

does not contribute to the second moment, and the calculation must be carried to at least the fourth moment in order to take into account the exchange interaction. In our case, however, the exchange interaction already contributes to the second moment. Hence the contributions from the fourth and still higher moments to the spin relaxation time will be relatively unimportant. In fact, even the calculation

of the second moment is quite laborious, and it will be practically impossible to calculate the fourth moment.

In conclusion, we should like to express our sincere thanks to Professor Masao Kotani for his encouragement and guidance. We also appreciate the helpful discussions of Mr. K. Tomita and Mr. S. Koide. For the publication of this paper, we are very much indebted to Professor Van Vleck for his interest and good offices.

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Spin-Spin Interaction*

R. E. TREES

University of Pennsylvania, Philadelphia, Pennsylvania

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Araki has suggested that spin-spin and spin-other-orbit interactions have an appreciable effect on the intervals of multiplets in spectra of heavy elements. He has shown that for a large number of elements the three intervals of a quartet (or the four of a quintet, etc.) can be calculated from a relation involving two arbitrary constants. We have calculated the matrix elements of spin-spin interaction for d^n configurations, so that comparison can be made between different multiplets. The results are applied to 8 multiplets of Fe III, taking account of nondiagonal spin-orbit elements with second-order perturbation theory. The agreement obtained seems to warrant the conclusion that spin-spin effects are appreciable. An analysis of the electrostatic interaction in the d^n configuration of Fe III has also been made.

I. INTRODUCTION

IT has been suggested that spin-spin and spin-other-orbit interactions are important in explaining the intervals of multiplets in atomic spectra even when the nuclear charge is large.¹ The demonstration offered consists in showing that for many elements the three intervals of a quartet (or the four of a quintet, etc.) can be calculated from a relation involving two arbitrary constants, one of which arises from spin-orbit and spin-other-orbit diagonal matrix elements and has a Landé dependence on J , and the other originating in spin-spin diagonal matrix elements with J entering in a more complex fashion (see relation (11) below). It has been pointed out² that the neglect of nondiagonal elements of spin-orbit interaction and the use of two parameters to explain each set of multiplet levels make this demonstration inconclusive. By calculating spin-spin and spin-other-orbit matrix elements completely, the different pairs of constants for each of the multiplets of a given configuration are expressible in terms of a much smaller number of radial parameters, and the intervals of triplets can also be analyzed. In the case of d^n configurations, spin-spin interaction and spin-other-orbit interaction are expressible in terms of two radial

parameters;³ and if the parameter for spin-orbit interaction is included, the number of parameters is thus reduced to three. In the present paper, only the matrix elements of spin-spin interaction for d^n configurations have been calculated.

II. THEORY

The calculation is simplified by the use of Racah's methods.⁴ The spin-spin interaction will be indicated by H_m^{II} as defined in Marvin.⁵ With a few minor redefinitions, Araki's results¹ show that this is a scalar product of the type considered in II (32'); i.e.,

$$H_m^{II} = \sum_{i>j} T_{ij}^{(2)} \cdot U_{ij}^{(2)}. \quad (1)$$

It follows from II (38) that

$$\begin{aligned} & (l^n \alpha S L J M | H_m^{II} | l^n \alpha' S' L' J M) \\ &= (-)^{S+L'-J} W(S L S' L'; J 2) \\ & \quad \times (l^n \alpha S L || T^{(22)} || l^n \alpha' S' L'), \quad (2) \end{aligned}$$

where $T^{(22)}$ is by definition the double tensor whose scalar part is given by (1) (see II §5). The function W is defined in II (36), and for diagonal elements has the

* Part of a dissertation presented to the faculty of The Graduate School of the University of Pennsylvania in candidacy for the degree of Doctor of Philosophy.

¹ G. Araki, *Prog. Theor. Phys.* **3**, 152 (1948); **3**, 262 (1948). Relation (1) has been given by L. Eisenbud and E. Wigner, *Proc. Natl. Acad. Sci. U.S.A.* **27**, 281 (1941).

² G. Reach, private communication.

³ This follows by extension of the arguments given by Aller, Ufford, and Van Vleck, *Astrophys. J.* **109**, 42 (1949).

⁴ G. Racah, *Phys. Rev.* **61**, 186 (1942); **62**, 438 (1942); **63**, 367 (1943); **76**, 1352 (1949). These will be referred to as I, II, III, and IV, respectively.

⁵ H. H. Marvin, *Phys. Rev.* **71**, 102 (1947). The radial parameters used in this paper are the ones defined by Marvin for d^n .

TABLE I. ($d^{\nu}vSL\|T^{(22)}\|d^{\nu}vS'L'$)

ν	SL	$S'L'$	$(d^{\nu}vSL\ T^{(22)}\ d^{\nu}vS'L')$
2	3P	3P	$-84(M_0+12M_2)$
2	3P	3F	$24(14)^{\frac{1}{2}}(M_0-13M_2)$
2	3F	3F	$12(14)^{\frac{1}{2}}(M_0-38M_2)$
3	2P	4P	$-4(42)^{\frac{1}{2}}(M_0-18M_2)$
3	2P	4F	$-2(3)^{\frac{1}{2}}(22M_0+104M_2)$
3	4P	4P	$56(6)^{\frac{1}{2}}(M_0-18M_2)$
3	4P	2D	$-8(105)^{\frac{1}{2}}(M_0+2M_2)$
3	4P	2F	$8(42)^{\frac{1}{2}}(M_0+32M_2)$
3	4P	4F	$-16(21)^{\frac{1}{2}}(2M_0-11M_2)$
3	2D	4F	$24(5)^{\frac{1}{2}}(M_0-48M_2)$
3	2F	4F	$-(42)^{\frac{1}{2}}(14M_0-52M_2)$
3	4F	4F	$-16(21)^{\frac{1}{2}}(M_0+7M_2)$
3	4F	2G	$-6(30)^{\frac{1}{2}}(3M_0-74M_2)$
3	4F	2H	$4(330)^{\frac{1}{2}}(M_0-8M_2)$
4	1S	5D	$-240(35)^{\frac{1}{2}}M_2$
4	3P	3P	$24(M_0-78M_2)$
4	3P	3D	$-6(10)^{\frac{1}{2}}(M_0+2M_2)$
4	3P	5D	$-18(70)^{\frac{1}{2}}(M_0+2M_2)$
4	3P	3F	$48(M_0-28M_2)$
4	1D	5D	$1800M_2$
4	3D	3D	$-30(21)^{\frac{1}{2}}/7(M_0-128M_2)$
4	3D	5D	$30(3)^{\frac{1}{2}}(3M_0-44M_2)$
4	3D	3F	$12(15)^{\frac{1}{2}}(3M_0-19M_2)$
4	3D	3G	$60(7)^{\frac{1}{2}}/7(M_0-93M_2)$
4	5D	5D	$-210(M_0-8M_2)$
4	5D	1F	$-300(14)^{\frac{1}{2}}M_2$
4	5D	3F	$12(105)^{\frac{1}{2}}(M_0-23M_2)$
4	5D	1G	$180(110)^{\frac{1}{2}}M_2$
4	5D	3G	$180(M_0-3M_2)$
4	3F	3F	$-12(14)^{\frac{1}{2}}(M_0+22M_2)$
4	3F	3G	$-24(10)^{\frac{1}{2}}(M_0-18M_2)$
4	3F	3H	$12(110)^{\frac{1}{2}}(M_0+7M_2)$
4	3G	3G	$-12(462)^{\frac{1}{2}}/7(M_0-58M_2)$
4	3G	3H	$12(22)^{\frac{1}{2}}(M_0-33M_2)$
4	3H	3H	$-12(143)^{\frac{1}{2}}(M_0-8M_2)$
5	2S	4D	$-6(10)^{\frac{1}{2}}(3M_0-104M_2)$
5	6S	2D	$240(105)^{\frac{1}{2}}M_2$
5	6S	4D	$42(30)^{\frac{1}{2}}(M_0-8M_2)$
5	2D	4D	$180(14)^{\frac{1}{2}}/7(M_0-18M_2)$
5	2D	4G	$-60(70)^{\frac{1}{2}}/7(M_0+24M_2)$
5	4D	4D	$120(14)^{\frac{1}{2}}/7(M_0+22M_2)$
5	4D	2F	$2400M_2$
5	4D	2G	$48(385)^{\frac{1}{2}}/7(M_0-18M_2)$
5	4D	4G	$-48(70)^{\frac{1}{2}}/7(2M_0+9M_2)$
5	2F	4G	$6(10)^{\frac{1}{2}}(7M_0-66M_2)$
5	2G	4G	$-30(14)^{\frac{1}{2}}/7(M_0+122M_2)$
5	4G	4G	$-240(77)^{\frac{1}{2}}/7(M_0-13M_2)$
5	4G	2I	$-12(65)^{\frac{1}{2}}(M_0+12M_2)$

form

$$W(SLSL; J2) = (-)^{S+L-J} 2 \left\{ \frac{(2S-2)!(2L-2)!}{(2S+3)!(2L+3)!} \right\}^{\frac{1}{2}} \\ \times [3K(K+1) - 4L(L+1)S(S+1)], \quad (3)$$

where

$$K = J(J+1) - L(L+1) - S(S+1),$$

which agrees with the J dependence given by Araki. Relation (2) need not be restricted to l^n configurations.

The calculation of the last factor on the right of (2) can be carried out by use of a formula suggested by IV(1). The tensor $T^{(22)}$ is of the form

$$T_n^{(pq)} = \sum_{i>j} t_{ij}^{(pq)}, \quad (4)$$

where the subscript "n" indicates a summation over all

pairs for n equivalent electrons. Because of the equivalence of the electrons, all terms in the sum contribute the same quantity to the total matrix element. If terms involving the n th electron are removed, the number of terms is reduced in the ratio $(n-2)/n$ so that

$$(l^n \alpha SL \| T_n^{(pq)} \| l^n \alpha' S' L') \\ = [n/(n-2)] (l^n \alpha SL \| T_{n-1}^{(pq)} \| l^n \alpha' S' L'). \quad (5)$$

(If the tensor were of the form II(61), i.e.,

$$T_n^{(pq)} = \sum_i t_i^{(pq)}, \quad (6)$$

then the factor $n/(n-2)$ would be replaced by $n/(n-1)$ in this and subsequent relations.) Because vector coupling formulas do not apply to configurations with more than two equivalent electrons, linear combinations of vector coupled eigenfunctions must be used if the explicit dependence of the state on the n th electron is to be indicated. Using eigenfunctions of the form III(8), it follows from (5) that

$$(l^n \alpha SL \| T_n^{(pq)} \| l^n \alpha' S' L') \\ = [n/(n-2)] \sum_{\substack{\alpha_1 S_1 L_1 \\ \alpha_2 S_2 L_2}} (l^n \alpha SL \| l^{n-1}(\alpha_1 S_1 L_1) l SL) \\ \times (l^{n-1}(\alpha_1 S_1 L_1) l_n SL \| T_{n-1}^{(pq)} \| l^{n-1}(\alpha_2 S_2 L_2) l_n S' L') \\ \times (l^{n-1}(\alpha_2 S_2 L_2) l S' L' \| l^n \alpha' S' L'). \quad (7)$$

A generalization of II(44a) can be made to get the relation

$$(\alpha s_1 l_1 s_2 l_2 SL \| T^{(pq)} \| \alpha' s_1' l_1' s_2' l_2' S' L') \\ = (-)^{s_2+l_2-s_1'-l_1'-s-L+p+q} [(2S+1)(2L+1) \\ \times (2S'+1)(2L'+1)]^{\frac{1}{2}} (\alpha s_1 l_1 \| T^{(pq)} \| \alpha' s_1' l_1') \\ \times W(s_1 S s_1' S'; s_2 p) W(l_1 L l_1' L'; l_2 q). \quad (8)$$

Relation (8) can be derived from the commutator relation II(23) using the $SLM_s M_L$ scheme in the same way as II(44a) was derived. Using (8) in (7) gives the desired relation:

$$(l^n \alpha SL \| T^{(pq)} \| l^n \alpha' S' L') \\ = (-)^{L+S-l-l'+p+q} [n/(n-2)] \\ \times [(2S+1)(2L+1)(2S'+1)(2L'+1)]^{\frac{1}{2}} \\ \times \sum_{\substack{\alpha_1 S_1 L_1 \\ \alpha_2 S_2 L_2}} (-1)^{L_2+S_2} (l^n \alpha SL \| l^{n-1}(\alpha_1 S_1 L_1) l SL) \\ \times (l^{n-1} \alpha_1 S_1 L_1 \| T^{(pq)} \| l^{n-1} \alpha_2 S_2 L_2) \\ \times (l^{n-1}(\alpha_2 S_2 L_2) l S' L' \| l^n \alpha' S' L') \\ \times W(S_1 S S_2 S'; \frac{1}{2} p) W(L_1 L L_2 L'; l q). \quad (9)$$

The matrix elements of spin-spin interaction for all two-electron configurations involving s , p , and d elec-

trons have been calculated by Marvin.⁵ The one element for p^3 has been calculated by Aller, Ufford, and Van Vleck.³ To calculate the elements for d^n configurations, Marvin's elements for d^2 are compared with (2) to obtain $(d^2 2SL \| T^{(22)} \| d^2 2S'L')$. Relation (9) is then used with $p=q=2$ and α replaced by the seniority number "v" (defined in III §6) to calculate $(d^2 vSL \| T^{(22)} \| d^2 vS'L')$. This procedure is repeated to obtain the elements for d^4 and d^6 configurations.

According to the results of this calculation, nonvanishing matrix elements exist only between states with the same seniority number, and the values of the elements in (5) are fully defined if vSL are given; i.e.,

$$(d^n vSL \| T^{(22)} \| d^n vS'L') = \delta_{vv'} (d^n vSL \| T^{(22)} \| d^n vS'L'). \quad (10)$$

The 48 quantities listed in Table I are therefore sufficient to calculate all of the spin-spin matrix elements for d^n configurations (there are 210 nonvanishing elements for the ten possible configurations). As an example, the diagonal element for the $J=4$ level of the $d^6 \ ^5D$ term ($v=4$) is, according to (2) and (10),

$$(d^6 \ ^5D_4M | H_m^{II} | d^6 \ ^5D_4M) = W(2222; 42) (d^4 \ ^5D \| T^{(22)} \| d^4 \ ^5D).$$

Substituting from (3) and Table I, we see this to be

$$(d^6 \ ^5D_4M | H_m^{II} | d^6 \ ^5D_4M) = -12(M_0 - 8M_2).$$

Similarly, for the $J=3$ level it can be shown that the matrix element has the value $24(M_0 - 8M_2)$, so that the interval between these two levels is altered by the amount $36(M_0 - 8M_2)$.

III. COMPARISON WITH EXPERIMENT

The d^6 configuration of the spectrum of Fe III was chosen for analysis,⁶ as the energy levels (with the exception of two high singlets) are all known and are so low that configuration interaction should be small. Moreover, d^6 and d^4 configurations have the largest number of multiplets with nonvanishing diagonal spin-spin elements to make comparison with.

To obtain the eigenfunctions for the five pairs of terms of the same kind that occur in the d^6 configuration, an analysis of the electrostatic interaction energy must first be made. The formulas for this energy have been taken in the same form as II(85), with "6A" replaced by a new constant, here indicated by "A." The data has been fitted by the method of least squares, and the results are given in Table II. The mean deviation is 876 cm^{-1} .

An analysis was first made considering only diagonal spin-orbit, diagonal spin-other-orbit, and diagonal spin-

TABLE II. Term values of the $3d^6$ configuration of Fe III (cm^{-1}).

Term	Obs.	Calc.	Diff.
5D	422	688	266
3P	20032	21642	1610
3H	20251	19321	-930
3F	21635	22115	480
3G	24837	24003	-834
1I	30355	28637	-1718
3D	30783	30558	-225
1G	30886	30320	-566
1S	34812	35152	340
1D	35803	37253	1450
1F	42896	42684	-212
$^3F'$	50260	50166	-94
$^3P'$	49992	50640	648
$^1G'$	57221	56848	-373
$^1D'$		76137	
$^1S'$		98720	
$A = 15F_0 - 14F_2 - 420F_4 = 20354.2$ $B = F_2 - 5F_4 = 936.49$ $C = 35F_4 = 3721.66$ Mean deviation = $\pm 876 \text{ cm}^{-1}$			

spin interactions. The procedure is the same as used by Araki,¹ and in his approximation the interval between the level "J" and "J-1" is of the form

$$\Gamma_J = E_J - E_{J-1} = C_1 J + C_2 J [2J^2 - 2L(L+1) - 2S(S+1) + 1]. \quad (11)$$

There are two constants in this expression which are determined from the two intervals for the triplets of d^6 . The four intervals of the 5D of d^6 can be combined in pairs to give three independent evaluations of these constants, thus giving an additional check on the consistency. The first five columns of Table III give the results of this analysis for 8 multiplets of the d^6 configuration of Fe III. The three independent determinations of the constants C_1 and C_2 furnished by the 5D are defined by the pairs of intervals Γ_4 and Γ_3 , Γ_3 and Γ_2 , and Γ_2 and Γ_1 , reading down in Table III. The sixth and seventh columns of Table III give the magnitudes of the two terms on the right side of Eq. (11), and have been called the spin-orbit part (it has C_1 as factor) and the spin-spin part (it has C_2 as factor) for brevity.

By assuming that the constant C_1 is determined chiefly by the spin-orbit interaction, one gets approximate values of the parameter ζ_d of spin-orbit interaction. The calculation is made using the relation III(25), and the resulting values of ζ_d are given in the final column of Table III. Partly owing to neglect of non-diagonal spin-orbit elements, the results are not very consistent and are particularly bad for the two 3F terms. If these two terms are omitted, the remaining six terms lead to a value $\zeta_d = 413 \pm 21$.

The effect of nondiagonal spin-orbit elements has been estimated by second-order perturbation theory, the experimental values being adjusted to the positions they would occupy if the effects of nondiagonal elements were absent. These revised energy levels are

⁶ B. Edlen and P. Swings, *Astrophys. J.* **95**, 532 (1942).

TABLE III. Analysis of intervals of multiplets of d^6 configuration of Fe III (no correction for nondiagonal spin-orbit elements).

Level	Energy	Interval	C_1	C_2	Sp. orb. part	Sp. sp. part	ζ_a
$^5D, J=4$	-0.8	-436.2	-103.8	-0.58	-415.3	-20.9	415.2
3	435.4	-302.7	-103.0	-0.42	-309.0	6.3	412.0
2	738.1	-193.5	-101.4	-0.31	-202.8	9.3	405.6
1	931.6	-94.9			-101.4	6.5	
0	1026.5						
$^3P, J=2$	19404.0	-1283.6	-621.5	-20.28	-1243.0	-40.6	421
1	20687.6	-520.1			-621.5	101.4	
0	21207.7						
$^3H, J=6$	20050.3	-249.7	-39.4	-0.24	-236.4	-13.3	394
5	20300.0	-181.1			-197.0	15.9	
4	20481.1						
$^3F, J=4$	21461.4	-237.7	-56.9	-0.5	-227.6	-10.0	566
3	21699.1	-157.3			-170.7	13.4	
2	21856.4						
$^3G, J=5$	24558.0	-382.1	-66.3	-1.45	-331.5	-50.6	442
4	24940.1	-201.5			-265.2	63.7	
3	25141.6						
$^3D, J=3$	30857.0	141.6	31.6	5.2	94.8	46.8	379
2	30715.4	-9.6			63.2	-72.8	
1	30725.0						
$^3F', J=4$	50275.3	-19.1	10.1	-2.98	40.4	-59.5	590
3	50294.4	110.3			30.3	80.0	
2	50184.1						
$^3P', J=2$	50411.5	835.4	419.6	-1.95	839.2	-3.8	429
1	49576.1	429.1			419.6	9.5	
0	49147.0						

defined by the relation

$$E^R(SLJ) = E^0(SLJ) + \sum_{S'L'} \frac{|(d^6SLJ | \sum L_i \cdot S_i | d^6S'L'J)|^2 \zeta_a^2}{E^0(S'L'J) - E^0(SLJ)}, \quad (12)$$

where $E^0(SLJ)$ are the energy levels given by experiment, and the sum is over all terms of the d^6 configuration of Fe III except the term that is to be adjusted. The value $\zeta_a=425$ was assumed, since this was found by trial to be more consistent than 413 with the value of ζ_a obtained from the corrected calculation. The values of the revised energy levels are given in the second column of Table IV. Except for the calculated values of C_2 and the calculated spin-spin parts, the other columns of Table IV are calculated from the revised energy levels in the same way as the corresponding columns of Table III were calculated from the original experimental data.

To calculate C_2 it is assumed that the spin-spin part is due solely to spin-spin interaction, which was the assumption made in the original derivation of Eq. (11). By use of Eqs. (2), (3), and (10), it may then be shown that the constant C_2 should theoretically have the value

$$C_2 = 12 \left\{ \frac{(2L-2)!(2S-2)!}{(2L+3)!(2S+3)!} \right\}^{\frac{1}{2}} (d^{\nu\nu}SL || T^{(22)} || d^{\nu\nu}SL) \quad (13)$$

for the terms occurring only once in d^6 ; thus, for the 5D we have

$$C_2 = -(M_0 - 8M_2).$$

For the other terms of d^6 , linear combinations of these

values must be taken appropriate to the eigenfunction considered. The two parameters M_0 and M_2 were determined by least squares with the spin-spin parts of Table IV as the experimental data and were found to be $M_0=0.304$ and $M_2=0.018$. With these values of the parameters, the calculated values of C_2 are determined from (13), and the calculated spin-spin part is the value of the second term on the right-hand side of (11).

Again omitting both 3F terms, the value of the spin-orbit parameter obtained from the values in column 8 of Table IV is $\zeta_a=429 \pm 16$, which is reasonably consistent with the assumed value of 425. The mean square value of the experimentally defined spin-spin parts in column 7 of Table IV is 9 cm^{-1} , while the mean deviation between the calculated and experimental values of the spin-spin parts is 4 cm^{-1} .

IV. DISCUSSION OF ERRORS

The major sources of error in the calculation occur in the correction for the nondiagonal elements of spin-orbit interaction. Most important is the uncertainty in the value of the radial parameter ζ_a which might possibly be in error by 4 percent. The average error in the spin-spin part would be about 3 cm^{-1} from the full error in ζ_a . The matrix elements also may be in error owing to errors in the choice of eigenfunctions. The agreement obtained between two calculations with widely different values of the parameters of electrostatic interaction indicates that the error will be less than 2 cm^{-1} for any reasonable values of the radial parameters. A third source of inaccuracy is the use of perturbation theory instead of solving for the eigenvalues of the matrices.

TABLE IV. Analysis of intervals of multiplets of d^6 configuration of Fe III (energy corrected for nondiagonal spin-orbit elements).

Level	Energy	Interval	C_1	C_2	Sp. orb. part	Sp. sp. part	ζ_d	C_2 (calc.)	Sp. sp. part (calc.)
${}^5D, J=4$	30.9	-422.1	-104.7	-0.10	-418.8	-3.3	419	-0.160	-5.8
3	453.0	-312.6	-104.4	-0.04	-313.2	0.6	418		2.4
2	765.6	-207.7	-103.0	0.06	-206.0	-1.7	412		4.8
1	973.3	-104.2			-103.0	-1.2			3.4
0	1077.5								
${}^3P, J=2$	19416.8	-1248.7	-620.8	-3.56	-1241.6	-7.1	421	-3.258	-6.5
1	20665.5	-603.0			-620.8	17.8			16.3
0	21268.5								
${}^3H, J=6$	20076.6	-284.5	-45.9	-0.17	-275.4	-9.1	459	-0.064	-3.5
5	20361.1	-218.4			-229.5	11.1			4.2
4	20579.5								
${}^3F, J=4$	21581.7	-177.4	-44.6	0.05	-178.4	1.0	444	-0.253	-5.1
3	21759.1	-135.0			-133.8	-1.2			6.8
2	21894.1								
${}^3G, J=5$	24496.9	-327.9	-65.8	0.03	-328.9	1.0	438	0.127	4.4
4	24824.8	-264.2			-253.0	-1.2			-5.6
3	25089.0								
${}^3D, J=3$	30876.4	109.9	33.6	1.02	100.8	9.1	403	0.857	7.7
2	30766.5	52.9			67.2	-14.3			-12.0
1	30713.6								
${}^3F', J=4$	50280.0	56.8	15.9	-0.34	63.6	-6.8	933	-0.175	-3.5
3	50223.2	56.5			47.4	9.1			4.7
2	50166.7								
${}^3P', J=2$	50389.6	821.7	414.5	-3.64	829.0	-7.3	425	-3.698	-7.4
1	49567.9	432.7			414.5	18.2			18.5
0	49135.2								

This would lead to only a small error, as the nondiagonal elements are of the order of a tenth the distance between levels at the largest. Further sources of error, such as configuration interaction, might also affect the results. An experimental check may be made by computing the spin-spin parts for the 5D using the two extreme values of C_2 (i.e., -0.10 and 0.06); the mean square difference between the two sets of spin-spin parts is 4 cm^{-1} . It seems safe to conclude that the mean square error of the spin-spin parts in column 7 of Table IV lies within the limits $2-6 \text{ cm}^{-1}$.

The very large value of ζ_d for the ${}^3F'$ level in Table IV seems to be caused by the smallness of C_1 . It was noted that the calculation of ζ_d depends strongly on the values chosen for the parameters of the electrostatic interaction; this is also true to some extent for the 3F level.

V. CONCLUSION

The preceding analysis of the d^6 configuration of Fe III is an effort to explain 18 deviations from the Landé rule. Although a spin-spin interaction was assumed in making the calculations, this is not essential as C_1 can be determined by least squares, and the part of the interval not following the Landé rule would be very nearly equal to the spin-spin parts of Tables III and IV.

Nondiagonal spin-orbit interaction is important in explaining deviations from the Landé rule. The mean square value of the spin-spin parts of Table III is 47 cm^{-1} , and this is reduced to 9 cm^{-1} when nondiagonal spin-orbit interactions are allowed for. Part of this

remaining deviation is, no doubt, due to the approximate methods used, but it seems unlikely that all the error is due to this.

By correcting for spin-spin interaction, the remaining deviation can be reduced from 9 cm^{-1} to 4 cm^{-1} . Half of the spin-spin parts of Table IV are greater than 7 cm^{-1} ; and in the case of the ${}^3F'$ and 3D they are more than 10 percent of the interval, so that the deviations to be explained are appreciable compared with known sources of error. Only two parameters were used to explain 18 deviations. There is an agreement in sign in all cases except the 3F and the 5D , and the latter would also agree if C_2 were taken as the lowest experimental value, -0.10 (the magnitudes of the spin-spin parts of the 5D would then agree much better also). The agreement in magnitude is only fair, however, as the difference is more than 50 percent of the experimental value for 4 of the 8 multiplets. The fact that the radial parameters are found to be positive and that $M_2 < M_0/7$ is in accord with the restrictions placed on these parameters by their definition in terms of radial integrals.^{5,7}

One can avoid the difficulty of separating a spin-spin part by calculating the matrix elements of spin-other-orbit interaction in a manner similar to that used for spin-spin interaction, so that the entire interval is then defined in terms of three parameters. Since the same

⁷ The estimate of C_2 for the $d^6 {}^5D$ of Fe III (-0.16) is much smaller than the value -0.475 ($\rho=0.95\pm 0.1$) obtained by M. H. L. Pryce [Phys. Rev. **80**, 1107 (1950)], neglecting spin-orbit nondiagonal elements. Equation (13) agrees with his Eq. (3) for the 5D of d^4 and d^8 , the 3F of d^2 and d^8 , and the 4F of d^8 and d^7 .

radial parameters are involved in spin-orbit interaction and spin-spin interaction, they will probably have effects of the same order of magnitude on the interval. It should then be possible to get more consistent values of ζ_d when C_1 is corrected for spin-orbit

interaction, and this would be a check on the preceding analysis.

I wish to thank Dr. C. W. Ufford for suggesting this problem and for many helpful discussions during the course of the work.

Half-Life of I^{129} and the Age of the Elements*

S. KATCOFF, O. A. SCHAEFFER, AND J. M. HASTINGS

Chemistry Department, Brookhaven National Laboratory, Upton, Long Island, New York

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The specific activities of several samples of methyl iodide containing I^{129} were measured with proportional counters, and the ratios of I^{129} to I^{127} were determined with a 60° sector type mass spectrometer. The half-life of I^{129} was found to be $(1.72 \pm 0.09) \times 10^7$ years. The time interval between the formation of the elements and the formation of the earth calculated from this value is 2.7×10^8 years. It was assumed that most of the Xe^{129} present on the earth at present originated from decay of I^{129} after the formation of the earth and that the original cosmic abundance of I^{129} was about equal to that of the stable I^{127} .

I. HALF-LIFE DETERMINATION

THE half-life of I^{129} was found by measuring the absolute disintegration rates, isotopic compositions, and total iodine contents of several samples obtained from fission product iodine that was separated from a uranium slug which had received a 4-year irradiation in the Oak Ridge pile and had cooled for 21 months.

For the chemical separation the uranium was dissolved in concentrated hydrochloric acid to which a few mg of iodine carrier had been added. After oxidation with hydrogen peroxide the elementary iodine was removed by counter-current extraction into carbon tetrachloride. It was purified by six or eight (see below) chemical cycles consisting of reduction to iodide, extraction into water, re-oxidation to iodine, and re-extraction into carbon tetrachloride. The iodine was finally precipitated as PdI_2 , which was washed and dried. Then it was decomposed by heating to 350° in an evacuated glass system; the evolved iodine vapor was collected in a tube containing methanol and red phosphorus. This mixture was heated at 110° for one hour to make methyl iodide, which was then passed over anhydrous calcium chloride to separate it from excess methanol. The methyl iodide was used for the activity measurements and the isotope ratio determinations.

The counters¹ were 2 cm in diameter and 30 cm long with silver cathodes and 2-mil wolfram center wires. They were operated in the proportional region with a 5000-volt power supply, a non-overloading pulse amplifier, and an Atomic Instrument Company scaler, model 101A. The counter gas was methane at one atmosphere. Preliminary experiments were performed

to study the effect of adding small amounts of methyl iodide to the methane. It was found that the counter plateau disappeared and that the counting rate of a Co^{60} γ -ray standard started to decrease as the partial pressure of methyl iodide was increased above 50 microns. Therefore, the measurements were made with the radioactive methyl iodide samples at partial pressures between 17 and 38 microns and with the counters operating at 3800 volts on both voltage and gain plateaus. Each sample was counted at least twice for periods of 20 to 150 minutes for total recorded counts $> 10^4$. Then the counter was cooled to -195° for one hour and the methane pumped off leaving the methyl iodide behind. This was then distilled, by warming the counter to room temperature, into a small tube containing a 30-mg piece of sodium and cooled with liquid nitrogen. This tube was set aside for the quantitative iodine determination. The counter was refilled with methane and the background counting rate determined. This was usually found to be somewhat higher than what it had been before the active methyl iodide had been in the counter. Apparently, anywhere, from 0 to 12 percent (average of 5 percent) of the methyl iodide remained in the counters. The backgrounds used in the calculations were those measured after the methyl iodide was distilled out. The operation of the counters was always checked by means of the Co^{60} standard. Its counting rate, corrected for I^{129} activity and background, remained the same within one percent, independent of the counter used and the amount of active methyl iodide therein. The total volumes and cathode volumes of the counters were measured at the conclusion of the experiments by adding water to them from a buret. It was shown by Bernstein and Ballentine¹ that the cathode volume is equal to the sensitive volume and that the observed counting rate is very nearly equal

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¹ W. Bernstein and R. Ballentine, *Rev. Sci. Instr.* **21**, 158 (1950).