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¹ Foote and Mohler, *Physic. Rev.*, **26**, 1925 (195-207); Mohler, Foote and Chenault, *Physic. Rev.*, **27**, 1926 (37-50).

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⁴ Smyth, *Physic. Rev.*, **25**, 1925 (452-468).

⁵ Witmer, *Proc. Nat. Acad. Sci.*, **12**, 1926 (238-243).

⁶ See Sommerfeld, "Atombau" 3d ed., Appendix 14.

⁷ Pauli, *Ann. Physik*, **68**, 1922 (177-240).

⁸ Niessen, *Ann. Physik*, **70**, 1923 (129-134).

⁹ Langmuir, *Science*, **52**, 1920 (433-437).

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SERIES AND IONIZATION POTENTIALS IN THE IRON SPECTRUM

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The iron spectrum has been extensively investigated especially by F. M. Walters² and by the writer.³ A brief discussion of the iron energy diagram as given in these papers from the viewpoint of the theory of spectra with several valence electrons⁴ was first given by F. Hund.⁵

It is the object of the following lines to discuss again the iron spectrum theoretically in a more detailed fashion than has been possible before, to show how far the theory enables us to predict not only the existence, but also the position of unknown terms, and finally to use these predictions for the establishment of several short series. We shall furthermore have the opportunity to demonstrate with a special group of terms the action of Pauli's equivalence principle.⁶ Anticipating the result, we may say that not only is the theory in complete agreement with empirical facts even in minute details, but also that it serves as an efficient tool for detecting new regularities.

Figure 1 shows the energy diagram of the iron spectrum in its present state. Compared with the other energy diagrams of Fe as published by W. F. Meggers⁷ or W. Grotrian⁸ several terms have been added, one of which was found by Dr. F. M. Walters and kindly put at the writer's disposal (³P at 23,000 cm.⁻¹), whereas others which are of importance here will be described and discussed later.

In explanation of figure 1, it may be said that the terms of equal apparent azimuthal quantum l are drawn on vertical lines. Each term is repre-

sented by a rectangle, whose vertical height corresponds to its separation in sublevels. Terms of different series systems are distinguished by their position on the vertical line, so that quintet terms (middle system) are drawn on the line, whereas triplet and septet terms are on the left and right sides of the line, respectively.

FIGURE 1

Primed and unprimed terms are put on different vertical lines and we have consequently two adjacent vertical lines for each l value. In terms of the old "dash" notation⁹ the arrangement of the terms from left to right is the following: $\bar{S}, \bar{P}, P, D, \bar{D}, \bar{F}, F, \dots$. A glance at the niveau scheme shows that $\bar{P}, D, \bar{F}$, etc., terms are low; $\bar{S} P \bar{D} F \dots$ terms are high; so that, as was proposed by Russell¹⁰ two sets of terms should be dis-

tinguished according to their position. In our arrangement the second, fourth and sixth vertical lines bear the low set, the first, third, . . . lines the higher set of terms, respectively.

This division into two sets can be explained in the following simple way. The low terms of an energy diagram correspond to a configuration of the

most stable electron "orbits," i.e., of type *s* and *d*; in other words they are obtained by adding *s* or *d* electrons, whereas the higher terms are generated by an addition of a *p* electron to the low energy states of the preceding ion. Thus terms of the same *l* value may arise from *s* and *d* electrons alone or else from *d* and one *p* or from *d*, *s* and one *p* electrons but they may be different by only one unit azimuthal quantum number.

The lowest term in the iron arc spectrum is a 5D —a result firmly supported by experimental facts and theoretical reasons¹¹—followed by quintet and triplet *P* and *F* terms. It is worth noticing that there is no low 3D appearing near 5D .

The terms of the second set appear in typical triads, indicated by dotted lines. Two triads consisting of terms with the same *l* values but different multiplicity, always appear together. Groups ${}^{7,5}(P\ D\ F)$, ${}^{5,3}(P\ D\ F)$ and ${}^{5,3}(D$

FIGURE 2

F G) are recognizable. The analysis of the spectrum, which is obviously getting more difficult for higher terms, has not so far advanced as to permit the allocation of the high 5S and 5P terms into triads.

D and *F* terms of a very high third set combining like the first have also been found; they are of special importance for the following. Unfortunately, their combinations are so weak and inconspicuous that it will be very difficult to complete this set of terms.

For the theoretical interpretation it is important to know the preceding spark spectrum, viz., Fe II, which has been investigated by H. N. Russell.¹²

For our purpose we need only a few of the lower terms. The normal state is a 6D , then follow 4F , 4D , 4P . 6D and 4D result from the configuration (d^6s^1); 4F and 4P come from (d^7).

Addition of a p electron to these furnishes the terms of the second set according to the following scheme:

The first six triads are readily identified with those marked on figure 1. The 5S term comes from 4P and thus belongs to (d^7p). Indications of other terms belonging to this triad have been found.

The terms of the low and of the very high set originate from the above-mentioned terms of the spark by addition of d and s electrons, the former by the addition of 3_3 and 4_1 , the latter of 4_3 and 5_1 electrons. For the third set this addition may be carried out according to the usual vector inequalities which were used by Russell and Saunders,¹³ whereas for the low metastable terms Pauli's equivalence principle must be taken into consideration.

Let us now consider the low terms. The following electron configurations and spectral terms have to be expected:

$$\begin{array}{c|c}
 d^6s^2 & {}^5D^3H \dots\dots \\
 d^7s & {}^5F^3F^5P^3P \dots\dots
 \end{array}$$

All these terms have actually been found. The F and P terms readily show their origin in a configuration with *one* s electron: always *two* close lying terms appear, having the same l value, but different multiplicities. They result from the addition of an s electron (4_1) to the above-mentioned 4F and 4P terms in the spark:

$$\begin{array}{c|cc}
 d^7 & {}^4F & {}^4P \\
 d^7s & \swarrow \quad \searrow & \swarrow \quad \searrow \\
 & {}^5F \quad {}^3F & {}^5P \quad {}^3P
 \end{array}$$

We should also have rather high terms, with the same combination properties, corresponding to an addition of s electrons with higher total quantum number; in other words we may expect four series of F and P terms, which in pairs converge to the generating spark terms 4F and 4P . Thus we assert, and shall prove later, that the terms 5F and 3F at about $49,000 \text{ cm.}^{-1}$ are the second members of a sequence of 5F and 3F terms, approaching 4F .

The 5D is the only prominent representative of the configuration (d^6s^2); it may be regarded as the result of the addition of an (equivalent) s electron

(4_1) to (d^6s^1). The second (unprimed) 5D term is situated much higher, at about $45,000 \text{ cm.}^{-1}$, and must be regarded as the second member of a term sequence in 5D , as was first pointed out by Gieseler and Grotrian.¹⁴ But a third, still higher 5D term, in figure 1 at $52,000 \text{ cm.}^{-1}$, was published soon after by Meggers.¹⁵ Gieseler and Grotrian's beautiful result now became very doubtful, since this third 5D lay much too close to the second one to be regarded as a third series member. With the aid of the new theory the explanation of this becomes evident; the most prominent terms of (d^7s) in Fe II are 6D and 4D ; and we obtain by addition of an s electron, disregarding Pauli's principle:

$$\begin{array}{c} \text{Fe II: } d^7s \\ \text{Fe I: } d^7s,s \end{array} \left| \begin{array}{cc} \begin{array}{c} ^6D \\ \swarrow \quad \searrow \\ ^7D \quad ^5D \end{array} & \begin{array}{c} ^4D \\ \swarrow \quad \searrow \\ ^5D \quad ^3D \end{array} \end{array} \right.$$

This ordinary vector addition is, of course, only allowed provided the total quantum of the s electron is >4 . Whereas among the low terms we have only *one* 5D (viz., the lowest term of Fe), we will obtain *four* D terms of multiplicity 7, 5, 5, 3 among the higher terms. This is actually the case, as a glance on figure 1, shows. The two high 5D terms thus become second members of two series, one converging to 6D and the other to 4D . Quantitative proof will be given below.

The dropping out of the 7D term at the low total quantum numbers is a direct consequence of Pauli's equivalence principle, and as such entirely similar to the dropping out of the 3S at lowest values of n in the spectra of the alkaline earths, as was pointed out by the author¹⁶ in 1924.

The very high 3D term at $54,000 \text{ cm.}^{-1}$ was not given before. Since it is of importance for the identification of all these *four* D terms as (d^7s, s) to prove the existence of 3D , its combinations with two second set terms, viz., a^3F and b^3D' are given below:

		3D		
		53747.45	54066.80	54386.10
a^3F	31307.27	22440.18		
		4455.037 (2u)		
	31805.10	21942.35	22261.70	
		4556.128 (3)?	4490.768 (2u)	
	32134.02	21613.43	21932.78	22252.08
			4558.110 (1)	4492.693 (1u)
b^3D	38175.38	15572.07	15891.42	
		6419.988 (3u)	6290.968 (3u)	
	38478.07	15069.38	15388.73	15708.03
			6496.62 (3)	6364.384 (1)
	38995.77		15071.03	15390.33
				6495.796 (2)

This 3D furthermore combines in three lines with a^3D and with b^3F of the second set.

Figure 2 illustrates more closely our identifications of the terms of Fe I and their way of approaching the low terms of Fe II. The terms of the second (middle) set are not drawn in, as no higher series members with $5z$, etc., electrons are known.

The crucial test is obviously the Rydberg formula. Since we know the differences between the spark terms, i.e., between the series limits, we have more empirical data than available constants. We shall work only with the sublevels of each term which has the highest j value.

(1) D series:

(α) a^5D and b^5D ; Gieseler-Grotrian series.

(In the author's old notation d^1 and d^2 , in that of Meggers A and T .)

$$a^5D_4 - b^5D_4 = 44,677.$$

$$\text{Hence } a^5D_4 - {}^6D_5^+ = 65,523 \quad \text{Rydberg corr. } \mu = 0.294$$

(β) a^5D and c^5D (in the notation of Meggers A and T')

$$a^5D_4 - c^5D_4 = 51,350$$

$$a^5D_4 - {}^4D_4^+ = 73,587 \quad \text{Rydberg corr. } \mu = 0.221$$

(2) F series:

(α) a^5F and b^5F (in the old notation of the author $\bar{f}^1$ and $\bar{f}^2$, in that of Meggers B and U),

$$a^5F_5 - b^5F_5 = 40,077$$

$$a^5F_5 - {}^4F_5^+ = 59,880 \quad \mu = 0.353.$$

a^3F and b^3F . (In the author's notation a^3F is $\bar{F}^1$, in that of Meggers C .) The term b^3F was not known before; the author predicted its position according to the above-explained ideas. The new term, b^3F , combines with almost every term of the second set, always giving weak lines; for its proof only the combinations with 3G and with a^3F may be given

		3F		
		47960.89	48531.82	48928.33
3G	35379.23	12581.66		
		7945.89 (7)		
	35767.59	12193.30	12764.23	
		8198.97 (2)	7832.24 (6)	
	36079.39	11881.6	12452.40	12848.94
			8028.37 (2)	7780.65 (5)
b^3F	36686.20	11274.74	11845.62	
		8866.94 (3)	8439.58 (3)	
	37162.76	10798.13	11369.06	11765.57
		9258.49	8793.37 (2)	8497.00 (2)
	37521.18		11010.64	11407.15
			9079.63	8763.97

Since the term value of a^3F_4 with respect to a^5D_4 is 11,976, the distance between the two alleged series members becomes $47,961 - 11,976 = 35,985$.

$$a^3F_4 - b^3F_4 = 35,985$$

$$a^3F_5 - {}^4F_5^+ = 54,767 \quad \mu = 0.415.$$

We have now obtained in four independent ways the distances of various arc and spark terms. By means of an application of the combination principle these distances can be reduced to the first ionization potential, namely, ${}^5D_4 - {}^6D_5^+$. Figure 2 will illustrate this procedure.

We obtain from (1 α)

$$a^5D_4 - {}^6D_5^+ = 65,523.$$

According to Russell's analysis of Fe^+ , we have

$${}^6D_5^+ - {}^4D_4^+ = 7955$$

hence from (1 β)

$$a^5D_4 - {}^6D_5^+ = 65,632.$$

The third value is deducible from (2 α) by means of the term difference in the arc spectrum

$$a^5D_4 - a^5F_5 = 6928$$

and one in the spark spectrum (Russell):

$${}^6D_5 - {}^6F_5 = 1873$$

we thus obtain:

$$a^5D_4 - {}^6D_5^+ = 64,935.$$

The term sequence in 3D_3 approaches the same limit ${}^6D_5^+$, as an application of Pauli's coördination rule shows. We obtain from (2 β), since the arc spectrum term difference

$$a^5D_5 - a^3D_4 = 11,976$$

a fourth value

$$a^5D_4 - {}^6D_5^+ = 64,870.$$

We may take as unweighted mean 65,240 which corresponds to an ionization of 8.06 volts.

We wish to leave undecided whether the above agreement of four independently obtained values is an argument against Gieseler and Grotrian's value $65,994 \pm 20 \text{ cm.}^{-1}$, and consequently against their third member of the series. In general we arrive at a confirmation of their idea about series in Fe.

The whole method resembles very much that applied by C. C. Kiess

and the author¹⁷ to the spectra of Cr, with the only difference that in Fe the spark spectrum is sufficiently investigated (Russell), whereas in Cr the discovered series regularities were used to find the normal state of Cr⁺.

Figure 2 shows how this procedure can be extended and how more series may be found. Thus two P terms will occur, which, together with the two low terms 5P and 3P at 20,000 form a series converging to ${}^4P(d^7)$. It is interesting to note in this connection, that since ${}^5F - {}^5P$ is almost equal to ${}^4F - {}^4P$ the sequence $n{}^5P$ will have the same Rydberg correction as has $n{}^5F$.

We are in agreement with a rule brought forward by Kiess and the author that the transition from arc to spark spectrum is always caused by a loss of an s electron,¹⁸ and furthermore confirm our identification of the k values of the terms in Fe I and Fe II, which to a certain extent deviated from that of Hund. Hund ascribed the 4F and 4P terms in Fe II, whose existence he was forced to assume from the second set terms of the arc spectrum, to the configuration (d^6s) instead, as we did, to (d^7) . The occurrence of terms belonging to the type (d^z) — z being the number of valence electrons—is an interesting and common phenomenon in first spark spectra; in several (e.g., Cr⁺, V⁺, Cu⁺?) they even exceed the terms of the other types, $(d^{z-1}s)$ and $(d^{z-2}s^2)$, in stability, and furnish the normal state.

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³ O. Laporte, *Zs. Physik*, **23**, 135; **26**, 1, 1924.

⁴ H. N. Russell and F. A. Saunders, *Astrophys. J.*, **61**, 38, 1925.

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⁶ W. Pauli, *Zs. Physik*, **31**, 765, 1925.

⁷ W. F. Meggers, *Astrophys. J.*, **60**, 60, 1924.

⁸ W. Grotrian, *Naturwissenschaften*, 1925.

⁹ O. Laporte, loc. cit.³

¹⁰ H. N. Russell, *Science*, 1924. From today's theoretical viewpoint this distinction appears as the only justified one. One should denote the terms of the second set, e.g., by a dot or circumflex, and abolish the dashes and primes entirely.

¹¹ O. Laporte, *Nature*, May 22, 1926.

¹² H. N. Russell, *Astrophys. J.*, **61**, 1925; *Mount Wilson Contrib.* No. 286, page 52. The writer is deeply indebted for the permission of using all his unpublished material on Fe II.

¹³ H. N. Russell and F. A. Saunders, *Astrophys. J.*, **61**, 60, 1925.

¹⁴ Gieseler and W. Grotrian, *Zs. Physik*, **25**, 165, 1924.

¹⁵ W. F. Meggers, loc. cit.⁷

¹⁶ *Zs. Physik*, **26**, 1, 1924, vide page 18.

¹⁷ C. C. Kiess and O. Laporte, *Science*, **63**, 234, 1926.

¹⁸ Loc. cit.