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Configuration Interaction in the Hydrogen Fluoride Molecule[1]

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A self-consistent field molecular orbital (SCF MO) calculation of the electronic structure of HF in the ground state and at the observed internuclear separation has been made. The MO's were approximated as linear combinations of atomic orbitals (LCAO's), and all electrons and the exact Hamiltonian were used. Both a single determinant MO and a configuration interaction (CI) treatment were carried out with single exponential Slater AO's as basis functions. The parameters for the single exponential basis set were chosen to be identical to those used by A. B. F. Duncan, and comparison is made with his work and that of others. The results including CI give 34.8% of the observed binding energy and a dipole moment of +0.6938 Debye unit (experimental value = +1.74 *D*).

Introduction

Recently a number of simple diatomic molecules[4-7] have been studied within the framework of the SCF LCAO–MO treatment formulated by Roothaan.[8] A calculation of the HF molecule has been made by Kastler[9] using a valence bond configuration to represent the ground state and superimposing on this a CI treatment. Discrepancies between the results of Duncan and Kastler, as well as other inconsistencies,[10] led us to reconsider the single determinant SCF method and to re-evaluate all integrals in a consistent manner. This work has been extended to include CI and an electron distribution analysis.

Atomic Orbitals and Method of Calculation.[12]—The atomic orbitals are those used by Duncan

$$h \equiv (1s)_{\mathrm{H}} = \left(\frac{1}{\pi}\right)^{1/2} \exp(-r_{\mathrm{H}})$$

$$s \equiv (1s)_{\mathrm{F}} = (c_1{}^3/\pi)^{1/2} \exp(-c_1 r_{\mathrm{F}})$$

$$S \equiv 1.02951(2s)_{\mathrm{F}} - 0.244726(1s)_{\mathrm{F}} \qquad (1)$$

$$[(2s)_{\mathrm{F}} = (c_2{}^5/3\pi)^{1/2}\, r_{\mathrm{F}} \exp(-c_2 r_{\mathrm{F}})]$$

$$z \equiv (2p_0)_{\mathrm{F}} = (c_2{}^5/\pi)^{1/2}\, r_{\mathrm{F}} \exp(-c_2 r_{\mathrm{F}})\ P_1{}^0 (\cos\theta)$$

$$\pi^{\pm} \equiv (2p_{\pm})_{\mathrm{F}} = (c_2{}^5/2\pi)^{1/2}\, r_{\mathrm{F}} \exp(-c_2 r_{\mathrm{F}}) P_1{}^1(\cos\theta)\ \exp(\pm i\phi)$$

$$c_1 = 8.7;\ c_2 = 2.6$$

These AO's form the basis for an orthonormal set of MO's, in particular, that set which minimizes the energy of the single Slater determinant representing the ground state molecular wave function.

All integrals were evaluated numerically on the MIT digital computer Whirlwind using programs written by F. J. Corbató.[13,14] The two-center one- and two-electron integrals were evaluated by the method of Barnett and Coulson[15] using the standard method of expanding an exponential function about another center. As programmed by Corbató this expansion in general form is

$$r\phi_{nlm}\,(k,r') = \sum_{j\,=\,|m|}^{\infty} (2j+1)\ \alpha_j(nlm|k|a|r) P_j{}^{|m|}(\cos\theta)\ \frac{e^{im\phi}}{\sqrt{2\pi}} \qquad (2)$$

where

$$\phi_{nlm}\,(k,r') = \left\{\left[\frac{(2k)^{2n+1}}{(2n)!}\right]^{1/2} r'^{\,n-1}\, e^{-kr'}\right\}$$
$$\left\{\left[\frac{2l+1}{2}\ \frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2} P_l{}^{|m|}\ (\cos\theta')\ \frac{e^{im\phi'}}{\sqrt{2\pi}}\right\} \qquad (2a)$$

and where the expansion functions, α_j, are appropriate combinations of spherical Bessel functions of half-integer order and imaginary argument. The spherical polar coördinates (r, θ, ϕ) and (r', θ', ϕ') refer, respectively, to the origin and to the center displaced by a distance a. The fluorine functions were generated using the limiting case $a = 0$, and the hydrogen 1s function was expanded about the fluorine center with $a = 1.7328$ atomic units, the observed equilibrium separation for HF. Simpson's rule integration was employed on a 101 point mesh. In general accuracy of the integrals was governed by the error in the integration method, so that the integrals are only tabulated to five places in the Appendix. The one-center kinetic energy integrals were evaluated analytically.[16]

The Roothaan procedure is an approach to a molecular Hartree–Fock solution in which the linear coefficients of a finite predetermined set of one-electron basis orbitals are evaluated variationally. The scheme has been described in detail elsewhere[8] and yields a set of orthonormal MO's expressed as a linear combination of the chosen basis AO's

$$\phi_i = \sum_p a_{ip}\chi_p \qquad (3)$$

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[4] C. W. Scherr, *J. Chem. Phys.*, **23**, 569 (1955), (N_2).

[5] R. C. Sahni, *ibid.*, **25**, 332 (1956), (BH).

[6] J. E. Faulkner, *ibid.*, **27**, 369 (1957), (Li_2).

[7] A. B. F. Duncan, THIS JOURNAL, **77**, 2107 (1955), (HF).

[8] C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

[9] D. Kastler, *J. chim. phys.*, **50**, 556 (1953).

[10] A. C. Hurley has pointed out in conversation that the molecular energy obtained by Kastler is higher than that reported by Duncan, even though Kastler's results were based on a somewhat more complete calculation involving CI and essentially the same basis orbitals as were used by Duncan. Roothaan[11] also found that with more variation parameters he obtained a higher F atom energy than that calculated by Duncan.

[11] C. C. J. Roothaan, Laboratory of Molecular Structure and Spectra, TR 1955 (University of Chicago, 1 Oct. 1954–30 Sept. 1955) p. 44.

[12] Atomic units are used throughout. $a_0 \equiv$ unit of length $\cong$0.5293 Å. Rydberg $\equiv$ unit of energy $\cong$ 13.602 e.v.

[13] F. J. Corbató, *J. Chem. Phys.*, **24**, 452 (1956).

[14] F. J. Corbató, Quarterly Progress Report, Solid-State and Molecular Theory Group, M.I.T., April 15, 1956, p. 33.

[15] M. P. Barnett and C. A. Coulson, *Phil. Trans.*, **A243**, 221 (1951).

[16] A comparison with Duncan's integrals shows a rather systematic discrepancy in the second and third decimal place for those integrals involving $(2s)_{\mathrm{F}}$ and slightly larger differences in a few other cases.

where the linear coefficients, a_{ip}, are solutions of the matrix equation

$$(H + G)a_i = \epsilon_i S a_i \qquad (4)$$

A program has been written for this process by A. Meckler and R. K. Nesbet for the M.I.T. digital computer, Whirlwind, and requires for input the one- and two-electron integrals and an initial estimate of the density matrix, ρ, ($\rho_{\lambda\nu} = \Sigma_i a_{\lambda i} a_{i\nu}{}^{+}$). Equation 4 must be solved iteratively, and the program accomplishes this by successive density matrix alterations and Hamiltonian matrix diagonalizations until a stationary density matrix is realized. The final SCF a_{ip}, $\rho_{\lambda\nu}$, the one- and two-electron integrals transformed to the orthonormal SCF MO basis, and the one-electron energy parameters are obtained as output from the computer.[17]

The Best Single Determinant Wave Function.—In Mulliken's notation the electronic configuration of the ground state of HF is $(1\sigma)^2(2\sigma)^2(3\sigma)^2\cdot(\pi^+)^2(\pi^-)^2$, $^1\Sigma^+$. The orthonormal set of MO's which solve eq. 4 are

$$\begin{aligned}
1\sigma &= -1.000147s - 0.015841S - 0.002431z + 0.004600h \\
2\sigma &= -0.021903s + 0.905020S + 0.089717z + 0.161492h \\
3\sigma &= +0.028309s + 0.459325S - 0.684695z + 0.579121h \\
4\sigma &= -0.053023s - 0.543582S - 0.808494z + 1.048445h \\
\pi^{\pm} &= (2p_{\pm})_F
\end{aligned} \qquad (5)$$

The orbital energies, the total molecular energy, and the resulting dissociation energy are given in Table I.

TABLE I

CALCULATED ENERGIES (RYDBERGS)

Orbital energies ϵ	
$\epsilon(1\sigma)$	− 52.290286
$\epsilon(2\sigma)$	− 2.962522
$\epsilon(3\sigma)$	− 1.136526
$\epsilon(4\sigma)$	0.943008
$\epsilon(\pi^{\pm})$	− 0.934659
Total electronic energy	−209.355025
Nuclear repulsion energy	10.387812
Total molecular energy	−198.967213
−(H + F atomic energy)	198.866503
Dissociation energy	− 0.100710
	(− 1.3699 e.v.)
Dissociation energy (exptl.)[a]	− 6.08 e.v.

[a] A. C. Hurley, *Proc. Phys. Soc. (London)*, A69, 301 (1956).

The energy of the F atom was calculated using the same AO's as were used in the molecular calculation. These results are in agreement with those of M. Krauss of the National Bureau of Standards,[18] who has also essentially repeated Duncan's single determinant calculation (the only difference being his use of 8.68 instead of 8.70 for the $(1s)_F$ exponent). He obtains a total molecular energy of −198.956 Rydbergs. With the fluorine nucleus taken at the origin, the dipole moment is given by

$$\mu = -e\int \phi^* \bar{r} \phi \, d\tau + e r_0 \qquad (6)$$

where ϕ is the antisymmetrized product of the occupied ground state MO's and r_0 is the equilibrium internuclear separation. It is found to be +0.8494 Debye unit. The most recent experimental value has been obtained by G. A. Kuipers of the Eastman Kodak Company[19] and is +1.74 *D*.

The negatives of the one-electron parameters approximate the ionization potentials of the molecule (Koopmans' theorem). From our results the first ionization potential would be about 12.7 e.v., but there are no experimental values with which to compare. Duncan[7] has given a brief summary of existing experimental excitation energies.

Configuration Interaction.—The single determinant molecular wave function can be only an approximation to the wave function representing the actual electron distribution in the ground state. A better approximation can be made by supplementing the ground state with a linear combination of configurations of appropriate ground state symmetry and multiplicity

$$\psi = \sum_r m_r \phi_r \qquad (7)$$

and applying to the undetermined coefficients, m_r, the standard variational treatment for minimizing the energy.

By choosing the SCF MO's already determined, the leading term in the expression will be the single determinant ground state function; and for this choice the leading coefficient will also be maximized. The digital computer program for the Roothaan scheme also constructs an unoccupied orthonormal MO (4σ), and this is used in the CI. All configurations which can be formed from the set of MO's at our disposal are included, with the restriction that the 1σ orbital remains filled.[20] One can show from second-order perturbation theory that little interaction occurs between highly excited states, formed by promoting 1σ electrons, and the ground state.

The ground state and the six excited configurations are listed in Table II with the coefficients, m_r, resulting from the complete CI treatment. The third column gives the binding energy resulting from the interaction of two through seven configurations added in order proceeding down the column. The first entry is the value obtained for the single determinant approximation.

TABLE II

MOLECULAR WAVE FUNCTION FROM CI

Configurations ϕ_r	Coeffs. m_r for seven configs.	Binding energy from CI (Rydbergs)
$\phi_1(1\sigma)^2(2\sigma)^2(3\sigma)^2(\pi^+)^2(\pi^-)^2$	0.990357	−0.10071
$\phi_2(1\sigma)^2(2\sigma)^2(4\sigma)^2(\pi^+)^2(\pi^-)^2$	− .125011	− .14123
$\phi_3(1\sigma)^2(3\sigma)^2(4\sigma)^2(\pi^+)^2(\pi^-)^2$	− .028254	− .14648
$\phi_4(1\sigma)^2(2\sigma)(3\sigma)(4\sigma)^2(\pi^+)^2(\pi^-)^2$	− .038659	− .15313
$\phi_5(1\sigma)^2(2\sigma)^2(3\sigma)(4\sigma)(\pi^+)^2(\pi^-)^2$	− .017433	− .15355
$\phi_6(1\sigma)^2(2\sigma)(3\sigma)^2(4\sigma)(\pi^+)^2(\pi^-)^2$	− .003143	− .15364
$\phi_7(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(\pi^+)(\pi^-)$	.030957	− .15561

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[17] See L. C. Allen, Solid-State and Molecular Theory Group, M.I.T., January 15, 1957, p. 10, for a description of the use and format of this program.

[18] Private communication.

[19] Private communication.

[20] Configurations ϕ_5 and ϕ_6 formed by excitation of a single electron from the ground state have no first-order interaction with the ground state, and, therefore, little effect in lowering the energy. They have been included so that an exact comparison can be made with another calculation of HF (to be published) which has been carried out over a wide range of internuclear distances using Hartree–Fock AO's on F. At larger internuclear distances second-order interactions become increasingly important.

Appendix

One-electron integrals

Orbitals	Overlap	Kinetic energy	Potential energy		Dipole moment
χ_p χ_q	$\int \chi_p(1)\chi_q(1)d\tau$	$\int \chi_p(1)\left(-\frac{\Delta}{2}\right)\chi_q(1)d\tau$	$\int \chi_p(1)\frac{1}{r_F}\chi_q(1)d\tau$	$\int \chi_p(1)\frac{1}{r_H}\chi_q(1)d\tau$	$\int \chi_p(1)(r_F\cos\theta)\chi_q(1)d\tau$
s s	1.00000	37.84500	8.70009	0.57711	0
S s	0.00000	−10.50364	−1.20734	.00000	0
S S	1.00000	4.06860	1.44775	.57274	0
z s	0	0	0	.01618	.04858
z S	0	0	0	.17883	.55964
z z	1.00000	3.38000	1.30001	.64933	0
h s	0.05485	0.00524	0.23920	.03266	.00281
h S	0.47227	.13199	.40702	.36812	.26792
h z	0.29894	.22198	.23700	.37145	.48681
h h	1.00000	.50000	.52782	1.00000	1.73288
π π	1.00000	3.38000	1.30001	0.53481	0

Two-electron integrals

$\chi_p\chi_q\chi_s\chi_t$	$\int \chi_p(1)\chi_q(1)\frac{1}{r_{12}}\chi_s(2)\chi_t(2)d\tau_{12}$	$\chi_p\chi_q\chi_s\chi_t$	$\int \chi_p(1)\chi_q(1)\frac{1}{r_{12}}\chi_s(2)\chi_t(2)d\tau_{12}$	$\chi_p\chi_q\chi_s\chi_t$	$\int \chi_p(1)\chi_q(1)\frac{1}{r_{12}}\chi_s(2)\chi_t(2)d\tau_{12}$
s s s s	5.43754	h S z S	0.04399	π s π s	0.03104
S s s s	−0.51635	h S z z	.36903	π S π s	.04061
S s S s	0.08215	h S h s	.02314	π S π S	.19954
S S s s	1.29513	h S h S	.16847	π z π z	.05484
S S S s	−0.02149	h z s s	.23674	π h π s	.01255
S S S S	.91807	h z S s	− .00047	π h π S	.06812
z s z s	.03104	h z S S	.20940	π h π z	.00955
z S z s	.04061	h z z s	.01567	π h π h	.02772
z S z S	.19954	h z z S	.09370		
z z s s	1.29076	h z z z	.22812		
z z S s	−0.01152	h z h s	.01372		
z z S S	0.92945	h z h S	.11716	π π s s	1.29076
z z z z	1.01767	h z h z	.11218	π π S s	−0.01152
h s s s	0.19482	h h s s	.52699	π π S S	.92945
h s S s	− .01213	h h S s	− .00062	π π z z	.90798
h s S S	.06655	h h S S	.50052	π π h s	.06811
h s z s	.00120	h h z s	.01060	π π h S	.35825
h s z S	.00210	h h z S	.10289	π π h z	.20203
h s z z	.06836	h h z z	.52783	π π h h	.48868
h s h s	.00826	h h h s	.02940		
h S s s	.41525	h h h S	.27157	π^+ π^- π^- π^+	0.10969
h S S s	.00033	h h h z	.23059	π^+ π^+ π^+ π^+	0.96283
h S S S	.35848	h h h h	.62500		
h S z s	.00599				

The complete dipole moment is given by

$$\mu = -e\int \psi^* \bar{r} \psi \, d\tau + er_0 \qquad (8)$$

and is found to be +0.6938 Debye unit.

Electron Population Analysis.—Mulliken[21] has shown that qualitative information concerning the electronic charge distribution can be obtained from an analysis of the overlap and atomic populations defined by the relations

$$\left.\begin{aligned} n(i;\ p_K, q_l) &= 2N(i)a_{ip_k}a_{iq_l}(\chi_{p_k}|\chi_{q_l}) \\ n(i) &= \sum_{p_k}\sum_{q_l} n(i;\ p_k, q_l) \\ n(p_k, q_l) &= \sum_i n(i;\ p_k, q_l) \\ n &= \sum_i n(i) \end{aligned}\right\}\text{overlap populations} \qquad (9)$$

$$\left.\begin{aligned} &N(i;\ p_k) = \\ &N(i)a_{ip_k}{}^2 + N(i) \sum_{k \mp l} a_{ip_k}a_{iq_l}(\chi_{p_k}|\chi_{q_l}) \\ &N(i) = \sum_{p_k} N(i;\ p_k) \\ &N(p_k) = \sum_i N(i;\ p_k) \end{aligned}\right\}\text{atomic populations} \qquad (10)$$

where a_{ip_k} is the SCF LCAO coefficient of χ_{p_k} in the ith filled MO, $N(i)$ the number of electrons in the ith MO, $(\chi_{p_k}|\chi_{q_l})$ the overlap integral for functions χ_p, χ_q on centers k and l. The bonding and antibonding nature of the ith MO is associated with the sign and magnitude of $n(i)$. The difference between the number of 2s electrons in the free F atom and the effective number in the molecule is said to define the amount of 2s-2p$_0$ promotion. The results of the electron population analysis for the single determinant wave functions are given in Tables III and IV.

Discussion of Results

The total energy found by Duncan for the ground state configuration (−199.4196 Ryd.) is considerably larger than our value (−198.9672 Ryd.). The difference probably can be accounted for by the previously mentioned discrepancies in the integrals. The molecular energies reported here are consistent with the results of a number of other calculations also using simple exponential Slater AO's.[4-6,9] In particular, Kastler's total energy (−199.0524 Ryd.) and dipole moment

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(21) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

TABLE III

AO POPULATIONS IN HF

	$N(i;\ 1s)$	$N(i;\ 2s)$	$N(i;\ 2p)$	$N(i;\ \mathrm{H})$	$N(i)$
1σ	2.00008	0.00043	0.00001	−0.00054	1.99998
2σ	0.00057	1.77617	0.02476	.19848	1.99998
3σ	−0.00020	0.17071	1.17469	.65479	1.99999
$N(p_k)$	2.00045	1.94731	1.19946	.85273	5.99995

$s - p$ promotion = 0.0522

TABLE IV

OVERLAP POPULATIONS IN HF

	$n(i;\ 1s,\ \mathrm{H})$	$n(i;\ 2s,\ \mathrm{H})$	$n(i;\ 2p,\ \mathrm{H})$	$n(i)$
1σ	−0.00101	−0.00014	−0.00001	−0.00116
2σ	− .00078	.27609	.01732	.29263
3σ	− .00360	− .50250	.47414	− .03196
$n(p_k,q_l)$	− .00539	− .22655	.49145	.25951

n(total overlap population) = 0.25951

(+0.9261 D) are quite near the results of our CI treatment. (Kastler's CI is equivalent to ours since 1s ≈ 1σ and because the omission of ϕ_7 and the slight differences in exponential AO parameters produce a negligible effect.) The calculated molecular energy is about two Rydbergs above the observed value. An appreciable fraction of the difference can be accounted for by the failure of Slater AO's to represent the F^- ion, with a resulting poor description of the F^-H^+ molecular state. Kastler showed that with his basis set the energy of F^- was higher than the F atom.[22] Qualitatively this may explain the small dipole moment obtained, since the high total energy of F^- implies inadequate charge on the fluorine center in the molecule. The fraction of the binding energy which is calculated and the amount of improvement contributed by CI is very nearly the same as that found in similar SCF calculations.

From the SCF LCAO coefficients as well as the electron distribution analysis the 1σ and 2σ MO's are seen to be formed almost completely from 1s and 2s fluorine AO's, respectively, and concentrated about the fluorine nucleus. The overlap population is large for the 2σ MO and it is therefore bonding. The electron population of the 3σ MO is distributed around both nuclei, with the overlap population such that this MO is slightly antibonding. These results are in agreement with what has been found for N_2, BH and Li_2.[4-6]

NOTE ADDED IN PROOF.—An ionization potential of 12.6 e.v. has been reported from the absorption spectrum of HF in the vacuum ultraviolet in good agreement with our predicted value of 12.7 e.v. (R. P. Iczkowski and J. L. Margrave, Symposium on Molecular Structure and Spectroscopy, The Ohio State University, June 16–20, 1958).

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[22] Similar results have been obtained by L. C. Allen, ref. 17, p. 4.

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The Crystal Structures of Some of the Rare Earth Carbides

BY F. H. SPEDDING, K. GSCHNEIDNER, JR.,[1] AND A. H. DAANE

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A study of the rare earth–carbon systems has been made. The existence of the reported LaC_2, CeC_2, PrC_2, NdC_2 and SmC_2, and the Ce_2C_3 has been confirmed. The existence of the tetragonal CaC_2 type structure for the other rare earth dicarbides has been shown. The lattice constants of these compounds decrease in a regular fashion, except for the YbC_2, whose lattice parameters lie between those of HoC_2 and ErC_2. The body-centered cubic Pu_2C_3 type structure has been found to exist in all of the rare earths from La to Ho. The lattice constants decrease in a normal manner, except for Ce_2C_3, whose lattice parameter is smaller than would be expected. A new rare earth carbide has been found, R_3C, which is similar to the face-centered cubic NaCl type structure, except that it is deficient in carbon. This compound appears to exist over a range of composition, *i.e.*, in the case of yttrium it was found to vary from $YC_{0.25}$ to $YC_{0.40}$. This compound has been found to exist in the rare earth–carbon systems of Sm to Lu, and the lattice parameters decrease in a regular manner. No X-ray evidence was found for the existence of this lower carbide in the La–, Ce–, Pr– and Nd–C systems.

Introduction

The crystal structures of several tetragonal rare earth dicarbides (LaC_2, CeC_2, PrC_2, NdC_2 and SmC_2) and a hexagonal YC_2 have been known for several years.[2] Recently the existence of other rare earth carbon compounds, CeC,[3] Ce_2C_3[3] and CeC_3,[4] have been reported. CeC was reported to be face-centered cubic (NaCl type) with a lattice constant of 5.130 Å.; Ce_2C_3 was found to be body-centered cubic (plutonium sesquicarbide type[5]) with a_0 = 8.455 Å., while no structural data have been reported for CeC_3. In a study of the lanthanum–carbon system[6] only two compounds were found, La_2C_3 and LaC_2. The structural details of these two carbides were determined using X-ray and neutron diffraction techniques.[7]

Experimental

Materials.—The rare earth metals, 99.9% pure, were prepared by metallothermic reduction methods described by Spedding and Daane.[8] In general, the metals were used in the form of filings or finely divided chips since it was easier to achieve homogeneous alloys by arc melting compressed cylinders of the metal filings and carbon powder. The carbon was prepared in the form of a powder by turning spectroscopic electrodes on a lathe.

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[1] Los Alamos Scientific Laboratory, Los Alamos, New Mexico· Based in part on a dissertation submitted by Karl Gschneidner, Jr., to the Graduate School, Iowa State College, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1957.

(2) M. von Stackelberg, *Z. Elektrochem.*, **37**, 542 (1931).

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(5) W. H. Zachariasen, *Acta Cryst.*, **5**, 17 (1952).

(6) F. H. Spedding, K. Gschneidner, Jr., and A. H. Daane, "The Lanthanum–Carbon System," to be published.

(7) M. Atoji, *et al.*, THIS JOURNAL, **80**, 1804 (1958).

(8) F. H. Spedding and A. H. Daane, *J. Metals*, **6**, 504 (1954).