# Spin-dependent interactions in Mn III $3d^5$ †

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An energy-level calculation of the $3d^5$ configuration of Mn III is carried out, including eleven newly observed energy levels. The calculation takes into account the "weak" spin-dependent interactions, namely the spin-other-orbit, the spin-spin, and the effective electrostatic-spin-orbit interactions, which are of special importance in the half-filled $3d$ shell. An excellent fit between the calculated and observed energy levels is obtained, with a mean error of 7 $cm^{-1}$, and a mean "$o$-$c$ spread" of 3 $cm^{-1}$ per multiplet. A ratio between effective electrostatic-spin-orbit interaction parameters $Q^2$ and $Q^4$ is established for the first time.

In a recent paper[1] we have presented the results of a systematic investigation on the effects of spin-dependent interactions (SDI) on the energy-level schemes of the $3d^N$ configurations ($N=2,\ldots,8$) in the third spectra of the iron group. The SDI considered, in addition to the ordinary spin-orbit interaction, were the spin-other-orbit (SOO), the spin-spin (SS), and the effective electrostatic-spin-orbit (effective EL-SO) interactions. The parameters $M^k$ ($k=0,2$) representing the mutual magnetic SOO and SS interactions were found to be decreasing functions of $k$. It is to be expected from the definition of the $Q^k$'s ($k=2,4$), which represent the effective EL-SO interaction [Eq. (11) of Ref. 1], that they, also, should be decreasing functions of $k$, since they involve the Slater parameters $R^k$, which are found to have this property. Nevertheless, in Ref. 1 the $Q^k$'s were constrained to be equal to each other in the least-squares procedure. This constraint was deduced from the following facts: (i) The values obtained for $Q^4$ in the separate least-squares calculations for each ion had large uncertainties and did not show a regular behavior along the row of the $3d^N$ configurations. (ii) Within these uncertainties, the $Q^4$ values were roughly the same as the corresponding values of $Q^2$.

The spectrum of Mn III $3d^5$, in the middle of the row, is of special interest as far as the SDI are concerned. The $3d$ shell is half-filled, and therefore the diagonal matrix elements of the spin-orbit interaction vanish. Consequently, the multiplet splittings are largely determined by the SDI. However, the experimental data for Mn III $3d^5$ used in Ref. 1 were rather limited, comprising only the terms $^4G$, $^4_3P$, $^4D$ (three levels), and $^4_3F$ (the $^6S$ term was omitted in Ref. 1 because of the large deviation from its calculated value). After the completion of the above-mentioned work, additional energy levels of Mn III $3d^5$ have been observed,[2] comprising the fourth level of $^4D$ and the $^2_5D$, $^2_3F$, $^2_3H$, $^2_5G$, $^2_5F$, and $^2_3D$ terms. We can now take advantage of the large number of experimentally known multiplets and of the special importance of the SDI in this configuration, and carry out a new energy-level calculation in order to determine the ratio $Q^4/Q^2$. The least-squares calculation involves ten free parameters. Of these, five represent the electrostatic interaction; these are the Racah parameters $A$, $B$, and $C$ [which are linear combinations of the Slater parameters $F^k(dd)$] and the two-electron effective interaction parameters $\alpha$ and $\beta$. The values of the three-electron effective interaction parameters $T$ and $T_x$ were taken from the general-least-squares (GLS) calculation of Ref. 1 and were fixed during the calculation, because in a half-filled shell they are (to a good approximation) linear combinations of the other electrostatic parameters. The other five parameters represent all the interactions that are spin dependent; that is, the spin-orbit parameter $\zeta$, the SOO and SS interaction parameters $M^0$ and $M^2$, and the effective EL-SO interaction parameters $Q^2$ and $Q^4$. There are 10 experimental terms that split into 27 levels. The five electrostatic parameters are determined by the 10 terms, while the five spin-dependent parameters are determined by the 17 multiplet splittings. A preliminary calculation resulted in a mean error of 27 $cm^{-1}$. It turned out that this large error is mainly due to the inclusion of the $^2_3D$ term in the least-squares calculation. A final calculation was therefore carried out, in which the $^2_3D$ term was not included. The deletion of this term drastically reduced the deviations $o_i-c_i$ of all the other levels, thus resulting in a mean error of 7 $cm^{-1}$. The results obtained are given in Tables I–III.

Table I includes the calculated energy levels, together with the observed levels, the deviations between the observed and the calculated levels ($o_i-c_i$), and the composition percentages of the eigenstates. It can be seen that the remaining

TABLE I. Observed and calculated energy levels of Mn III $3d^5$, in $cm^{-1}$.

| Term composition | $J$ | Obs. | Calc. | $o-c$ | $o-c$ spread | $o-c$ | $o-c$ spread without SDI |
|---|---|---|---|---|---|---|---|
| $^6S$ 100% | $\frac{5}{2}$ | (0.0) [a] | −298 | (298) | | | |
| $^4G$ 100% | $\frac{11}{2}$ | 26 824.5 | 26 828 | −3 | | −32 | |
| 100% | $\frac{9}{2}$ | 26 852.4 | 26 855 | −3 | 1 | −9 | 54 |
| 100% | $\frac{7}{2}$ | 26 860.3 | 26 863 | −3 | | 9 | |
| 100% | $\frac{5}{2}$ | 26 856.9 | 26 859 | −2 | | 22 | |
| $^4_3P$ 97% | $\frac{5}{2}$ | 29 168.9 | 29 161 | 8 | | 7 | |
| 98% | $\frac{3}{2}$ | 29 207.6 | 29 202 | 6 | 4 | 7 | 5 |
| 99% | $\frac{1}{2}$ | 29 243.0 | 29 239 | 4 | | 2 | |
| $^4D$ 100% | $\frac{7}{2}$ | 32 308.9 | 32 306 | 3 | | −2 | |
| 97% | $\frac{5}{2}$ | 32 385.7 | 32 383 | 3 | | −3 | |
| 98% | $\frac{3}{2}$ | 32 384.0 | 32 385 | −1 | 5 | 1 | 17 |
| 99% | $\frac{1}{2}$ | 32 368.9 | 32 365 | 4 | | 14 | |
| $^2I$ 99% | $\frac{11}{2}$ | | 39 230 | | | | |
| 100% | $\frac{13}{2}$ | | 39 233 | | | | |
| $^2_5D$ 58% + $^2_3F$ 22% + $^2_1D$ 19% | $\frac{5}{2}$ | 41 238.1 | 41 247 | −9 | | −3 | |
| $^2_5D$ 73% + $^2_1D$ 24% | $\frac{3}{2}$ | 41 569.8 | 41 580 | −10 | 1 | −17 | 14 |
| $^2_3F$ 98% | $\frac{7}{2}$ | 42 606.5 | 42 607 | 0 | | −10 | |
| $^2_3F$ 72% + $^2_5D$ 14% | $\frac{5}{2}$ | 43 105.4 | 43 109 | −4 | 4 | 8 | 18 |
| $^4_3F$ 99% | $\frac{9}{2}$ | 43 574.2 | 43 580 | −6 | | 0 | |
| 99% | $\frac{7}{2}$ | 43 604.2 | 43 608 | −4 | | 0 | |
| 90% | $\frac{5}{2}$ | 43 670.5 | 43 673 | −2 | 4 | −2 | 14 |
| 96% | $\frac{3}{2}$ | 43 675.6 | 43 678 | −2 | | −14 | |
| $^2_3H$ 92% | $\frac{9}{2}$ | 46 515.9 | 46 508 | 8 | | 17 | |
| 99% | $\frac{11}{2}$ | 46 670.7 | 46 661 | 10 | 2 | 1 | 16 |
| $^2_5G$ 99% | $\frac{7}{2}$ | 47 842.0 | 47 845 | −3 | | −15 | |
| 91% | $\frac{9}{2}$ | 48 005.2 | 48 011 | −6 | 3 | 2 | 17 |

TABLE I. *(Continued)*

| Term Composition | $J$ | Obs. | Calc. | $o-c$ | $o-c$ spread | $o-c$ $o-c$ spread without SDI | |
|---|---|---|---|---|---|---|---|
| $^2_5F$ 99% | $\frac{5}{2}$ | 51 002.7 | 50 994 | 9 | 2 | 19 | 21 |
| 99% | $\frac{7}{2}$ | 51 059.7 | 51 053 | 7 | | −2 | |
| $^2S$ 100% | $\frac{1}{2}$ | | 55 651 | | | | |
| $^2_3D$ 100% | $\frac{3}{2}$ | (61 580.2)[a] | 61 481 | (99) | | (148) | |
| 100% | $\frac{5}{2}$ | (61 603.8)[a] | 61 495 | (109) | | (95) | |
| $^2_3G$ 100% | $\frac{9}{2}$ | | 68 782 | | | | |
| 100% | $\frac{7}{2}$ | | 68 764 | | | | |
| $^2_3P$ 100% | $\frac{3}{2}$ | | 83 088 | | | | |
| 100% | $\frac{1}{2}$ | | 83 071 | | | | |
| $^2_1D$ 76% + $^2_5D$ 24% | $\frac{5}{2}$ | | 89 411 | | | | |
| $^2_1D$ 75% + $^2_5D$ 24% | $\frac{3}{2}$ | | 89 395 | | | | |

[a] Not included in the calculation.

(small) $o$-$c$ deviations are nearly the same for all the levels belonging to the same multiplet, which means that they are of electrostatic origin. This fact is reflected by the quantity named "$o$-$c$ spread," which was introduced in Ref. 1 as a measure of that part of the deviations which is spin dependent. The $o$-$c$ spreads of the various multiplets range from 1 cm$^{-1}$ ($^4G$, $^2_5D$) to 5 cm$^{-1}$ ($^4D$) with an average of 3 cm$^{-1}$ per multiplet, which is very small (see Table I).

In order to bring out the importance of the SDI, an additional energy-level calculation has been carried out, in which these interactions were excluded. The $o_i$-$c_i$ increased considerably, resulting in a mean error of 14 cm$^{-1}$. As could be expected, the absence of the SDI affected even more the $o$-$c$ spreads, which range in this case from 5 cm$^{-1}$ ($^4_3P$) to 54 cm$^{-1}$ ($^4G$), with an average $o$-$c$ spread of 20 cm$^{-1}$ per multiplet. The $o_i$-$c_i$ and the $o$-$c$ spreads of this calculation are listed in the last two columns of Table I.

The importance of the SDI in reproducing the correct multiplet structure is clearly seen in the case of $^4G$. The $o$-$c$ spread of this term, when excluding the SDI, is 54 cm$^{-1}$, which is larger than its over-all experimental splitting (36 cm$^{-1}$). The inclusion of the SDI reduces the $o$-$c$ spread of $^4G$ to 1 cm$^{-1}$. The same fact can also be seen by considering the detailed structure of this term.

TABLE II. Interaction-parameter values of Mn III $3d^5$.

| Parameter | Value (cm$^{-1}$) |
|---|---|
| $A$ | 31 471 ± 9 |
| $B$ | 916.2 ± 0.3 |
| $C$ | 3486.8 ± 1.1 |
| $\alpha$ | 31.93 ± 0.20 |
| $\beta$ | −470.6 ± 2.1 |
| $T$ | −4.63 (fixed) |
| $T_x$ | −1.77 (fixed) |
| $\zeta$ | 320.4 ± 2.5 |
| $M^0_{SS}=M^0_{SOO}$ | 1.465 ± 0.219 |
| $M^2_{SS}=M^2_{SOO}$ | 0.789 ± 0.270 |
| $Q^2$ | 44.6 ± 8.2 |
| $Q^4$ | 27.7 ± 15.8 |

TABLE III. Spin-dependent interaction parameters of Mn III $3d^5$, in cm$^{-1}$.

| Parameter | Value | GLS 2 value[a] | Hartree-Fock value[b] |
|---|---|---|---|
| $\zeta$ | 320 ± 2 | 318 | 333 |
| $M^0_{SS}=M^0_{SOO}$ | 1.465 ± 0.219 | 1.452 | 1.433 |
| $M^2_{SS}=M^2_{SOO}$ | 0.789 ± 0.270 | 0.808 | 0.783 |
| $Q^2$ | 44.6 ± 8.2 | 40.5 | ... |
| $Q^4$ | 27.7 ± 15.8 | | ... |

[a] See Ref. 1.
[b] See Ref. 3.

Experimentally, it is roughly an inverted term: $(^4G_{11/2} - {}^4G_{5/2})_{obs} = -32\ cm^{-1}$ (as is also reproduced by the calculation including the SDI). On the other hand, the calculation in which the SDI are excluded results in a roughly "normal" $^4G$: $(^4G_{11/2} - {}^4G_{5/2})_{calc} = 22\ cm^{-1}$.

Table II includes the values of the various interaction parameters. As seen from this table, the values of the $Q^k$'s decrease with $k$, as was expected, the ratio $Q^4/Q^2$ being 0.62.

In Table III the values of all the spin-dependent interaction parameters, including $\zeta$, obtained in the present work are compared with those resulting from GLS 2 of Ref. 1 and also with the corresponding values calculated using the Hartree-Fock method.[3] The excellent agreement between the three sets of parameters is further evidence of the reliability of the results obtained in this work.

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