Calculations of Configurations of Doubly Ionized Copper (Cu III)

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The energy levels belonging to the configurations $3d^{7}4s^{2}$ and $3d^{8}n^f$ ($n^f = 4s, 5s, 4p, 5p, 4d, 5d, 4f$, and $5g$) have been calculated. The radial energy integrals were treated as parameters and adjusted to give a least-squares fit to the observed levels. Two- and three-body effective electrostatic interactions for equivalent electrons were included, as well as two-body effective interactions for inequivalent electrons. Strong configuration interaction between $3d^{7}4s^{2}$ and $3d^{8}4d$ was taken into account. Values of the parameters are given for all the above configurations, and the calculated levels are given for all except $3d^{8}4s$ and $3d^{8}4p$ (for which essentially equivalent results have been published). Leading eigenvector percentages are given in appropriate coupling schemes.

Key words: Atomic energy levels; atomic spectra; atomic theory; copper; doubly ionized copper; electron configuration.

1. Introduction

A great extension of the analysis of Cu III has recently been achieved by Shenstone [1]. In this work he determined nearly all the levels of the configurations $3d^{7}4s^{2}$ and $3d^{8}n^f$ for $n^f = 4d, 5d, 5s, 6s, 5p, 4f$, and much of $3d^{8}5g$. In the course of this analysis we provided calculations of the level structures and continually refined them as new data were obtained. The final result is a set of calculations for all the known configurations of this ion (with the exception of $3d^{7}4s4p$) that are internally consistent so far as common radial integrals (parameters) are concerned and that include all the effective electrostatic interactions, as well as the usual Slater and spin-orbit interactions, that have so far been considered in the iron group.

2. Method

Calculations of the energy matrices for these configurations, as well as the matrix diagonalizations and level fitting, were carried out on the NBS Univac 1108 computer. The computer programs were originally obtained from the Laboratoire Aimé Cotton (Orsay, France). Successive diagonalizations and variations of the radial parameters were performed until a least-squares fit of the energy levels was achieved. Final values for the parameters, the standard error for each parameter, and the rms error of the least-squares fit for each configuration are given in table 1. (See ref. [2], for example, for more details of the general procedure.) The rms error is defined as

$$[\sum_{i=1}^{n} \delta_i^2/(n-m)]^{1/2},$$

where $\delta$ is the difference between the experimental and calculated positions for a level, $n$ is the number of levels used in the fitting, and $m$ is the number of free parameters. The standard error for a parameter value (in parentheses following the value) indicates how well the value is “defined” by the equations and the experimental levels.

In our initial calculations we were guided by the theoretical study of the even configurations of the third spectra of the iron group by Shadmi, Caspi, and Oreg [3] and by a similar work on the odd configurations by Roth [2]. These papers included calculations of the almost completely known $3d^{n}4s$ and $3d^{n}4p$ configurations of Cu III. Most of the parameters we use, including the effective two-body interactions ($\alpha$ and $\beta$) and three-body interactions ($T$ and $T_x$) for equivalent electrons, are defined in these papers or in reference [4]. In addition we introduced the two-body effective interactions for inequivalent electrons, denoted here as $D^k$ and $X^k$. 
Table 1. Fitted radial parameters for configurations of Cu III. Units are cm$^{-1}$. Standard errors are given in parentheses except for those parameters whose values were fixed in the least-squares calculation.

| Parameter | $3d^4s$ | $3d^45s$ | $3d^46s$ | $3d^4p$ | $3d^5p$ | $3d^4d$ | $3d^5d$ | $3d^4f$ | $3d^5g$ | $3d^4s^2$ |
|-----------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| $A$       | 74956(28) | 204843(40) | 249188(41) | 145275(67) | 231897(38) | 208143(74) | 251877(38) | 245483(25) | 268577(17) | 186606(98) |
| $B$       | 12074.3(3.4) | 12343.4(4.3) | 12311.3(3.7) | 12179.3(3.8) | 12373.1(19) | 12355.2(9.2) | 12379.1(1.8) | 12471.1(1.0) | 1247(1.0) | 12949.7(5.5) |
| $C$       | 5024(28) | 5059(36) | 5115(24) | 5006(11) | 5051(24) | 5073(13) | 50674(7.2) | 49.2(0.9) | 49.2(0.9) | 53.16(49) |
| $\alpha$  | 48.8(3.4) | 50.4(4.6) | 49.8(2.4) | 41.0(2.8) | 48.9(1.3) | 48.8(2.5) | 50.2(1.2) | 49.2(0.9) | 49.2(0.9) | 53.16(49) |
| $\beta$   | 7120.7(3.4) | 12343.4(4.3) | 12311.3(3.7) | 12179.3(3.8) | 12373.1(19) | 12355.2(9.2) | 12379.1(1.8) | 12471.1(1.0) | 1247(1.0) | 12949.7(5.5) |
| $T$       | -5.63 | -5.63 | -5.63 | -5.63 | -5.63 | -5.63 | -5.63 | -5.63 | -5.63 | -5.63 |
| $T_e$     | 5024(28) | 5059(36) | 5115(24) | 5006(11) | 5051(24) | 5073(13) | 50674(7.2) | 49.2(0.9) | 49.2(0.9) | 53.16(49) |
| $F^2$     | 9488(60) | 2292(95) | 819(80) | 6250(55) | 1643(35) | 2820(140) | 1412(62) | 87(120) | 195(91) | 195(91) |
| $F^4$     | 12074.3(3.4) | 12343.4(4.3) | 12311.3(3.7) | 12179.3(3.8) | 12373.1(19) | 12355.2(9.2) | 12379.1(1.8) | 12471.1(1.0) | 1247(1.0) | 12949.7(5.5) |
| $G^3$     | 9488(60) | 2292(95) | 819(80) | 6250(55) | 1643(35) | 2820(140) | 1412(62) | 87(120) | 195(91) | 195(91) |
| $G^4$     | -648(98) | -313(50) | -390(110) | -990(280) | -570(110) | -570(110) | -570(110) | -570(110) | -570(110) | -570(110) |
| $G^5$     | 901(15) | 901(24) | 918(10) | 1420(580) | 1450(520) | 910.8(6.7) | 911.7(5.1) | 907.7(3.4) | 913.7(6.0) | 973(25) |
| $X^2$     | 901(15) | 901(24) | 918(10) | 1420(580) | 1450(520) | 910.8(6.7) | 911.7(5.1) | 907.7(3.4) | 913.7(6.0) | 973(25) |
| $R^2(d^4d)$ | 53 | 32 | 10 | 72 | 34 | 4930(170) | 77 | 35 | 28 | 4930(170) |
| $R^2(d^4s^2)$ | 53 | 32 | 10 | 72 | 34 | 4930(170) | 77 | 35 | 28 | 4930(170) |
| rms dev.  | 53 | 32 | 10 | 72 | 34 | 4930(170) | 77 | 35 | 28 | 4930(170) |
for the direct and exchange parts [5]. We found these to be significant for the $3d^4p$, $3d^5p$ and $3d^4d$ configurations.

3. Parameters of the $3d^8$ Core

All configurations treated except $3d^44s^2$ are built on the $3d^8$ core. It is evident from the parameter values (table 1) that the core parameters are little affected by the additional outer electron of these configurations. The electrostatic parameters $B$, $C$, and $\alpha$ were freely varied in all cases except $3d^85g$; their fitted values are nearly identical for each configuration. The seniority parameter $\beta$ could be meaningfully evaluated only for $3d^44s$ and $3d^44p$, for which the doublet built on the $3d^8 1s^2$ core state is now known [1]. Its value was nearly the same in both cases and was also close to the value derived by Shadmi et al. [3] in their general treatment of the third spectra. It was therefore fixed at the value $-496$ cm$^{-1}$, derived from $3d^85s$, in all configurations of Cu III. Since most of the $3d^85g$ levels known with certainty are based on the $3p^6$ core term, all core parameters except the spin-orbit parameter $\zeta(3d)$ were fixed at average values derived from the other configurations. The fitted value of $\zeta(3d)$ for each of the $3d^8nl$ configurations was practically unchanged.

The effective 3-body parameter $T$ includes the interaction of $3s^33d^8$ with $3s3d^9$ and has a non-zero matrix element only for the $1D$ state of $3d^8$. This parameter cannot be freely determined for $3d^8$ because the number of core parameters exceeds the number of core terms; we therefore fixed it at the value $-5.63$ cm$^{-1}$ deduced by Shadmi et al. [3]. The significance of $T$ is demonstrated by the fact that the omission of this particular parameter leads to values for the parameters $C$, $\alpha$, and $\beta$ of the $3d^8nl$ configurations that are totally inconsistent with those derived from the general treatment of third spectra in references [2] and [3]. The second three-body parameter $T_x$, had no effect on the $d^8nl$ configurations and was omitted. This parameter was included for $3d^44s^2$, where (along with $T$) it is an independent interaction. It was not possible to obtain meaningful fitted values for $T$ and $T_x$ in $3d^44s^2$, probably because their effect is small and this configuration is strongly distorted by near-configuration interaction. The fixed values used for them were estimated from the results of Shadmi et al. [3].

4. The Two-Body Effective Interaction for Inequivalent Electrons

The interaction is represented here by the parameters $D_k$ and $X_k$ calculated according to the formulas of Goldschmidt and Starkand [5]. They are the coefficients of the scalar products of unit operators, $D_k$ for the direct and $X_k$ for the exchange interaction. The allowed parameters for $d^8p$ are $D^1$ and $X^2$, and for $d^8d$ they are $D^1$, $D^2$, $X^1$, and $X^3$. In the case of $3d^44p$ and $3d^5p$ both effective parameters are well defined by a least-squares fit. Only $D^1$ and $D^2$ were defined for $3d^4d$, perhaps because the far-configuration effects were partly masked by the interaction with $3d^44s^2$. Our attempts to include this type of interaction by least-squares fits in the other configurations of Cu III were unsuccessful, but it is surely important for all $3d^44p$ and $3d^44d$ configurations of the iron period.

5. Results

An indication of the success of these calculations is the low rms error reached for all configurations (table 1), always less than 100 cm$^{-1}$ and usually much less. This is particularly significant for the highly mixed $3d^44d$ and $3d^44s^2$ configurations where large deviations present in single-configuration calculations are considerably reduced by the introduction of a single parameter $R^2(d^8,ss)$ for configuration interaction. The inclusion of the effective parameters $D_k$ and $X_k$ in the $3d^44d$ configuration appears to be their first use for $3d^44d$. As a further test we introduced them in a calculation of $3d^44d$ of V III and found a reduction of the rms error from 117 cm$^{-1}$ reported by Spector [6] to 67 cm$^{-1}$. We repeated the calculation of $3d^44p$ of Cu III by Roth [2] who obtained an rms error of 126 cm$^{-1}$; with the inclusion of $D^1$ and $X^2$ the rms error was reduced to $72$ cm$^{-1}$ (table 1).

Tables 2 through 8 contain the calculated levels obtained with the parameters of table 1. (The $3d^44s$ and $3d^44p$ results are not included because they are essentially the same as appear in references [2] and [3].)

All observed levels are from Shenstone [1], the values being rounded off to the nearest cm$^{-1}$. Observed levels followed by a question mark were so denoted by Shenstone to indicate that these levels may not be real. The “Leading Percentages” refer to squared eigenvector components given as percentages following the term symbols, and rounded off to the nearest percent. The “average %” given at the end of a “Leading Percentage” column is the average purity of the levels for the indicated coupling scheme. The $3d^8$ parent terms for LS-coupling designations are given in parentheses.

5.1. ($3d^44d + 3d^44s^2$) and $3d^45s$

The calculated levels for these even configurations are in tables 2 and 3, respectively. The two leading percentages in LS coupling are given for each level, any second percentage less than 0.5 percent being omitted. In table 2, the two $3d^44s^2$ 2$D$ terms are labeled 1 and 2 as in Nielson and Koster [7].

Shenstone [1] has described his method of assigning LS names to the levels, beginning with the $3d^8$, $3d^8s$, and $3d^44p$ levels and proceeding to name the levels

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1 These authors use the notations $-F$ and $-G$ for the parameters here designated $D^p$ and $X^s$, respectively ($k=4$).
2 With $T$ omitted, these parameters take the following values for Cu III $3d^44s$: $C = 4686 (28)$ cm$^{-1}$, $\alpha = 91(3)$ cm$^{-1}$, and $\beta = -45(36)$ cm$^{-1}$.
3 The following values were obtained for V III by least-squares fitting: $D^1 = -728(88)$ cm$^{-1}$, $D^2 = -1099(200)$ cm$^{-1}$, $X^1 = -327(100)$ cm$^{-1}$, and $X^3 = -678(170)$ cm$^{-1}$.
| J   | Levels (cm⁻¹) | O–C | Leading percentages | Remarks |
|-----|---------------|-----|---------------------|---------|
|     | Observed      | Calculated |                  |         |
| 1/2 | 189695        | 193945       | ¹P 95            | ²P 3    |
|     | 195723        | 195743       | ²P 91            | ¹P 9    |
|     | 197200        | 197198       |                    |         |
|     | 198034        | 198041       |                    |         |
|     | 211286        | 211296       |                    |         |
|     | 212209        | 212137       |                    |         |
|     | 213142        | 213148       |                    |         |
|     | 215762        | 215730       |                    |         |
|     | 216834        | 216794       |                    |         |
| 3/2 | 169608        | 169571       | ¹F 99            |         |
|     | 194684        | 194670       | ²P 91            | ³P 8    |
|     | 196100        | 196095       | ²P 76            | ³D 2    |
|     | 196806        | 196745       | ²P 61            | ³F 10   |
|     | 197986        | 198005       | ²P 19            | ³D 14   |
|     | 201732        | 201751       | ²P 51            | ³F 27   |
|     | 21124         | 211073       | ²P 48            | ³P 19   |
|     | 211652        | 211634       | ²P 74            | ³F 26   |
|     | 213312        | 213264       | ²P 61            | ³P 20   |
|     | 215197        | 215172       | ²P 25            | ³D 4    |
|     | 215807        | 215758       | ²P 24            | ³D 2    |
|     | 218235        | 216063       | ²P 172           | ³F 19   |
|     | 224504        | 224479       | ²P 92            | ³D 4    |
|     | 240176        | 256250       | ²P 92            | ³D 4    |
| 5/2 | 168857        | 168834       | ²P 98            | ³F 2    |
|     | 193885        | 193911       | ²P 56            | ³F 30   |
|     | 195340        | 195255       | ²P 51            | ³F 28   |
|     | 196220        | 196232       | ²D 59            | ³D 37   |
|     | 196731        | 196768       | ²P 34            | ³D 30   |
|     | 197901        | 197932       | ²P 49            | ³D 24   |
|     | 198061        | 198070       | ²P 56            | ³D 24   |
|     | 201215        | 201118       | ²P 79            | ³D 13   |
|     | 210159        | 210205       | ²P 45            | ³D 23   |
|     | 211680        | 211172       | ²P 34            | ³D 19   |
|     | 213134        | 213117       | ²P 51            | ³D 19   |
|     | 213515        | 213317       | ²P 73            | ³D 19   |
|     | 214990        | 214952       | ²P 45            | ³D 23   |
|     | 215100        | 215042       | ²P 83            | ³F 23   |
|     | 216145        | 216146       | ²P 77            | ³F 23   |
|     | 216376        | 216448       | ²P 68            | ³F 22   |
|     | 221879        | 221882       | ²P 98            | ³F 22   |
|     | 223787        | 223869       | ²P 73            | ³D 23   |
|     | 240945        | 256273       | ²P 99            | ³D 23   |
| 7/2 | 167739        | 167741       | ²F 100           |         |
|     | 189603        | 189616       | ²G 98            | ³F 2    |
|     | 193521        | 193536       | ²P 93            | ³D 24   |
|     | 195344        | 195374       | ²D 53            | ³F 24   |
|     | 196742        | 196740       | ²F 36            | ³D 24   |
|     | 197055        | 197063       | ²F 47            | ³D 24   |
|     | 197594        | 197605       | ²F 40            | ³D 24   |
|     | 198930        | 198988       | ²F 81            | ³D 24   |
|     | 210240        | 210309       | ²F 69            | ³D 24   |
Table 2. Calculated energy levels and leading percentages (LS coupling) for the interacting 3d^44d and 3d^44s^2 configurations. States of 3d^44s^2 are distinguishable by the absence of parentage. The meaning of the letters under “Remarks” is explained in the text (5.1) — Continued

| J         | Levels (cm\(^{-1}\)) | O–C (cm\(^{-1}\)) | Leading percentages | Remarks |
|-----------|----------------------|-------------------|---------------------|---------|
|           |                      |                   |                     |         |
|           | Observed             | Calculated        |                     |         |
| 1/2       | 211217               | 211271            | 54                  | (^3)D^F^G 83 (^3)P^F^F 10 |
|           | 212752               | 212860            | –108                | (^3)P^F^F 72 (^3)D^F^F 19 |
|           | 213816               | 213988            | –172                | (^3)F 56 (^3)P^F^F 23 |
|           | 214845               | 214901            | –56                 | (^3)P^F^F 90 (^3)D^F^F 3 |
|           | 215977               | 216090            | –113                | (^3)P^F^F 65 (^3)D^F^F 2 |
|           | 221861               | 221876            | –15                 | (^3)G^F^F 98 (^3)D^F^F 1 |
|           | 223174               | 223190            | –24                 | (^3)G^F^F 99 (^3)D^F^F 1 |
| 9/2       | 166160               | 166210            | –50                 | (^3)F 99 |
|           | 188098               | 188116            | –18                 | (^3)G 94 (^3)H 3 |
|           | 195062               | 195086            | –24                 | (^3)F^G^F 39 (^3)F^F^F 36 |
|           | 195518               | 195415            | 103                 | (^3)F^F^F 33 (^3)F^F^F 21 |
|           | 196029               | 196167            | –138                | (^3)H 30 (^3)F^G^F 23 |
|           | 196796               | 196675            | 121                 | (^3)F^F^H 65 (^3)F^G^F 18 |
|           | 197376               | 197573            | –197                | (^3)F^F^G 49 (^3)F^G^F 26 |
|           | 198687               | 198561            | 126                 | (^3)F^F^H 60 (^3)H 26 |
|           | 211314               | 211259            | 55                  | (^3)D^F^G 82 (^3)P^F^F 16 |
|           | 214748               | 214782            | –34                 | (^3)P^F^F 83 (^3)D^G^F 16 |
|           | 223090               | 223101            | –11                 | (^3)G^F^H 91 (^3)G^F^G 9 |
|           | 223201               | 223217            | –16                 | (^3)G^F^G 90 (^3)G^F^H 9 |
| 11/2      | 194033               | 194017            | 16                  | (^3)F^F^H 51 (^3)H 35 |
|           | 194818               | 194816            | 2                   | (^3)F^G^F 68 (^3)F^H^G 27 |
|           | 195758               | 195745            | 13                  | (^3)F^H^H 41 (^3)H 31 |
|           | 197039               | 197000            | 39                  | (^3)F^F^H 47 (^3)H 31 |
|           | 220311               | 220291            | 20                  | (^3)G^F^F 100 |
|           | 223175               | 223173            | 2                   | (^3)G^F^F 100 |
| 13/2      | 194332               | 194320            | 12                  | (^3)F^H^F 100 |
|           | 220414               | 220379            | 35                  | (^3)G^F^F 100 |

This level was found by Shenstone after publication of his paper [1]. The more exact value is 196220.49 cm\(^{-1}\).

Table 3. Calculated energy levels and leading percentages (LS coupling) for the 3d^55s configuration.

| J         | Levels (cm\(^{-1}\)) | O–C (cm\(^{-1}\)) | Leading percentages |
|-----------|----------------------|-------------------|---------------------|
|           |                      |                   |                     |         |
|           | Observed             | Calculated        |                     |         |
| 1/2       | 213418               | 213408            | 10                  | (^3)P^P^P 98 (^3)P^P^P 2 |
|           | 214730               | 214709            | 23                  | (^3)P^P^P 98 (^3)P^P^P 2 |
|           |                      | 254805            |                     |         |
| 3/2       | 196442               | 196406            | 36                  | (^3)F^F 99 (^3)D^D 1 |
|           | 210033               | 210035            | –2                  | (^3)D^P 86 (^3)P^P^P 10 |
|           | 213127               | 213155            | –28                 | (^3)P^P^P 94 (^3)D^D 5 |
|           | 214265               | 214256            | 29                  | (^3)P^P^P 90 (^3)D^D 8 |
| 5/2       | 195555               | 195524            | 31                  | (^3)F^F 89 (^3)F^F 11 |
|           | 197400               | 197444            | –44                 | (^3)F^F^F 88 (^3)F^F^F 11 |
|           | 209875               | 209860            | 15                  | (^3)D^D^P 77 (^3)P^P^P 22 |
|           | 212951               | 212995            | –44                 | (^3)P^P^P 78 (^3)D^D 22 |
| 7/2       | 194117               | 194140            | –23                 | (^3)F^F 64 (^3)F^F^F 36 |
|           | 195789               | 195792            | –3                  | (^3)F^F 64 (^3)F^F^F 36 |
|           | 220569               | 220566            | 3                   | (^3)G^G^G 100 |
| 9/2       | 193371               | 193363            | 8                   | (^3)F^F^P 100 |
|           | 220564               | 220565            | –1                  | (^3)G^G^G 100 |

Average % ____________________________________________ 89

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| J  | Levels (cm⁻¹) | O-C (cm⁻¹) | Leading percentages |
|----|---------------|-------------|---------------------|
|    | Observed      | Calculated  | LS                   |
| 1/2|    |             |             | (L,S,)(J,J) | 3F₃,3/2 | 99 |
|    | 215161       | 215155      | 6           | (F)D | 99  |
|    | 229054       | 229142      | -88         | (D)P | 75  |
|    | 231298?      | 231304      | -6          | (P)P | 91  |
|    | 232620       |             |             | (P)D | 97  |
|    | 233591       |             |             | (P)P | 86  |
|    | 234189       |             |             | (P)S | 95  |
|    | 273668       |             |             | (S)P | 100 |
|    |              |             |             | (S)₁/₂ | 100 |
| 3/2|    |             |             | (F)D | 88  |
|    | 214358       | 214351      | 7           | (F)F | 90  |
|    | 215783       | 215777      | 6           | (F)F | 90  |
|    | 216449       | 216463      | -14         | (F)D | 90  |
|    | 228469       | 228465      | 4           | (D)P | 57  |
|    | 229430       | 229430      | 75          | (D)P | 55  |
|    | 231438       | 231429      | 29          | (P)P | 73  |
|    | 232478?      | 232499      | -21         | (P)D | 87  |
|    | 232814       | 232847      | -33         | (P)P | 85  |
|    | 233654       | 233581      | 73          | (P)P | 87  |
|    | 234036       | 234059      | -23         | (P)F | 90  |
|    | 274085       |             |             | (S)P | 100 |
|    |              |             |             | (S)₁/₂ | 100 |
| 5/2|    |             |             | (F)D | 73  |
|    | 213026       | 213024      | 2           | (F)F | 39  |
|    | 214703       | 214704      | -1          | (F)F | 38  |
|    | 214766       | 214768      | -2          | (F)D | 38  |
|    | 215417       | 215410      | 7           | (F)G | 60  |
|    | 216566       | 216583      | -17         | (F)F | 76  |
|    | 228424       | 228436      | -12         | (D)P | 52  |
|    | 228960       | 228962      | -2          | (D)F | 62  |
|    | 231333       | 231371      | -38         | (P)P | 72  |
|    | 232458       | 232391      | 67          | (P)D | 71  |
|    | 233057       |             |             | (P)D | 75  |
|    | 239149       | 239125      | 24          | (G)F | 99  |
|    |              |             |             | (G)₁/₂ | 99  |
| 7/2|    |             |             | (F)D | 91  |
|    | 211821       | 211821      | 0           | (F)F | 36  |
|    | 213312       | 213313      | -1          | (F)F | 36  |
|    | 214328       | 214327      | 1           | (F)G | 59  |
|    | 215000       | 214998      | 2           | (F)F | 46  |
|    | 216018       | 216030      | -12         | (F)G | 65  |
|    | 229098       | 229074      | 24          | (D)F | 81  |
|    | 223436       | 223499      | -52         | (P)D | 82  |
|    | 238834       | 238829      | 5           | (G)F | 98  |
|    | 240786       | 240786      | 0           | (G)G | 99  |
|    |              |             |             | (G)₁/₂ | 68  |
| 9/2|    |             |             | (F)D | 42  |
|    | 212415       | 212418      | -3          | (F)F | 67  |
|    | 212995       | 213004      | -9          | (F)F | 67  |
|    | 214588       | 214581      | 7           | (F)G | 56  |
|    | 238788       | 238807      | -19         | (G)H | 99  |
|    | 240853       | 240853      | 0           | (G)G | 99  |
| 11/2|    |             |             | (F)G | 74  |
|    | 212525       | 212510      | 15          | (F)H | 100 |
|    | 239142       | 239154      | -12         | (G)H | 100 |

Average % .............................................. 77 71

* This tentative level was not entered into the least-squares adjustment of the parameters. See text (5.2).
Table 5. Calculated energy levels and leading percentages for the 3d^86s configuration

| J   | Levels (cm⁻¹)       | O–C (cm⁻¹) | Leading percentages |
|-----|---------------------|------------|---------------------|
|     | Observed            | Calculated |                      |
| 1/2 | 258291              | 258785     |                     |
|     | 299796              |            |                     |
| 3/2 | 241392              | 241135     | 7                   |
|     | 254694              | 254703     | −9                  |
|     | 258046              | 258380     |                     |
| 5/2 | 240326              | 240330     | −4                  |
|     | 241694              | 241699     | −5                  |
|     | 254640              | 254630     | 10                  |
|     | 257866              | 257887     | −1                  |
| 7/2 | 238638              | 238629     | 9                   |
|     | 240303              | 240306     | −3                  |
|     | 265293              | 265294     |                     |

Average %........................................................................ 84 85

Table 6. Calculated energy levels and leading percentages for the 3d^85d configuration

| J   | Levels (cm⁻¹)       | O–C (cm⁻¹) | Leading percentages |
|-----|---------------------|------------|---------------------|
|     | Observed            | Calculated |                      |
| 1/2 | 240764              | 240806     | −42                 |
|     | 241900              | 241901     | −1                  |
|     | 242247              | 242272     | −25                 |
|     | 255515              | 255851     |                     |
|     | 258312              | 259847     |                     |
| 3/2 | 239327              | 239311     | 16                  |
|     | 240795              | 240834     | −39                 |
|     | 241328              | 241334     | −6                  |
|     | 242219              | 242222     | −3                  |
|     | 244619              | 244535     | 84                  |
|     | 255562              |            |                     |
|     | 255750              | 255756     | −5                  |
|     | 258386              | 258931     |                     |
|     | 259830              |            |                     |
|     | 259957              |            |                     |
|     | 260426              |            |                     |
| 5/2 | 267310              | 267320     | −10                 |
|     | 300578              |            |                     |

Average %........................................................................ 84 85

Table 6. Calculated energy levels and leading percentages for the 3d^85d configuration

| J   | Levels (cm⁻¹)       | O–C (cm⁻¹) | Leading percentages |
|-----|---------------------|------------|---------------------|
|     | Observed            | Calculated |                      |
| 1/2 | 388819              | 388835     | −16                 |
|     | 240063              | 240042     | 21                  |
|     | 240995              | 240982     | 13                  |
|     | 242007              | 241987     | 20                  |
|     | 242290              | 242279     | 11                  |
|     | 243780              | 243755     | 25                  |
|     | 255176              | 255686     | 7                   |
| 3/2 | 238819              | 388835     | −16                 |
|     | 240063              | 240042     | 21                  |
|     | 240995              | 240982     | 13                  |
|     | 242007              | 241987     | 20                  |
|     | 242290              | 242279     | 11                  |
|     | 243780              | 243755     | 25                  |
|     | 255176              | 255686     | 7                   |
| 5/2 | 238819              | 238835     | −16                 |
|     | 240063              | 240042     | 21                  |
|     | 240995              | 240982     | 13                  |
|     | 242007              | 241987     | 20                  |
|     | 242290              | 242279     | 11                  |
|     | 243780              | 243755     | 25                  |
|     | 255176              | 255686     | 7                   |

Average %........................................................................ 84 85

Table 6. Calculated energy levels and leading percentages for the 3d^85d configuration

| J   | Levels (cm⁻¹)       | O–C (cm⁻¹) | Leading percentages |
|-----|---------------------|------------|---------------------|
|     | Observed            | Calculated |                      |
| 1/2 | 258291              | 258785     |                     |
|     | 299796              |            |                     |
| 3/2 | 241392              | 241135     | 7                   |
|     | 254694              | 254703     | −9                  |
|     | 258046              | 258380     |                     |
| 5/2 | 240326              | 240330     | −4                  |
|     | 241694              | 241699     | −5                  |
|     | 254640              | 254630     | 10                  |
|     | 257866              | 257887     | −1                  |
| 7/2 | 238638              | 238629     | 9                   |
|     | 240303              | 240306     | −3                  |
|     | 265293              | 265294     |                     |

Average %........................................................................ 84 85
### Table 6. Calculated energy levels and leading percentages for the 3d^55d configuration—Cont.

| J     | Levels (cm⁻¹) | O–C       | Leading percentages |
|-------|---------------|-----------|---------------------|
|       | Observed      | Calculated| LS                  | \((L_S) J J [K]\) |
| 7/2   | 266092        | 266088    | 4                   | \((G) F F 99 \ G_{5/2} 72\) |
|       | 267034        | 267094    | -63                 | \((G) F D 91 \ G_{3/2} 67\) |
|       | 300561        |           |                     | \((S) D 100 \ S_{5/2} 100\) |
| 9/2   | 238731        | 238774    | -43                 | \((F) F D 86 \ F_{5/2} 49\) |
|       | 239441        | 239439    | 2                   | \((F) F F 59 \ F_{5/2} 49\) |
|       | 241074        | 241069    | 5                   | \((F) G 44 \ F_{3/2} 91\) |
|       | 241250        | 241250    | 0                   | \((F) H 71 \ F_{3/2} 88\) |
|       | 242089        | 242053    | 36                  | \((F) G 69 \ F_{5/2} 69\) |
|       | 242610        | 242666    | -56                 | \((D) F F 77 \ D_{5/2} 66\) |
|       | 255173        | 255162    | 11                  | \((D) G G 83 \ D_{3/2} 71\) |
|       | 255487        | 255486    | 39                  | \((P) F D 80 \ P_{5/2} 54\) |
|       | 256199        | 256199    | 0                   | \((P) F F 80 \ P_{3/2} 53\) |
|       | 259018        | 258986    | 32                  | \((P) F F 81 \ P_{5/2} 44\) |
|       | 260680        | 260687    | 7                   | \((G) F F 100 \ G_{3/2} 52\) |
|       | 266643        | 266649    | -6                  | \((G) G 100 \ G_{3/2} 52\) |

**Average %..........................................................** 72 68

### Table 7. Calculated energy levels and leading percentages for the 3d^44f configuration

| J     | Levels (cm⁻¹) | O–C       | Leading percentages |
|-------|---------------|-----------|---------------------|
|       | Observed      | Calculated| LS                  | \((L_S) J J [K]\) |
| 1/2   | 234531        | 234510    | 21                  | \(3F_{1}[1] 100 \ F F S 45\) |
|       | 236324        | 236319    | 5                   | \(3F_{1}[1] 75 \ F F F D 40\) |
|       | 236371        | 236368    | 3                   | \(3F_{1}[0] 74 \ F F P 42\) |
|       | 237591        | 237586    | 5                   | \(3F_{1}[1] 99 \ F F P 36\) |
|       | 251062        |            |                     | \(D_{5/2} 83 \ D F P 83\) |
|       | 254662        |            |                     | \(F_{2}[1] 84 \ F F F P 84\) |
|       | 260986        |            |                     | \(G_{1}[1] 100 \ G F P 100\) |
| 3/2   | 234427        | 234458    | -31                 | \(3F_{1}[1] 84 \ F F P 49\) |
|       | 234661        | 234649    | 12                  | \(3F_{1}[2] 84 \ F F F 48\) |
|       | 236395        | 236405    | -10                 | \(3F_{1}[1] 71 \ F F F D 36\) |
|       | 236485        | 236488    | -3                  | \(3F_{1}[2] 71 \ F F F 39\) |
|       | 237559        | 237563    | -24                 | \(3F_{1}[1] 74 \ F F F P 36\) |
|       | 237734        | 237733    | 1                   | \(3F_{1}[2] 74 \ F F D 41\) |
|       | 250942        |            |                     | \(D_{2}[2] 81 \ D F F 81\) |
|       | 251070        |            |                     | \(D_{2}[1] 83 \ D F P 83\) |
|       | 254178        |            |                     | \(F_{2}[2] 72 \ P F F 87\) |
| 5/2   | 234491        | 234489    | 2                   | \(3F_{1}[2] 88 \ F F D 45\) |
|       | 234775        | 234771    | 4                   | \(3F_{1}[3] 88 \ F F D 50\) |
| J       | Levels (cm⁻¹) | O - C (cm⁻¹) | Leading percentages |
|---------|--------------|--------------|---------------------|
|         |              |              | (L₃S₃J₃/₁K₃)       | LS       |
|         |              |              | L, S, l, J/₁K      |          |
|         | Observed     | Calculated   |                     |          |
| 7/2     | 234562       | 234566       | -4                  |          |
|         | 234813       | 234802       | 11                  |          |
|         | 236512       | 236494       | 18                  |          |
|         | 236611       | 236607       | 4                   |          |
|         | 237731       | 237761       | -10                 |          |
|         | 250734       | 250732       | 2                   |          |
|         | 250818       | 250859       | -41                 |          |
|         | 254132       | 254103       | 29                  |          |
|         | 254221       |              |                     |          |
|         | 254772       | 254737       | 35                  |          |
|         | 254927       | 254914       | 13                  |          |
|         | 255131       |              |                     |          |
|         | 261563       | 261508       | 55                  |          |
|         | 261763       | 261798       | -35                 |          |
| 9/2     | 234655       | 234674       | -19                 |          |
|         | 234775       | 234753       | 22                  |          |
|         | 236337       | 236529       | 8                   |          |
|         | 236550       | 236656       | -15                 |          |
|         | 237645       | 237613       | 32                  |          |
|         | 237779       | 237789       | -10                 |          |
|         | 250734       | 250730       | 4                   |          |
|         | 251000       | 250946       | 54                  |          |
|         | 253831       | 254070       | -39                 |          |
|         | 254449       | 254508       | -59                 |          |
|         | 254784       | 254729       | 55                  |          |
|         | 261757       | 261800       | -43                 |          |
|         | 261996       | 261966       | 30                  |          |
| 11/2    | 234681       | 234695       | -14                 |          |
|         | 234717       | 234752       | -35                 |          |
|         | 236419       | 236407       | 12                  |          |
|         | 236532       | 236540       | -8                  |          |
|         | 237641       | 237645       | -4                  |          |
|         | 251011       | 250949       | 62                  |          |
|         | 254468       | 254492       | -24                 |          |
|         | 261829       | 261837       | -17                 |          |
|         | 261998       | 261969       | 20                  |          |
| 13/2    | 234533       | 234553       | -20                 |          |
|         | 234671       | 234670       | 1                   |          |
|         | 236418       | 236403       | 15                  |          |
|         | 261710       | 261159       | 11                  |          |
|         | 261812       | 261843       | -31                 |          |
| 15/2    | 234337       | 234520       | 17                  |          |
|         | 261168       | 261165       | 3                   |          |

Average % .................................................................................. 88 67
| J   | Levels (cm⁻¹) | O−C (cm⁻¹) | Leading percentages |
|-----|---------------|-------------|---------------------|
| 1/2 |               |             | (L,S,) J, j [K]     |
|     | Observed      | Calculated  |                     |
| 1/2 | 257495        | 257407      | 88                  |
|     | 257491        | 257391      |                     |
|     | 284186        | 284229      |                     |
| 3/2 | 257560        | 257540      | 19                  |
|     | 257584        | 259363      |                     |
|     | 259433        | 259376      | 57                  |
|     | 260612        | 273899      |                     |
|     | 277499        | 284219      |                     |
|     | 284303        |             |                     |
| 5/2 | 257489        | 257464      | 25                  |
|     | 257672        | 257673      | 1                   |
|     | 259441        | 259463      | 7                   |
|     | 260545        | 260724      |                     |
|     | 273812        | 273899      |                     |
|     | 277466        | 277633      |                     |
|     | 284291        | 284410      |                     |
| 7/2 | 257515        | 257506      | 9                   |
|     | 257668?       | 257701      |                     |
|     | 259421        | 259565      |                     |
|     | 260625        | 260741      |                     |
|     | 273724        | 273843      |                     |
|     | 277176        | 277361      |                     |
|     | 277650        | 277744      |                     |
|     | 277996        | 284403      |                     |
|     | 284542        | 318914      |                     |
| 9/2 | 257574?       | 257546      | 28                  |
|     | 257626        | 257655      |                     |
|     | 259403?       | 259414      |                     |
|     | 259480        | 260654      |                     |
|     | 260676?       | 273692      |                     |
|     | 273807        | 277141      |                     |
|     | 277236        | 277630      |                     |
|     | 277866        | 284539      |                     |
|     | 284662        | 318908      |                     |
| 11/2| 257531        | 257575      | 44                  |
|     | 257556        | 257586      |                     |
|     | 259404        | 259415      |                     |
|     | 259418        | 259434      |                     |
|     | 260591        | 260564      |                     |

Table 8. Calculated energy levels and leading percentages for the 3d⁵5g configuration.
of the higher configurations on the basis of the relative intensities of their transitions. His designations are usually in agreement with our calculations for those levels whose assigned eigenvectors yield meaningful LS names. As examples of the nature of such discrepancies as exist, we have added a column to table 2 for remarks on the designations of the levels. (Shenstone draws attention to the \((3d^8 4d + 3d^7 4s^2)\) group in this connection.) The eigenvectors for the observed levels in table 2 given without a letter in the final column confirm the names assigned by Shenstone.\(^5\) The letters in the final column have the following meanings:

A. The leading component of the eigenvector indicates a designation different from that assigned by Shenstone.

B. The eigenvector yields no theoretically satisfactory single-configuration single-term designation.\(^5\)

C. Indicates pairs of neighboring levels whose eigenvectors might possibly be interchanged.

The low \(3d^8(2F) 4d\) \(4P\) and \(4D\) terms overlap, but the \(4D\) term is lower according to our calculations; this accounts for the first six “A” notations in the table. The several B notations for the \(J = 9/2\) and \(J = 11/2\) levels mainly arise because of the strong admixtures of \(3d^7 4s^2\) \(2H\) components, which are so distributed amongst these levels that no level for either \(J\) value can meaningfully be assigned to this term. The very similar compositions of the \(J = 11/2\) levels at 194033 and 197039 cm\(^{-1}\) may be noted; these prevent a designation for either level according to our criteria.

5.2. \(3d^85p\), \(3d^86s\), and \(3d^85d\).

The results for these configurations are given in tables 4, 5, and 6. The leading percentage for each level is given in LS coupling and in a \((L, S_1, J, K)_{1/2}\) coupling scheme. The notations for the latter scheme have the
3d<sup>n</sup> parent level (in LS coupling) followed by the j value of the outer electron. Most of the levels have meaningful names in either scheme. The average purity in LS coupling is a little higher than the J<sub>1</sub><sub>j</sub> purity (3d<sup>n</sup>5p and 3d<sup>n</sup>5d), or the purities in the two schemes are practically equal (3d<sup>n</sup>6s); the LS names are probably more generally useful.

Shenstone assigned some 25 odd levels to the 3d<sup>f</sup>4s4p configuration [1]. We calculated this large configuration, but the results of the level fitting were inconclusive because of the lack of sufficient data. Shenstone assigned a tentative level at 232990 cm<sup>-1</sup> to 3d<sup>f</sup>7(4F)4s4p (3P<sup>0</sup>) 2D<sub>3/2</sub> and a level at 233286 cm<sup>-1</sup> to 3d<sup>g</sup>8(3P)5p 2D<sub>5/2</sub>. The lower of these levels is closer to our prediction for 3d<sup>f</sup>8 (3P) 5p 2D<sub>5/2</sub> but we used neither level in the least-squares calculations. Although the good fit obtained for the 3d<sup>n</sup>5p levels indicates that the general configuration interaction with 3d<sup>f</sup>4s4p is weak, the closeness of these two 2D<sub>5/2</sub> levels might result in significant configuration mixing.

5.3. 3d<sup>n</sup>4f and 3d<sup>n</sup>5g

Shenstone pointed out that the level structure of the 3d<sup>n</sup> parent configuration could usually be discerned in the pattern of the 3d<sup>n</sup>nl levels. "In 5g the scheme [in which the parent J value is defined] reaches an extreme which makes it possible to identify some, but not all of the levels. In fact, the number of combinations of a level is reduced in most cases to just two . . . " A small number of combinations is one effect of pair coupling and, as is evident from tables 7 and 8, the 3d<sup>n</sup>4f and 3d<sup>n</sup>5g configurations are best described by the J<sub>1</sub><sub>j</sub> coupling scheme. The designations for this scheme have the 3d<sup>n</sup> parent level (L, S, and J) preceding the bracketed K value (obtained by coupling J<sub>1</sub> and the l vector of the outer electron) [8]. Shenstone was able to deduce LS names for the 4f and 5g levels in some accordance with the intensities of their transitions, but many of the LS designations have meaning only in that connection. Only two of the eigenvectors for 3d<sup>n</sup>4f have leading percentages less than 50 percent in J<sub>1</sub><sub>j</sub> coupling, whereas there are 23 such eigenvectors in LS coupling; for 3d<sup>n</sup>5g, the equivalent numbers are 4 and 26.

6. References

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