. Chim. Acta, 27,* 253 (1978).
4 E. Clementi and D. L. Raimondi, *J. Chem. Phys., 38,* 2686 (1963).
5 C. E. Moore, "Ionization Potentials and Ionization Limits Derived from the Analyses of Optical Spectra", Natl. Bur. Std. (U.S.), Circ. NSRDS-NBS 34, Sept. 1970, and references therein.
6 D. S. Sutton, "Electronic Spectra of Transition Metal Complexes", McGraw–Hill, London (1968), p. 60.
7 P. George and D. S. McClure, *Prog. Inorg.Chem., 1,* 381 (1959).
8 R. D. Shannon and C. T. Prewitt, *Acta Cryst., B25,* 925 (1969).
9 S. P. Sinha, *Inorg. Chim. Acta, 22,* L5 (1977).