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SOME THEORETICAL ESTIMATES OF THE
PHYSICAL PROPERTIES OF THE RARE EARTH METALS

by

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MASTER

Abstract:

Recent determinations of the non-relativistic Hartree atomic wave functions¹ have permitted us to estimate which electronic configuration of the free lanthanide atoms is more stable and to make theoretical estimates of physical quantities such as the spin-orbital splitting parameter, Slater F^2 integral, diamagnetic susceptibility, atomic scattering factor and L emission spectra. Calculations of the equilibrium Wigner-Seitz radius ρ and the compressibilities χ were recalculated by the Fröhlich-Raimes method. This method has been extended to obtain the deviations from Vegard's law for a number of cerium based alloys.

Hartree Calculations:

Until quite recently the self-consistent field (SCF) method Hartree² employed for obtaining atomic wave functions ψ_{nl} and eigenvalues E_{nl} has been applied to only a few scattered elements with atomic numbers Z larger than 42. Mrs. Ridley³ published in 1960 calculations for Pr^{+3} and Tm^{+3} . Using her data, Freeman and Watson⁴ obtained Hartree-Fock wave functions for the trivalent lanthanide ions; that is, wave functions corrected for exchange. Recently Holm⁵ independently determined Hartree eigenfunctions and eigenvalues for the neutral ytterbium atom. Aside from these atoms, SCF information has been determined by Hartree and co-workers for a few elements each side of mercury.

Energy eigenvalues E_{nl} for the free lanthanide atoms were computed for the configurations $4f^{n-5}d6s^2$ and $4f^{n-1}6s^2$. These are summarized in Fig. 1. Although two curves are shown for E_{4f} and E_{6s} , only one curve is appropriate for E_{5d} . The binding energy ($-E_{4f}$) of the 4f electrons increases with Z . Most of the decrease in binding energy due to the change from $4f^{n-5}d6s^2$ to $4f^{n-1}6s^2$ can be attributed to an increased repulsion between 4f electrons. The potential field that these electrons experience is modified by the loss of the 5d electron. Presumably the shift in E_{4f} due to this factor is small.

According to Koopman's theorem, the ionization potential for a given electron is approximately equal to its eigenvalue. Coulson and Sharma⁶ pointed out that the 4f shell of the lanthanides would begin to fill when E_{4f} lies below (or the binding energy above) the first

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ionization potential. It is interesting to compare the beginning of the 4f transition elements deduced from the present eigenvalues with those previously available.

In 1955, Latter⁷ used the Thomas-Fermi statistical distribution of electrons to obtain the several eigenvalues for all of the elements. In addition he employed the Dirac or exchange correction to the TF model. In 1961, Coulson and Sharma⁶ made an important correction for self-interaction of the 4f electron. The 4f eigenvalues determined by these three treatments of the statistical model are presented in Fig. 2. In addition, the experimental ionization potential I_1 and the present Hartree values of E_{4f} are plotted in this figure.

On the basis of this comparison the lanthanide series would start at erbium, using Latter's TF values, and at promethium using his TFD values. The Coulson-Sharma improvement leads to samarium as the first member. The Hartree method, however, yields more realistic values since the series starts between lanthanum and cerium.

A detailed study of the energy of different configurations of the free cerium atom was made because several estimates of the valence of metallic cerium have been published. Gschneidner and Smoluchowski⁸ after reviewing the available data on atomic radius, magnetic susceptibility, Hall coefficients, etc. conclude that the metallic valence of cerium in the room temperature γ -modification is not significantly different from 3 but that in the low temperature or collapsed α -form, the valence is not 4 but approximately 3.6. That is, in the γ -phase, three ($5d6s^2$) electrons become conduction electrons and the ion core has a localized 4f electron, whereas in the α -phase, the 4f electron has been promoted from approximately 40 per cent of the ion cores into the conduction or valence band. Hartree eigenvalues and radial density functions were obtained for a series of configurations of the form $4f^x 5d^{2-x} 6s^2$. The variation of eigenvalues as a function of x, the occupancy of the 4f subshell is shown in Fig. 3. The change of approximately 13 electron-volts (nearly one Rydberg) in E_{4f} as x increased, is surprising. It can be concluded that much of the decrease in the binding energy of the 4f electrons with increasing x is due to increased electrostatic repulsion. However as the number of 5d electrons ($2-x$) increases, their electrostatic repulsion is more than offset by the reduced screening of the nuclear charge by the 4f electrons.

Derived Quantities:

The total binding energy E_t can be crudely estimated by summing the total eigenvalues and subtracting the interaction energies given by the Slater F^0 integrals⁹. It is assumed that the electrons move in a central field of spherical symmetry, which is the same assumption upon which the Hartree and Hartree-Fock methods are based. The present values of E_t indicate that the configuration with 0.5 of a 4f electrons,

i.e. $x = 0.5$, is more stable than any of the configurations computed. However, consideration of E_t leads one to conclude that the arrangement $4f^n 5d 6s^2$ is more stable than $4f^{n+1} 6s^2$ for the lanthanides. This is contrary to the recent atomic beam results reported by Smith and Spalding¹⁰. It should be mentioned that the inclusion of the appropriate linear combinations of Slater F^k and G^k integrals in computing the interaction energies¹⁴ i.e., the two-electron contributions to the total of one-electron energies, may remove this discrepancy.

Plots of the radial density function $r^2 |\psi(r)|^2$ for the free cerium atom have been made for the three values of the occupancy x . To meet the Wigner-Seitz boundary condition, the derivative of ψ_{nl} must vanish at radius ρ , a substantial fraction of the 6s electrons must be compressed to lie within the Wigner-Seitz sphere. Thus because of enhanced electrostatic repulsion, E_{6s} will be substantially reduced in magnitude. The effect on the 5d electrons will be lesser as can readily be seen. The conclusion of Watson and Freeman⁴, that the 4f would be buried radially and thus relatively unaffected by the environment, would appear to be substantiated. The behavior of the 4f electron in cerium metal might be substantially different from that in other lanthanide metals, because the eigenvalues of 4f, 5d and 6s electrons are so similar in the case of cerium. However, no firm conclusion that the 4f electron is only slightly affected by environment can be made until at least Hartree wave functions have been obtained which are subject to the Wigner-Seitz boundary conditions. Band calculations would be a further substantial improvement.

Typical values of the spin-orbital splitting parameter ζ for the 4f electrons from Hartree calculations by Boyd and Waber¹¹ are 641 cm^{-1} for Ce and 2480 for Er whereas the experimental values fitted to spectral data are 640 and 2470 respectively as quoted by Freeman and Watson⁴. The Hartree-Fock values⁴ are from 30 to 14 per cent higher than experimental.

Blume and Watson¹² recently pointed out that the spin orbit coupling parameter is not correctly given by $\langle r^{-1} dV/dr \rangle$ when determinantal wave functions are used, such as in the Hartree-Fock method. Inclusion of certain exchange type terms they have subsequently shown, leads to excellent agreement between calculations and experiments for atoms containing 3d and 4p outer electrons. Unfortunately their calculations have not been published for the lanthanides.

The configuration of the free atom used was $4f^n 5d 6s^2$ since this has the same number of f electrons as Freeman and Watson⁴ used. The correctness of their assumption about the behavior of the 4f electrons is supported by comparing our results for the neutral atom with the results of Ridley's similar calculation for trivalent ions. Our interpolated values for Pr and Tm are 773 and 2740. Her values³ are 785 for

Pr^{+3} and 2742 for Tm^{+3} .

The Slater integrals identified as F^2 obtained by Boyd and Waber¹¹ have been compared with values fitted by Judd and Lindgren¹³ as well as by Crozier and Runciman¹⁴ to spectral data. Although calculations by Boyd and Waber are 21 to 28 per cent higher than the "experimental" values, they are closer than the Hartree-Fock values. The latter, obtained by Freeman and Watson⁴ are 40 to 48 per cent higher.

Atomic scattering factors have been obtained using the Hartree wave functions and will be reported elsewhere. It is interesting that values calculated with two configurations differ by several tenths of an electron in useful range of $\sin \theta/\lambda$ values. Probably the present calculations are more realistic than the Thomas-Fermi-Dirac values tabulated by Ibers¹⁵.

From the calculated Hartree energy eigenvalues and the spin-orbital splitting energies, it is possible to obtain the energies corresponding to the L-emission spectra. A comparison of the present results with X-ray spectroscopic values¹⁶ indicates that the non-relativistic values for cerium are from 3.8 to 4.2 per cent low.

The major error comes from the fact that both of the 2p levels will have even greater binding energy than the 3d levels in the relativistic case; any improvement in the spin orbit splitting will have a small influence on the emission energy.

Van Vleck¹⁷ noted that molar diamagnetic susceptibility of a free atom is given by

$$\chi_{\text{dia}} = -0.790 \times 10^{-6} (\sum \overline{r^2}) \quad (1)$$

where $\overline{r^2}$, the expectation value of r^2 for each electron shell, is summed over all of the shells and weighted according to the number of electrons in each. Values of the quantity $(-\chi \cdot 10^6)$ range from 95.3 for Ce to 78.7 for Yb in the $4f^{n-5}d^6s^2$ configuration and from 94.2 for Ce and 75.1 for Yb in the $4f^{n-1}6s^2$ configuration. These are larger than the values suggested by the Thomas-Fermi model, namely $10^{-6} Z^{1/3}$. However, they are difficult to compare with experimental values since the latter are observed for solids rather than for free atoms. The diamagnetic susceptibility depends mainly on the wave functions of the outermost electrons and these are strongly perturbed in a solid. Values for two other configurations of Ce namely 95.1 in $4f^{0.5}d^{1.5}6s^2$ and 94.8 in $5d^26s^2$. These suggest that the major influence of the 4f electron is in shielding the nuclear charge.

Cohesive Energy Calculation:

In the calculation by Bernstein and Smith¹⁸ of the cohesive energy

of the lanthanides, the experimental values of the third ionization potential I_3 were used, where available, to obtain the parameter r_0 which determines the ground state energy in the method of Fröhlich¹⁹ and Raimes²⁰. In other cases, they assumed that r_0 was larger than the ionic radius r_i by a constant amount m . For tetravalent cerium and divalent europium, they estimated the ionic radius from the trivalent radius using Pauling's empirical equation²¹ and used this quantity in an equation they derived involving a Prokofjew potential²⁷ for the ion core. Larson and Waber²³ recalculated the cohesive energy, compressibility χ and the equilibrium Wigner-Seitz radius ρ for a number of rare earths using the most recent values of I_3 and a modification of the transcendental equation all previous investigators had employed to determine r_0 . Values are compared in Table VI with the values of Bernstein and Smith and with the observed values. Calculations for trivalent Eu and Yb as well as for divalent Lu are also presented. It will be seen that agreement between calculated and experimental Wigner-Seitz radii has been improved although Larson and Waber²³ observed that values of ρ are about 10 per cent larger than experimental. This tendency is supported by Table I.

	Wigner-Seitz Radius (Bohr Units)			Compressibility $-\chi \cdot 10^6$ kg/cm ²			Parameter r_0 (Bohr Units)		
	BS	LW	Obs.	BS	LW	Obs.	LW	BS	Equation BS used
Sc(3)	3.69	3.635	3.427	1.37	1.27	-	2.540	2.56	Raimes
Y(3)	4.40	4.358	3.760	2.69	2.44	2.25	3.198	3.20	Raimes
La(3)	4.70	4.653	3.921	3.47	3.22	4.13	3.466	3.47	Raimes
Ce(3)	4.65	4.464	3.81(γ)	3.29	2.75	4.10(γ)	3.295	3.42	$r_i + m$
Ce(4)	4.31	3.480	3.57(α)	1.58	0.61	4.72(α)	2.387	3.09	Shielding
Sm(3)	4.50	4.174	3.761	2.88	2.15	3.52	3.031	3.28	$r_i + m$
Eu(2)	4.84	4.829	4.290	8.13	7.76	4.91	3.715	3.67	Both
Eu(3)	-	4.088	4.290	-	1.98	4.91	2.953	-	-
Yb(2)	4.54	4.485	4.044	6.33	5.92	7.84	3.389	3.28	Raimes
Yb(3)	-	3.986	4.044	-	1.80	7.84	2.860	-	-
Lu(3)	4.25	3.771	3.628	2.36	2.51	2.33	3.198	3.06	$r_i + m$
Lu(2)	-	4.358	3.628	-	3.10	2.33	2.701	-	-

It is interesting to compare as in Fig. 4 the energies for trivalent and tetravalent cerium which enter into these calculations. The ground state energy (in atomic units) is

$$E_0 = \frac{n}{r_s} \left[3 - \left(\frac{r_s}{r_0} \right)^2 \right] \quad (2)$$

where n is the valence, r_s the radius of the Wigner-Seitz sphere and r_0 the Fröhlich-Raimes parameter. The interaction energy E_I is composed of the electrostatic self energy of the $(n-1)$ remaining valence electrons, as well as their Fermi, exchange and correlation energies. The experimental values of ρ are also indicated in Fig. 4 for the alpha and gamma forms of cerium. It will be seen that ρ calculated for tetravalent cerium is smaller than the experimental value for α -phase suggesting that 4 is too high a valence. Generally the metals were calculated to be more incompressible than they are in nature. Inclusion of repulsion between the ionic cores was recently studied by Larson and Waber²¹. This tends to make them more compressible at low pressure, and more incompressible at high pressures. Unfortunately the calculated values of ρ would be even larger.

The Fröhlich-Raimes method can be applied to alloys. The ground state energy was then assumed to be given by

$$E_0 = \frac{c_A n_A}{r_s} \left[3 - \left(\frac{r_s}{r_{0A}} \right)^2 \right] + \frac{c_B n_B}{r_s} \left[3 - \left(\frac{r_s}{r_{0B}} \right)^2 \right] \quad (3)$$

where c_A , n_A and r_{0A} are respectively the atomic concentration, the valence and the Fröhlich-Raimes parameter for component A. For the interaction energy the mean number $c_A n_A + c_B n_B$ of valence electrons was used. Values of the total energy E_t , radius ρ , and compressibility K have been obtained as a function of concentration for a large number of alloys. Most of these results will be reported elsewhere. One interesting result is summarized here.

It has become common for metallurgists to compare the observed average lattice spacing of alloys with the spacing obtained by averaging the lattice spacings of the components. We have assessed this deviation from Vegard's law by computing

$$y(c_A) = \rho(c_A) - (c_A \rho_A + c_B \rho_B) \quad (4)$$

The relative deviations $1000 y(c_A)/\rho_A$ can be used to reduce confusion about units; values are presented below for cerium based alloys containing 10 per cent of several solutes.

Solute	Alpha Ce	Gamma Ce
Magnesium	- 1.47	+ 6.75
Aluminum	+ 2.07	+ 4.57
Lanthanum	- 1.84	- 0.09
Zirconium	+ 0.32	- 2.29
Thorium	+ 2.73	- 0.89

The relative deviations have the correct sign in both thorium poor solid solutions when compared with the recent data of Waber, Harris and Raynor²². They are smaller in magnitude than the observed values (4.14 for α and -1.31 for γ). The relative deviations computed by them using Friedel's elastic model²⁵ are similar (3.14 for α and -0.57 for γ).

In general, only experimental data for the gamma phase are available. The sign of $y(c_A)$ does agree with that reported by Gschneidner at this Conference for dilute magnesium alloys but does not agree with the recent findings of Harris and Raynor²⁶ for cerium dissolved in alpha-zirconium. The sign of $y(c_A)$ for lanthanum does not agree with the positive deviations discussed by Gschneidner and Vineyard²⁷ for various rare earth additions to cerium. Further verification of the change in the sign of $y(c_A)$ on cooling to form alpha phase alloys would be desirable.

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BINDING ENERGIES, RYDBERGS

COMPARISON OF
EIGENVALUES FOR
4f ELECTRONS

2.4

2.2

2.0

1.8

1.6

1.4

1.2

1.0

0.8

0.6

0.4

0.2

0

THOMAS-FERMI-DIRAC
(AFTER LATTER)

THOMAS-FERMI WITH
SELF INTERACTION
(AFTER COULSON-
SHARMA)

HARTREE

EXPERIMENTAL
IONIZATION
POTENTIAL

THOMAS-FERMI
(AFTER LATTER)

La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

58

60

62

64

66

68

70

ATOMIC NUMBER