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Detailed Crossover Studies of Transition Metal Ions

I. The Octahedral and Tetrahedral d^4 and d^6 Electron Configurations

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The complete ligand field, interelectronic repulsion, and spin-orbit interaction matrices were solved for the octahedral and tetrahedral d^4 and d^6 electron configurations. The results are employed in a detailed study of the crossover region. It is demonstrated that, close to the crossover, complicated mixing and interaction patterns may arise. A sharp crossover is encountered in the octahedral d^6 system exclusively where Γ_1 and Γ_5 levels are involved. In all situations where the two ground levels transform according to the same irreducible representation, the crossover is redefined by that value of $10Dq$ where both ground terms participate in the lowest level to equal amounts.

Die vollständigen Matrizen des Ligandenfeldes, der Elektronenwechselwirkung und der Spin-Bahn-Kopplung wurden für die Elektronenkonfigurationen d^4 und d^6 in Feldern oktaedrischer und tetraedrischer Symmetrie diagonalisiert. Die Ergebnisse werden in einer eingehenden Untersuchung des "crossover"-Bereiches eingesetzt. Es wird gezeigt, daß komplizierte Mischungs- und Wechselwirkungsstrukturen in der Nähe des Überschneidungspunktes der Grundterme auftreten können. Ein scharfer Schnittpunkt wird allein im oktaedrischen d^6-System erhalten, wobei die Niveaus Γ_1 und Γ_5 unmittelbar beteiligt sind. In allen Fällen, in denen sich die zwei tiefsten Niveaus der zwei Grundterme nach derselben irreduziblen Darstellung transformieren, wird der Überschneidungspunkt durch denjenigen Wert von $10Dq$ neu definiert, bei dem beide Grundterme zum tiefsten Niveau zu gleichen Teilen beitragen.

1. Introduction

It is a peculiar property of the d^4, d^5, d^6, and d^7 electron configurations in a field of octahedral symmetry that, depending on field strength, one of two possible ground terms may be stabilized. The two terms are characterized by a different symmetry transformation property and a different value of the total spin S. A similar situation is encountered with the configurations d^4, d^5, and d^6 within tetrahedral symmetry. The concept of spin-pairing energy [1] has been introduced as the particular value of the octahedral or tetrahedral ligand field splitting parameter $\Delta = 10Dq$ at the crossover of ground terms. However, the spin-pairing energy is well defined only as far as spin-orbit interaction is completely neglected.

The effect of spin-orbit coupling is, in general, to produce an additional splitting of all but a few terms and to give rise to a significant interaction between the levels thus formed. The interaction becomes the more marked the more the crossover is being approached. Under specific circumstances, complicated splitting and interaction patterns may arise which may extend over an energy range of $1000\ \text{cm}^{-1}$ or more. As a consequence, the original crossover concept becomes much less well founded than usually assumed and, in some cases, a modified definition of the crossover is called for.

Recently [2], we have considered in some detail the disposition of the lowest-energy spin-orbit levels in an octahedral d^6 ion close to the $^5T_2 - {}^1A_1$ crossover of ground terms. Additional studies demonstrate that this particular situation is one of the most simple ones to be expected. In the present investigation, we therefore examine the octahedral and tetrahedral d^4 and d^6 electron configurations side by side. The results should exemplify the complications arising close to the crossover and should serve to stimulate more accurate physical measurements on suitable transition metal containing systems. To this end and in contrast to our earlier study [2], values of the interelectronic repulsion parameters will be employed which should facilitate direct comparison with experiment.

2. Calculation Procedures and Results

The calculations including the ligand field, interelectronic repulsion, and spin-orbit interaction were performed within the complete configuration interaction approach. The appropriate Hamiltonian may be written

$$\mathcal{H} = \sum_i \left\{ -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{Ze^2}{r_i} + \kappa \zeta_i \boldsymbol{l}_i \cdot \boldsymbol{s}_i \right\} + \sum_{i>j} \frac{e^2}{r_{ij}} + V_{LF} \tag{1}$$

where the summation extends over the d electrons and where all the quantities have their usual meaning. Both the strong-field and the weak-field methods were applied, and complete agreement of all results was achieved. In the strong-field approach, the methods outlined by Griffith [3] were generally followed. These procedures were described in detail previously [2, 4]. In the weak-field approach, use has been made of Racah algebraic methods, and these we have briefly delineated elsewhere [4]. The complete octahedral and tetrahedral d^4 and d^6 electron problems thus generate, within the strong-field as well as in the weak-field approach, an overall 91×91 matrix. The resulting secular problems which may be partly factorized on the basis of symmetry were solved. From the results, eigenvalues and eigenvectors pertinent to the lowest energy levels in the direct neighborhood of the crossover were extracted.

It is well known that octahedral and tetrahedral fields give rise to a splitting into the same groups of levels, e and t_2, although their order is inverted and the sign of their separation is reversed, viz.

$$Dq_{\text{tet}} = -\tfrac{4}{9} Dq_{\text{oct}} \,. \tag{2}$$

Since confusion is not likely to occur, we will drop the suffix of Dq used in Eq. (2), negative values indicating always tetrahedral Dq and positive values indicating octahedral Dq. The sign changes of Dq and ζ required in applications of the matrices to the problems at hand have been discussed elsewhere [4].

Fig. 1 shows the central region of the complete ligand field and spin-orbit interaction diagram for an octahedral d^4 electron system and, in Fig. 2, the cor-

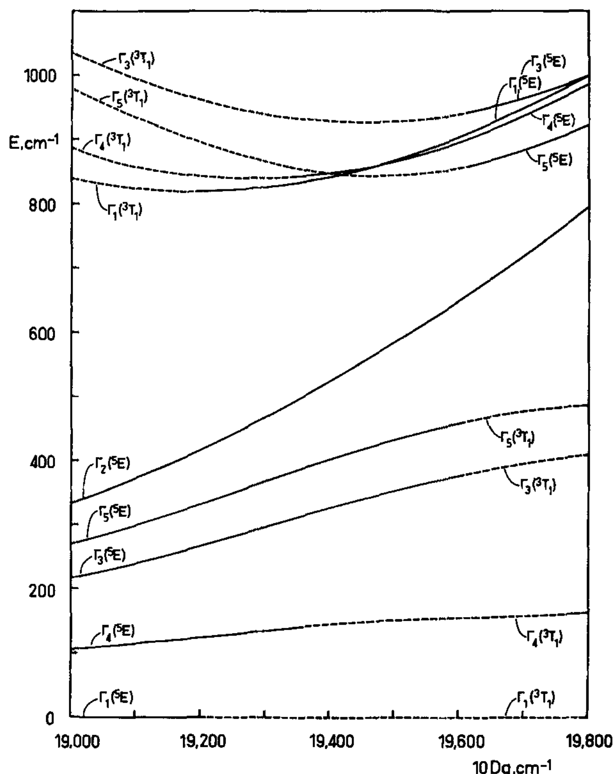

Fig. 1

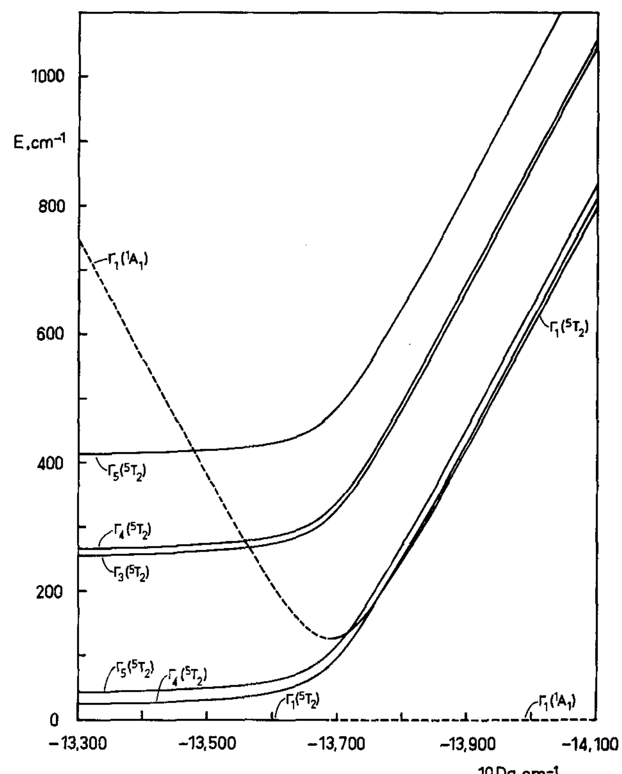

Fig. 2

Fig. 1. Lowest energy levels originating in the terms ^5E (t_2^3 ($^4A_2$) e) (full lines) and $^3T_1$ (t_2^4) (broken lines) of an octahedral d^4 system ($B = 800$ cm^{-1}, $C = 4B$, $\zeta = 290$ cm^{-1}) in the region of the crossover (i.e. $10Dq = 19210$ cm^{-1})

Fig. 2. Lowest energy levels originating in the terms $^5T_2$ (e^2 ($^3A_2$) t_2^2 ($^3T_1$)) (full lines) and $^1A_1$ (e^4) (broken line) of a tetrahedral d^4 system ($B = 800$ cm^{-1}, $C = 4B$, $\zeta = 290$ cm^{-1}) in the region of the crossover (i.e. $10Dq = -13689$ cm^{-1})

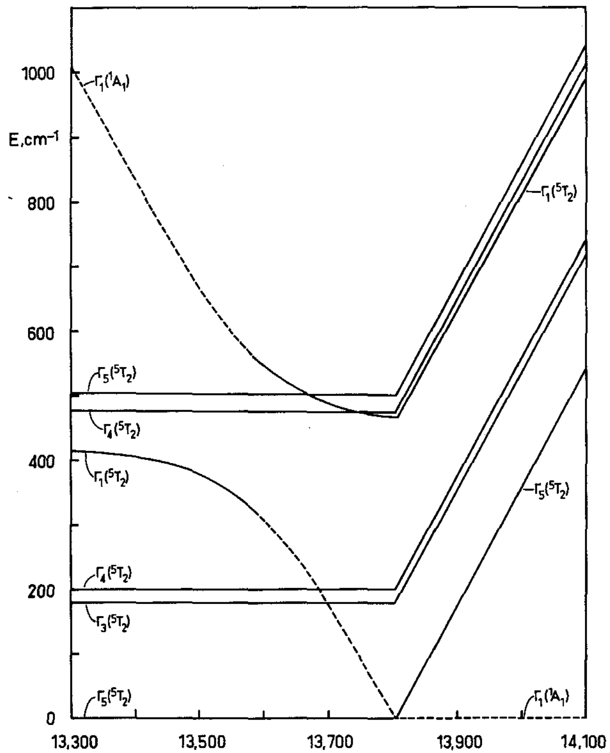

Fig. 3

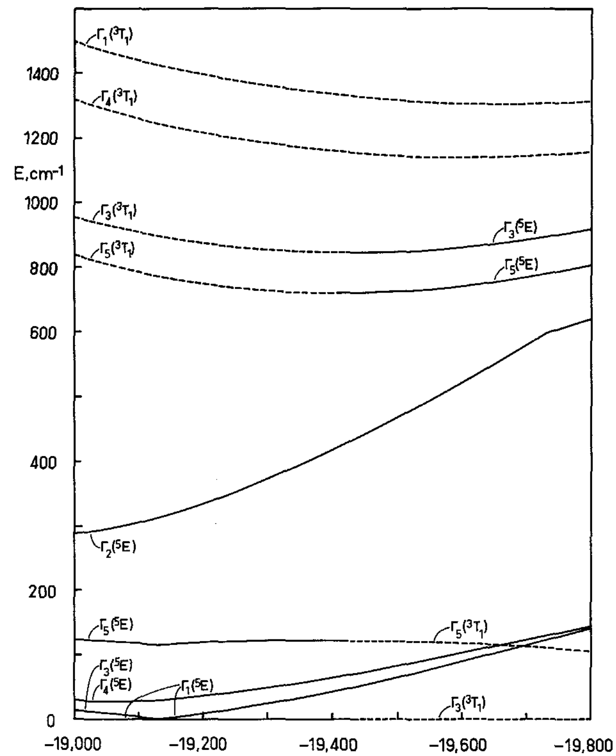

Fig. 4

Fig. 3. Lowest energy levels originating in the terms $^5T_2$ (t_2^4 ($^3T_1$) e^2 ($^3A_2$)) (full lines) and $^1A_1$ (t_2^6) (broken line) of an octahedral d^6 system ($B = 806$ cm^{-1}, $C = 4B$, $\zeta = 420$ cm^{-1}) in the region of the crossover (i.e. $10Dq = 13\,804.5$ cm^{-1})

Fig. 4. Lowest energy levels originating in the terms ^5E (e^3 t_2^3 ($^4A_2$)) (full lines) and $^3T_1$ (e^4 t_2^2) (broken lines) of a tetrahedral d^6 system ($B = 806$ cm^{-1}, $C = 4B$, $\zeta = 420$ cm^{-1}) in the region of the crossover (i.e. $10Dq = -19440$ cm^{-1})

responding plot for a tetrahedral d^4 ion is presented. The parameter values employed in the underlying calculations are $B=800\,cm^{-1}$, $C=4B$, and $\zeta=290\,cm^{-1}$ thus corresponding approximately to, e.g., a hexaquoion of Cr^{2+} or Mn^{3+}.[1] Fig. 3 and Fig. 4 display similar diagrams pertinent to the octahedral and tetrahedral d^6 electron configuration, respectively. Here we assumed $B=806\,cm^{-1}$, $C=4B$, and $\zeta=420\,cm^{-1}$ again corresponding roughly to the hexaquoions of Fe^{2+} and Co^{3+}.[2] The magnetic behavior of these systems has likewise been calculated and is discussed elsewhere [4]. The full ligand field and spin-orbit interaction diagrams for the octahedral and tetrahedral d^4 and d^6 electron configurations will be presented in a forthcoming publication [5].

3. Delineation of the Lowest Levels Close to the Crossover

Octahedral d^4 System

In the octahedral d^4 electron system, the two terms involved in the crossover are ${}^5E(t_2^3({}^4A_2)\,e)$ and ${}^3T_1(t_2^4)$, both being g on the basis of parity. The ${}^3T_1(t_2^4)$ term interacts with six higher energy ${}^3T_1$ terms via configuration interaction, while the ${}^5E$ is pure. If spin-orbit coupling is included, the splitting is according to ${}^3T_1 \rightarrow \Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5$ and ${}^5E \rightarrow \Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4 + \Gamma_5$. A peculiar property of the system is that, in the neighborhood of the crossover, all levels resulting from the two terms except Γ_2 are considerably mixed by spin-orbit interaction. With $10Dq$ approaching the crossover more closely, the amount of intermixing rises progressively. Thus, if $10Dq = 18\,700\,cm^{-1}$ is assumed, the lowest level Γ_1 at $0.0\,cm^{-1}$ consists of 75.17% $|{}^5E(t_2^3({}^4A_2)\,e)\rangle$, 24.06% $|{}^3T_1(t_2^4)\rangle$, and 0.77% various other contributions, whereas the Γ_1 level at $948.4\,cm^{-1}$ is composed of 73.08% $|{}^3T_1(t_2^4)\rangle$, 24.76% $|{}^5E(t_2^3({}^4A_2)\,e)\rangle$, and 2.16% other contributions, cf. Fig. 1. The next highest amount of intermixing arises with the Γ_4 levels, the lower one at $78.9\,cm^{-1}$ being essentially 83.13 % $|{}^5E(t_2^3({}^4A_2)\,e)\rangle$ and 16.35% $|{}^3T_1(t_2^4)\rangle$, whereas the higher one at $1018.3\,cm^{-1}$ is 80.79% $|{}^3T_1(t_2^4)\rangle$ and 16.82% $|{}^5E(t_2^3({}^4A_2)\,e)\rangle$. There is apparent, in addition, an appreciable mixing of the Γ_3 and Γ_5 levels of the two terms.

Consequently, *the actual crossover is much less well defined than, e.g., in the octahedral d^6 problem.* To clearly demonstrate this situation let us consider Fig. 1 again. The lowest level Γ_1 at $0.0\,cm^{-1}$ consists, at $10Dq = 19\,200\,cm^{-1}$, of 49.94% $|{}^5E(t_2^3({}^4A_2)\,e)\rangle$ and 48.63% $|{}^3T_1(t_2^4)\rangle$, whereas, at $10Dq = 19\,300\,cm^{-1}$, its composition is determined by 54.29% $|{}^3T_1(t_2^4)\rangle$ and 44.13% $|{}^5E(t_2^3({}^4A_2)\,e)\rangle$. If we decide to define the crossover by that value of $10Dq$ where, in the lowest Γ_1 level, equal contributions from the ${}^5E(t_2^3({}^4A_2)\,e)$ and ${}^3T_1(t_2^4)$ terms are involved, the crossover appears at $19\,210\,cm^{-1}$. However, we then have to accept the fact that in higher levels Γ_j, $j = 3, 4, 5$, the condition of equal contributions will be satisfied,

[1] We assumed $B_{free}(Cr^{2+}) = 899\,cm^{-1}$, $B_{free}(Mn^{3+}) = 1083\,cm^{-1}$ which values are based on a least square fit of the free ion spectra ($C_{free}(Cr^{2+}) = 3147\,cm^{-1}$, $C_{free}(Mn^{3+}) = 3916\,cm^{-1}$) and the nephelauxetic ratios $\beta = 0.88$ and $\beta = 0.75$ for $M(H_2O)_6^{n+}$ ions where $n=2$ and $n=3$, respectively. With $\zeta(Cr^{2+}) = 226\,cm^{-1}$ and $\zeta(Mn^{3+}) = 346\,cm^{-1}$, the above average values follow.

[2] We assumed $B_{free}(Fe^{2+}) = 916\,cm^{-1}$ based on a least square fit of the free ion sepctrum ($C_{free}(Fe^{2+}) = 3867\,cm^{-1}$) and $\beta = 0.88$ as above. The resulting $B = \beta \cdot B_{free}$ applies approximately also in a $Co(H_2O)_6^{3+}$ ion if $B_{free}(Co^{3+}) = 1100\,cm^{-1}$ and $\beta = 0.75$ are used. $\zeta = 420\,cm^{-1}$ is the free ion Fe^{2+} value.

in general, at higher values of $10Dq$. Thus, e.g., at $10Dq = 19300\ cm^{-1}$, the lower Γ_4 level (at $134.5\ cm^{-1}$) consists essentially of 53.44% $|^5E(t_2^3(^4A_2)\,e)\rangle$ and 45.26% $|^3T_1(t_2^4)\rangle$, whereas, at $10Dq = 19400\ cm^{-1}$, the composition of the Γ_4 level (now at $142.9\ cm^{-1}$) is 51.88% $|^3T_1(t_2^4)\rangle$ and 46.65% $|^5E(t_2^3(^4A_2)\,e)\rangle$, the "crossover" of the two Γ_4 levels then being at $19360\ cm^{-1}$. Likewise, at $10Dq = 19600\ cm^{-1}$, the lower Γ_3 level (at $375.5\ cm^{-1}$) is formed essentially of 51.70% $|^5E(t_2^3(^4A_2)\,e)\rangle$ and 46.91% $|^3T_1(t_2^4)\rangle$, whereas if $10Dq = 16700\ cm^{-1}$, the composition of that level (now at $395.5\ cm^{-1}$) is 55.07% $|^3T_1(t_2^4)\rangle$ and 43.30% $|^5E(t_2^3(^4A_2)\,e)\rangle$, the "crossover" of the Γ_3 levels resulting close to $19610\ cm^{-1}$. Finally, at $10Dq = 19600\ cm^{-1}$, the lower Γ_5 level (at $457.3\ cm^{-1}$) consists of 51.68% $|^5E(t_2^3(^4A_2)\,e)\rangle$ and 46.90% $|^3T_1(t_2^4)\rangle$, the corresponding values being, at $10Dq = 19700\ cm^{-1}$, 39.93% and 58.32%, respectively (level Γ_5 at $475.7\ cm^{-1}$). This then fixes the "crossover" of Γ_5 levels again close to $19610\ cm^{-1}$. Thus, in the example studied here, cf. the octahedral d^4 configuration, there is a region extending over about $400\ cm^{-1}$ (i.e. from $10Dq = 19210\ cm^{-1}$ to $19610\ cm^{-1}$) within that the levels Γ_j, $j = 1, 3, 4, 5$, resulting from the terms $^5E(t_2^3(^4A_2)\,e)$ and $^3T_1(t_2^4)$ cross[3].

Tetrahedral d^4 System

A considerably more simple situation is encountered if the d^4 electron system is subject to a field of tetrahedral symmetry. The ground terms involved are, in this case, $^1A_1(e^4)$ and $^5T_2(e^2(^3A_2)\,t_2^2(^3T_1))$, the $^1A_1(e^4)$ interacting with four higher energy $^1A_1$ terms via configuration interaction, whereas the $^5T_2(e^2(^3A_2)\,t_2^2(^3T_1))$ is pure. The splitting by spin-orbit interaction is according to $^5T_2 \to \Gamma_1 + \Gamma_3 + 2\Gamma_4 + 2\Gamma_5$ and $^1A_1 \to \Gamma_1$. Thus only the two Γ_1-levels are expected to be mixed via spin-orbit coupling. This is, indeed, clearly apparent from Fig. 2 where the lowest levels close to the crossover are displayed. In somewhat more detail then the intermixing is not significant at some distance from the crossover. If $10Dq = -13300\ cm^{-1}$, e.g., is assumed, the lowest level Γ_1 at $0.0\ cm^{-1}$ is 98.26% $|^5T_2(e^2(^3A_2)\,t_2^2(^3T_1))\rangle$, 0.99% $|^3T_1(e^3t_2)\rangle$, and only 0.59% $|^1A_1(e^4)\rangle$ etc., while the Γ_1 level at $745.8\ cm^{-1}$ is made up to 93.61% of $|^1A_1(e^4)\rangle$, 3.37% $|^1A_1(e^2(^1A_1)\,t_2^2(^1A_1))\rangle$, and no larger amount from the $^5T_2$ term. As the crossover is approached more closely the intermixing increases drastically. At $10Dq = -13680\ cm^{-1}$, the Γ_1 level at $0.0\ cm^{-1}$ is now composed of 54.47% $|^5T_2(e^2(^3A_2)\,t_2^2(^3T_1))\rangle$, 41.32% $|^1A_1(e^4)\rangle$, and 4.21% various other contributions. Conversely, the level Γ_1 at $127.5\ cm^{-1}$ consists of 53.27% $|^1A_1(e^4)\rangle$, 44.51% $|^5T_2(e^2t_2^2)\rangle$, and 2.22% other contributions. On the other hand, if $10Dq = -13700\ cm^{-1}$, the Γ_1 level at $0.0\ cm^{-1}$ consists of 55.32% $|^1A_1(e^4)\rangle$ and 39.84% $|^5T_2(e^2t_2^2)\rangle$, whereas the contributions to that at $128.9\ cm^{-1}$ are 39.29% and 59.13%, respectively. It follows that the crossover should be close to $10Dq = -13689\ cm^{-1}$. In the tetrahedral d^4 electron configuration then the crossover is rather *precisely defined* by that value of $10Dq$ where *equal contributions* from

[3] We would like to point out the fact that the contributions to the crossing levels are not reciprocal. The values listed above apply to the lower member of the pair in consideration. The contributions to the higher member of a pair are, in general, somewhat different due to additional mixing with higher energy levels.

the $^1A_1(e^4)$ and $^5T_2(e^2(^3A_2)\,t_2^2(^3T_1))$ terms are encountered in the lowest energy Γ_1 level. We would like to point out that both the two Γ_4 and the two Γ_5 levels originating in the $^5T_2$ ground term are highly intermixed, this mixing, however, is not particularly dependent on $10Dq$.

Octahedral d^6 System

The behavior of the octahedral d^6 electron system close to the crossover has been treated previously [2] and will be discussed here, therefore, only briefly. The terms involved in the crossover which are all g are $^1A_1(t_2^6)$ and $^5T_2(t_2^4(^3T_1)\,e^2(^3A_2))$, configuration interaction being the reason for mixing of the $^1A_1(t_2^6)$ and four higher $^1A_1$ terms, while the $^5T_2$ is pure. The splitting by spin-orbit coupling is according to $^5T_2 \rightarrow \Gamma_1+\Gamma_3+2\Gamma_4+2\Gamma_5$ and $^1A_1 \rightarrow \Gamma_1$ and thus only the two Γ_1 levels interact. The maximum of this interaction is observed at $10Dq = 13\,593\ \mathrm{cm}^{-1}$ (cf. Fig. 3) where the two levels $\Gamma_1[^1A_1(t_2^6)]$ and $\Gamma_1[^5T_2(t_2^4(^3T_1)\,e^2(^3A_2))]$ change their labels. The crossover, however, which is defined by the intersection of the former level with $\Gamma_5[^5T_2(t_2^4(^3T_1)\,e^2(^3A_2))]$ occurs at about $10Dq = 13\,804.5\ \mathrm{cm}^{-1}$. It should be noted that these two levels neither interact on the basis of spin-orbit coupling nor on that of configuration interaction. This is the reason that, of the four systems studied at present, the crossover is most precisely established in the octahedral d^6 electron configuration.

Tetrahedral d^6 System

Finally, we turn to the example of the tetrahedral d^6 electron system where the terms involved in the crossover are $^3T_1(e^4t_2^2)$ and $^5E(e^3t_2^3(^4A_2))$. The $^3T_1(e^4t_2^2)$ interacts with six higher $^3T_1$ terms on the basis of configuration interaction, whereas the ^5E is pure. The splitting due to spin-orbit coupling is according to $^3T_1 \rightarrow \Gamma_1+\Gamma_3+\Gamma_4+\Gamma_5$ and $^5E \rightarrow \Gamma_1+\Gamma_2+\Gamma_3+\Gamma_4+\Gamma_5$ having the consequence that all levels except Γ_2 interact at the crossover. The situation here is thus roughly similar to that in the octahedral d^4 system, although differences exist in detail. Again the amount of intermixing rises as $10Dq$ approaches the crossover. At $10Dq = -19\,100\ \mathrm{cm}^{-1}$, e.g., the lowest level Γ_1 at $0.0\ \mathrm{cm}^{-1}$ consists of 79.86% $|^5E(e^3t_2^3(^4A_2))\rangle$, 19.42% $|^3T_1(e^4t_2^2)\rangle$, and 0.72% various other contributions, whereas the Γ_1 level at $1442.0\ \mathrm{cm}^{-1}$ is formed of 77.13% $|^3T_1(e^4t_2^2)\rangle$, 20.02% $|^5E(e^3t_2^3(^4A_2))\rangle$, and 2.85% other contributions (cf. Fig. 4). An even higher amount of mixing is encountered in the Γ_3 levels, the lower one at only $2.94\ \mathrm{cm}^{-1}$ being essentially 67.35% $|^5E(e^3t_2^3(^4A_2))\rangle$ and 31.64% $|^3T_1(e^4t_2^2)\rangle$, whereas the higher energy counterpart at $905.9\ \mathrm{cm}^{-1}$ is 65.49% $|^3T_1(e^4t_2^2)\rangle$ and 32.57% $|^5E(e^3t_2^3(^4A_2))\rangle$. In addition, the Γ_4 and Γ_5 levels are likewise intermixed, the amount of mixing being intermediate between that of the Γ_1 and that of the Γ_3 level. At about $10Dq = -19\,130\ \mathrm{cm}^{-1}$ the lowest two levels, viz. Γ_1 and Γ_3, change their positions or, more accurately, Γ_1 is only $0.79\ \mathrm{cm}^{-1}$ above Γ_3 at this value of $10Dq$. The actual crossover then arises between the Γ_3 levels $\Gamma_3[^5E(e^3t_2^3(^4A_2))]$ and $\Gamma_3[^3T_1(e^4t_2^2)]$. If, in analogy to the octahedral d^4 system, the crossover is taken again as that value of $10Dq$ where equal contributions of these two levels are involved, the crossover occurs quite accurately at $10Dq = -19440\,cm^{-1}$. At this field value, the lower Γ_3 level at $0.0\,cm^{-1}$ contains 49.29% $|^5E(e^3t_2^3(^4A_2))\rangle$ and 49.22% $|^3T_1(e^4t_2^2)\rangle$ and, incidentally, the higher one (at $846.8\,cm^{-1}$) consists of 50.63% and 47.97%, respectively. With this definition of the crossover, we again have to accept that the condition of equal contributions will be fulfilled, in the higher levels (resulting from the ground term) Γ_j, $j=1, 4, 5$, at different values of $10Dq$. Thus, e.g., we find that, at $10Dq = -19400\,cm^{-1}$, the composition of the lower Γ_5 level (at $122.0\,cm^{-1}$) is 51.20% $|^5E(e^3t_2^3(^4A_2))\rangle$ and 47.33% $|^3T_1(e^4t_2^2)\rangle$, whereas, at $10Dq = -19450\,cm^{-1}$, the Γ_5 level (now at $121.6\,cm^{-1}$) consists of the contributions of 47.21% and 51.22%, respectively. Interpolation results in a "crossover" of the Γ_5 levels at $10Dq = -19425\,cm^{-1}$. The corresponding situation with the Γ_4 levels may be experienced at $10Dq = -19800\,cm^{-1}$ where the lower level at $143.7\,cm^{-1}$ is formed of 51.62% $|^5E(e^3t_2^3(^4A_2))\rangle$ and 46.93% $|^3T_1(e^4t_2^2)\rangle$ and where, at $10Dq = -19900\,cm^{-1}$, the contributions have changed to 46.92% and 51.51%, respectively (the Γ_4 level is now at $163.8\,cm^{-1}$), cf. Fig. 4. Here, the "crossover" of Γ_4 levels obtains at about $10Dq = -19850\,cm^{-1}$. Finally, at $10Dq = -20000\,cm^{-1}$, the lower Γ_1 level at $195.0\,cm^{-1}$ consists of 50.19% $|^5E(e^3t_2^3(^4A_2))\rangle$ and 48.21% $|^3T_1(e^4t_2^2)\rangle$, the corresponding values at $10Dq = -20100\,cm^{-1}$ (Γ_1 level at $221.0\,cm^{-1}$) being 46.08% and 52.20%, respectively. This then gives the "crossover" of Γ_1 levels at approximately $10Dq = -20020\,cm^{-1}$. It follows that there is, in fact, a region of about $600\,cm^{-1}$ (i.e. 19425 to $20020\,cm^{-1}$) in $10Dq$ within that the levels Γ_j, $j=1, 3, 4, 5$, resulting from the two ground terms intersect.

4. Generalizations and Conclusions

It has been shown above that, due to spin-orbit interaction, the detailed situation close to the crossover in octahedral and tetrahedral d^4 and d^6 electron systems is considerably more complicated than usually appreciated. In particular, the levels originating in the two ground terms which are involved in the crossover may be significantly spin-mixed and intersections between corresponding levels may be spread out over a region of up to $600\,cm^{-1}$ in $10Dq$. According to this study, the crossover is precisely defined only if the two levels participating in the crossover transform according to different irreducible representations, e.g. $\Gamma_1[^1A_1(t_2^6)]$ and $\Gamma_5[^5T_2(t_2^4(^3T_1)\,e^2(^3A_2))]$ within the d^6 octahedral system. If both levels transform according to the same irreducible representation, however, it is best to redefine the crossover by that value of $10Dq$ where the two ground terms participate to equal amounts in the lowest level. This definition is suggested by the situations discussed above under the octahedral d^4 and the tetrahedral d^4 and d^6 systems.

Recently, we calculated the spin-pairing energy in d^4, d^5, d^6, and d^7 configurations of octahedral and tetrahedral symmetry in absence of spin-orbit interaction [1]. It may be of some interest to compare the $10Dq$-values at the crossovers which result if spin-orbit coupling is or is not taken into account in the present systems. The corresponding values are compiled in Table 1. It should be apparent that the results are indeed affected to some extent, the values of $10Dq$ at the crossover being shifted by up to $230\,cm^{-1}$, viz. the octahedral d^4 system.

Table 1. Values of $10\,Dq$ (in cm^{-1}) at the crossover in octahedral and tetrahedral d^4 and d^6 electron systems. The results are from complete configuration interaction calculations with or without spin-orbit coupling (d^4: $B = 800\,cm^{-1}$, $C = 4B$, $\zeta = 290\,cm^{-1}$; d^6: $B = 806\,cm^{-1}$, $C = 4B$, $\zeta = 420\,cm^{-1}$)

System	With spin-orbit coupling [present work]	Without spin-orbit coupling [1]
d^4 octahedral	19210	19440
d^6 octahedral	13804.5	13702
d^4 tetrahedral[a]	−13689	−13600
d^6 tetrahedral[a]	−19440	−19586

[a] Values listed are $10Dq_{tet}$. To convert to $10Dq_{oct}$ multiply by (4/9).

Examples for more or less octahedrally coordinated complexes of iron(II) which are close to the crossover are abundant in literature [6]. In view of the present results it is not surprising that, in all these systems, essentially pure ground states $^1A_1(t_2^6)$ and $^5T_2(t_2^4e^2)$ are observed experimentally [7–10], their ratio being dependent on temperature [9, 10] as well as on pressure [11, 12]. This may now be understood as consequence of the sharp intersection between the two levels $\Gamma_1[^1A_1(t_2^6)]$ and $\Gamma_5[^5T_2(t_2^4(^3T_1)\,e^2(^3A_2))]$ within the octahedral d^6 configuration, cf. Fig. 3.

On the other hand, there is recent evidence [13] that some almost octahedral complexes of manganese(III) are fairly close to the crossover. Since, in the octahedral d^4 configuration, the behavior of the lowest levels is rather complicated (cf. Fig. 1 and the discussion in Section (3) above), physical properties characteristic of spin-mixed ground states should be expected. Although the magnetic moments of the compounds are somewhat unusual, a detailed comparison with theory must await the results of more sophisticated physical measurements. In particular, far infrared spectroscopy should provide means to observe direct transitions between the low energy levels involved.

Finally, the complicated crossover behavior in some of the systems affects directly the magnetic and spectroscopic properties. These aspects of the present problem will be discussed separately [4, 5].

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