Supplementary Information

Energy Levels in Pentacoordinate d^5 to d^9 Complexes

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Table S1. Reduction and selection rules for d^5 configuration, Fe(III)

D_{3h}, trigonal bipyramid	**C_{4v}**, square pyramid
Reduction of IRs on **$R_3 \rightarrow D_{3h}$**	Reduction of IRs on **$R_3 \rightarrow C_{4v}$**
$P \rightarrow A_2'' + E'$	$P \rightarrow A_1 + E$
$D \rightarrow A_1' + E' + E''$	$D \rightarrow A_1 + B_1 + B_2 + E$
$G \rightarrow A_1' + A_1'' + A_2'' + 2E' + E''$	$G \rightarrow 2A_1 + A_2 + B_1 + B_2 + 2E$
Dipole components in **D_{3h}**	Dipole components in **C_{4v}**
$A_2'' \in z$, $E' \in (x, y)$	$A_1 \in z$, $E \in (x, y)$
Selection rules in **D_{3h}**	Selection rules in **C_{4v}**
1: $A_1' \otimes E'' = E''$, (30.6)	1: $A_1 \otimes A_2 = A_2$, (30.3)
2: $A_1' \otimes A_1'' = A_1''$, (34.2)	1': $A_1 \otimes E = E \in (x, y)$, 32.5
2': $A_1' \otimes A_2'' = A_2'' \in z$, 34.2	2: $A_1 \otimes B_2 = B_2$, (34.1)
3: $A_1' \otimes E' = E' \in (x, y)$, 34.5	2': $A_1 \otimes E = E \in (x, y)$, 34.3
4: $A_1' \otimes E' = E' \in (x, y)$, 34.8	3: $A_1 \otimes B_1 = B_1$, (34.7)
5: $A_1' \otimes A_1' = A_1'$, 34.8	3': $A_1 \otimes A_1 = A_1 \in z$, 34.8
	4: $A_1 \otimes A_1 = A_1 \in z$, 34.8

GCF calculations for Fe(III) with B = 1122 cm^{-1}, C = 4712 cm^{-1}, ξ = 460 cm^{-1}. All excitation energies are spin forbidden at the weak crystal field.
Hereafter: all weak-field poles F_4 = 5000 cm^{-1} and F_2 = 0; numbers refer to excitation energies in units of 10^3 cm^{-1}.

Angular momentum in **D_{3h}**	Angular momentum in **C_{4v}**
$A_2' \in L_z$, $E'' \in L_{x,y}$	$A_2 \in L_z$, $E \in L_{x,y}$
Active excitations	Active excitations
1: $A_1' \otimes E'' = E'' \in L_{x,y}$, 30.6	1: $A_1 \otimes A_2 = A_2 \in L_z$, 30.3
2: $A_1' \otimes A_1'' = A_1''$, (34.2)	1': $A_1 \otimes E = E \in (x, y)$, 32.5
2': $A_1' \otimes A_2'' = A_2'' \in z$, 34.2	2: $A_1 \otimes B_2 = B_2$, (34.1)
3: $A_1' \otimes E' = E'$, (34.5)	2': $A_1 \otimes E = E \in (x, y)$, 34.3
4: $A_1' \otimes E' = E'$, (34.8)	3: $A_1 \otimes B_1 = B_1$, (34.7)
5: $A_1' \otimes A_1' = A_1'$, (34.8)	3': $A_1 \otimes A_1 = A_1$, (34.8)
	4: $A_1 \otimes A_1 = A_1$, (34.8)
Excitation energies are in units of 10^3 cm^{-1}.	

Reduction of IRs	Reduction of IRs
on **$D_{3h} \rightarrow [D_3] \rightarrow D_3$'**	on **$C_{4v} \rightarrow C_{4v}$'**
$A_1 \rightarrow \Gamma_1$, S=5/2 $\rightarrow 2\Gamma_4 + (\Gamma_5 + \Gamma_6)$	$A_1 \rightarrow \Gamma_1$, S=5/2 $\rightarrow \Gamma_6 + 2\Gamma_7$
$\Gamma_1 \otimes (2\Gamma_4 + \Gamma_5 + \Gamma_6) = 2\Gamma_4 + \Gamma_5 + \Gamma_6$	$\Gamma_1 \otimes (\Gamma_6 + 2\Gamma_7) = \Gamma_6 + 2\Gamma_7$
$E \rightarrow \Gamma_3$, S=3/2 $\rightarrow \Gamma_4 + (\Gamma_5 + \Gamma_6)$	$A_2 \rightarrow \Gamma_2$, S=3/2 $\rightarrow \Gamma_6 + \Gamma_7$
$\Gamma_3 \otimes (\Gamma_4 + \Gamma_5 + \Gamma_6) = 3\Gamma_4 + \Gamma_5$	$\Gamma_1 \otimes (\Gamma_6 + \Gamma_7) = \Gamma_6 + \Gamma_7$

Table S2. Reduction and selection rules for d^6 configuration, Fe(II)

D_{3h}, trigonal bipyramid	**C_{4v}**, square pyramid
Reduction of IRs on **R_3** → **D_{3h}**	Reduction of IRs on **R_3** → **C_{4v}**
$D \to A_1'+E'+E''$	$D \to A_1+B_1+B_2+E$
$H \to A_1'+A_2'+A_2''+2E'+2E''$	$H \to 2A_1+A_2+B_1+B_2+3E$
Dipole components in **D_{3h}**	Dipole components in **C_{4v}**
$A_2'' \in z, E' \in (x,y)$	$A_1 \in z, E \in (x,y)$
Selection rules in **D_{3h}**	Selection rules in **C_{4v}**
1: $E'' \otimes E' = ... + A_2'' \in z$, 3.7	0: $B_2 \otimes E = E \in (x,y)$, 1.7
2: $E'' \otimes A_1' = E''$, (7.4)	1: $B_2 \otimes A_1 = B_2$, (5.7)
3: $E'' \otimes A_2'' = E' \in (x,y)$, (16.8)	1': $B_2 \otimes B_1 = A_2$, (7.4)
4: $E'' \otimes E' = ... + A_2'' \in z$, (18.9)	2: $B_2 \otimes E = E \in (x,y)$, (18.0)
Transitions 3, 4, etc. are spin forbidden	2': $B_2 \otimes A_1 = B_2$, ()
	Transitions 2, 2', etc. are spin forbidden

GCF calculations for Fe(II) with B = 897 cm^{-1}, C = 3857 cm^{-1}, ξ = 400 cm^{-1}.

Angular momentum in **D_{3h}**	Angular momentum in **C_{4v}**
$A_2' \in L_z, E'' \in L_{x,y}$	$A_2 \in L_z, E \in L_{x,y}$
Active excitations	Active excitations
1: $E'' \otimes E' = ... + E'' \in L_{x,y}$, 3.7	0: $B_2 \otimes E = E \in L_{x,y}$, 1.7
2: $E'' \otimes A_1' = E'' \in L_{x,y}$, 7.4	1: $B_2 \otimes A_1 = B_2$, (5.7)
	1': $B_2 \otimes B_1 = A_2 \in L_z$, 7.4
Excitation energies are in units of 10^3 cm^{-1}.	

Reduction of IRs on **D_{3h}** → **[D_3]** → **D_3'**	Reduction of IRs on **C_{4v}** → **C_{4v}'**
E'' → Γ_3, S=2 → $\Gamma_1 + 2\Gamma_3$	B_2 → Γ_4, S=2 → $\Gamma_1+\Gamma_3+\Gamma_4+\Gamma_5$
$\Gamma_3 \otimes (\Gamma_1 + 2\Gamma_3) = 2\Gamma_1 + 2\Gamma_2+3\Gamma_3$	$\Gamma_4 \otimes (\Gamma_1+\Gamma_3+\Gamma_4+\Gamma_5) = \Gamma_1+\Gamma_2+\Gamma_4+\Gamma_5$
E' → Γ_3, S=2 → $\Gamma_1 + 2\Gamma_3$	E → Γ_5, S=2 → $\Gamma_1+\Gamma_3+\Gamma_4+\Gamma_5$
$\Gamma_3 \otimes (\Gamma_1 + 2\Gamma_3) = 2\Gamma_1 + 2\Gamma_2+3\Gamma_3$	$\Gamma_5 \otimes (\Gamma_1+\Gamma_3+\Gamma_4+\Gamma_5)$ $= \Gamma_1+\Gamma_2+\Gamma_3+\Gamma_4+3\Gamma_5$

Table S3. Reduction and selection rules for d^7 configuration, Co(II)

D_{3h}, trigonal bipyramid	**C_{4v}**, square pyramid
Reduction of IRs on **R_3 → D_{3h}**	Reduction of IRs on **R_3 → C_{4v}**
$P \rightarrow A_2'' + E'$	$P \rightarrow A_1 + E$
$F \rightarrow A_1' + A_2' + A_2'' + E' + E''$	$F \rightarrow A_1 + B_1 + B_2 + 2E$
Dipole components in **D_{3h}**	Dipole components in **C_{4v}**
$A_2'' \in z$, $E' \in (x, y)$	$A_1 \in z$, $E \in (x, y)$
Selection rules in **D_{3h}**	Selection rules in **C_{4v}**
1a: $A_2'' \otimes A_1' = A_2'' \in z$, 2.7	0: $E \otimes A_1 = E \in (x, y)$, 1.5
1b: $A_2'' \otimes A_2' = A_1''$, (2.7)	1: $E \otimes B_1 = E \in (x, y)$, 3.1
2: $A_2'' \otimes E' = E''$, (4.0)	1': $E \otimes E = ... + A_1 \in z$, 6.1
3: $A_2'' \otimes E'' = E' \in (x, y)$, 10.1	2: $E \otimes B_2 = E \in (x, y)$, 10.5
4: $A_2'' \otimes E' = E''$, (20.0)	3: $E \otimes A_1 = E \in (x, y)$, 19.0
4': $A_2'' \otimes A_2'' = A_1'$, (20.2)	3': $E \otimes E = ... + A_1 \in z$, 19.2

GCF calculations for Co(II) with B = 989 cm^{-1}, C = 4253 cm^{-1}, ξ = 515 cm^{-1}.

Reduction of IRs on **R_3 → D_{3h}**	Reduction of IRs on **R_3 → C_{4v}**
$P \rightarrow A_2'' + E'$	$P \rightarrow A_1 + E$
$F \rightarrow A_1' + A_2' + A_2'' + E' + E''$	$F \rightarrow A_1 + B_1 + B_2 + 2E$
	$D \rightarrow A_1 + B_1 + B_2 + E$
	$G \rightarrow 2A_1 + A_2 + B_1 + B_2 + 2E$
Angular momentum in **D_{3h}**	Angular momentum in **C_{4v}**
$A_2' \in L_z$, $E'' \in L_{x,y}$	$A_2 \in L_z$, $E \in L_{x,y}$
Excitations within daughters of F-term	Excitations within daughters of F-term
1: $A_2'' \otimes A_1' = A_2''$, (2.7)	0: $E \otimes A_1 = E \in L_{x,y}$, 1.5
1': $A_2'' \otimes A_2' = A_1''$, (2.7)	1: $E \otimes B_1 = E \in L_{x,y}$, 3.2
2: $A_2'' \otimes E' = E'' \in L_{x,y}$, 4.0	1': $E \otimes E = ... + A_2 \in L_z$, 6.1
3: $A_2'' \otimes E'' = E'$, (10.1)	2: $E \otimes B_2 = E \in L_{x,y}$, 10.5
4: $A_2'' \otimes E' = E'' \in L_{x,y}$, 20.0	3: $E \otimes A_1 = E \in L_{x,y}$, 19.0
	3': $E \otimes E = ... + A_2 \in L_z$, 19.2

Reduction of IRs on **D_{3h} → [D_3] → D_3'**	Reduction of IRs on **C_{4v} → [C_{4v}'] → C_{4v}'**
$A_2 \rightarrow \Gamma_2$, S=3/2 → $\Gamma_4 + (\Gamma_5 + \Gamma_6)$	$E \rightarrow \Gamma_5$, S=3/2 → $\Gamma_6 + \Gamma_7$
$\Gamma_2 \otimes [\Gamma_4 + (\Gamma_5 + \Gamma_6)] = \Gamma_4 + (\Gamma_6 + \Gamma_5)$	$\Gamma_5 \otimes (\Gamma_6 + \Gamma_7) = 2\Gamma_6 + 2\Gamma_7$
$A_1 \rightarrow \Gamma_1$, S=3/2 → $\Gamma_4 + (\Gamma_5 + \Gamma_6)$	$A_1 \rightarrow \Gamma_1$, S=3/2 → $\Gamma_6 + \Gamma_7$
$\Gamma_1 \otimes [\Gamma_4 + (\Gamma_5 + \Gamma_6)] = \Gamma_4 + (\Gamma_5 + \Gamma_6)$	$\Gamma_1 \otimes (\Gamma_6 + \Gamma_7) = \Gamma_6 + \Gamma_7$

Table S4. Reduction and selection rules for d^8 configuration, Ni(II)

D_{3h}, trigonal bipyramid	**C_{4v}**, square pyramid
Reduction of IRs on **R_3 → D_{3h}**	Reduction of IRs on **R_3 → C_{4v}**
$P \rightarrow A_2''+E'$	$P \rightarrow A_1+E$
$F \rightarrow A_1'+A_2'+A_2''+E'+E''$	$F \rightarrow A_1+B_1+B_2+2E$
Dipole components in **D_{3h}**	Dipole components in **C_{4v}**
$A_2'' \in z$, $E' \in (x,y)$	$A_1 \in z$, $E \in (x,y)$
Selection rules in **D_{3h}**	Selection rules in **C_{4v}**
1: $E'' \otimes E' = A_1''+A_2''+E'' \in z$, 5.7	1: $B_2 \otimes E = E \in (x,y)$, 4.4
2a: $E'' \otimes A_1' = E''$, (7.4)	1': $B_2 \otimes B_1 = A_2$, (7.4)
2b: $E'' \otimes A_2' = E''$, (7.4)	2: $B_2 \otimes A_1 = B_2$, (8.7)
3: $E'' \otimes A_2'' = E' \in (x,y)$, 8.9	2': $B_2 \otimes E = E \in (x,y)$, 9.7
4: $E'' \otimes E' = A_1''+A_2''+E'' \in z$, 21.1	3: $B_2 \otimes A_1 = B_2$, 22.3
4': $E'' \otimes A_2'' = E' \in (x,y)$, 21.6	3': $B_2 \otimes E = E \in (x,y)$, 22.6

GCF calculations for Ni(II) with B = 1042 cm^{-1}, C = 4585 cm^{-1}, ξ = 630 cm^{-1}.

Reduction of IRs on **R_3 → D_{3h}**	Reduction of IRs on **R_3 → C_{4v}**
$P \rightarrow A_2''+E'$	$P \rightarrow A_1+E$
$F \rightarrow A_1'+A_2'+A_2''+E'+E''$	$F \rightarrow A_1+B_1+B_2+2E$
Angular momentum in **D_{3h}**	Angular momentum in **C_{4v}**
$A_2' \in L_z$, $E'' \in L_{x,y}$	$A_2 \in L_z$, $E \in L_{x,y}$
Excitations within daughters of F-term	Excitations within daughters of F-term
1: $E'' \otimes E' = A_1''+A_2''+E'' \in L_{x,y}$, 5.7	1: $B_2 \otimes E = E \in L_{x,y}$, 4.4
2a: $E'' \otimes A_1' = E'' \in L_{x,y}$, 7.4	1': $B_2 \otimes B_1 = A_2 \in L_z$, 7.4
2b: $E'' \otimes A_2' = E'' \in L_{x,y}$, 7.4	2: $B_2 \otimes A_1 = B_2$, (8.7)
3: $E'' \otimes A_2'' = E'$, (8.9)	2': $B_2 \otimes E = E \in L_{x,y}$, 9.7

Reduction of IRs on **D_{3h} → [D_3] → D_3'**	Reduction of IRs on **C_{4v} → C_{4v}'**
$E \rightarrow \Gamma_3$, S=1 → $\Gamma_2 + \Gamma_3$	$B_2 \rightarrow \Gamma_4$, S=1 → $\Gamma_2 + \Gamma_5$
$\Gamma_3 \otimes (\Gamma_2 + \Gamma_3) = \Gamma_3 + \Gamma_1 + \Gamma_2 + \Gamma_3$	$\Gamma_4 \otimes (\Gamma_2 + \Gamma_5) = \Gamma_3 + \Gamma_5$
$E \rightarrow \Gamma_3$, S=1 → $\Gamma_2 + \Gamma_3$	$E \rightarrow \Gamma_5$, S=1 → $\Gamma_2 + \Gamma_5$
$\Gamma_3 \otimes (\Gamma_2 + \Gamma_3) = \Gamma_3 + \Gamma_1 + \Gamma_2 + \Gamma_3$	$\Gamma_5 \otimes (\Gamma_2 + \Gamma_5)$ $= \Gamma_5 + \Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_2$

Table S5. Reduction and selection rules for d^9 configuration, Cu(II)

D_{3h}, trigonal bipyramid	**C_{4v}**, square pyramid
Reduction of IRs on **R_3 → D_{3h}**	Reduction of IRs on **R_3 → C_{4v}**
$D \rightarrow A_1'+E'+E''$	$D \rightarrow A_1+B_1+B_2+E$
Dipole components in **D_{3h}**	Dipole components in **C_{4v}**
$A_2'' \in z, E' \in (x,y)$	$A_1 \in z, E \in (x,y)$
Selection rules in **D_{3h}**	Selection rules in **C_{4v}**
1: $A_1' \otimes E' = E' \in (x,y)$, 3.7	1: $B_1 \otimes A_1 = B_1$, (1.7)
2: $A_1' \otimes E'' = E''$, (7.4)	2: $B_1 \otimes E = E \in (x,y)$, 5.7
	3: $B_1 \otimes B_2 = A_2$, (7.4)

GCF calculations for Cu(II) with B = 1240 cm^{-1}, C = 4712 cm^{-1}, ξ = 830 cm^{-1}.

Reduction of IRs on **R_3 → D_{3h}**	Reduction of IRs on **R_3 → C_{4v}**
$D \rightarrow A_1'+E'+E''$	$D \rightarrow A_1+B_1+B_2+E$
Angular momentum in **D_{3h}**	Angular momentum in **C_{4v}**
$A_2' \in L_z, E'' \in L_{x,y}$	$A_2 \in L_z, E \in L_{x,y}$
Active excitations	Active excitations
1: $A_1' \otimes E' = E'$, (3.7)	1: $B_1 \otimes A_1 = B_1$ (1.7)
2: $A_1' \otimes E'' = E'' \in L_{x,y}$, 7.4	2: $B_1 \otimes E = E \in L_{x,y}$, 5.7
	3: $B_1 \otimes B_2 = A_2 \in L_z$, 7.4

Reduction of IRs on **D_{3h} → [D_3] → D_3'**	Reduction of IRs on **C_{4v} → C_{4v}'**
$A_1 \rightarrow \Gamma_1$, S=1/2 → Γ_4	$B_1 \rightarrow \Gamma_3$, S=1/2 → Γ_6
$\Gamma_1 \otimes \Gamma_4 = \Gamma_4$	$\Gamma_3 \otimes \Gamma_6 = \Gamma_7$
$E \rightarrow \Gamma_3$, S=1/2 → Γ_4	$A_1 \rightarrow \Gamma_1$, S=1/2 → Γ_6
$\Gamma_3 \otimes \Gamma_4 = \Gamma_4 + \Gamma_5$	$\Gamma_1 \otimes \Gamma_6 = \Gamma_6$

Table S6. Reduction of the $(2S + 1)$ states of R_3 and R_3' to irreducible representations of point groups.

S or J	0	1/2	1	3/2	2	5/2
For D_3, D_3'	Γ_1	Γ_4	$\Gamma_2+\Gamma_3$	$\Gamma_4+\Gamma_5+\Gamma_6$	$\Gamma_1+2\Gamma_3$	$2\Gamma_4+\Gamma_5+\Gamma_6$
For D_4, C_{4v}'	Γ_1	Γ_6	$\Gamma_2+\Gamma_5$	$\Gamma_6+\Gamma_7$	$\Gamma_1+\Gamma_3+\Gamma_4+\Gamma_5$	$\Gamma_6+2\Gamma_7$

Table S7. Decomposition of the direct product of irreducible representations $\Gamma_i \otimes \Gamma_j$ in double groups

a) group D_3' $(h = 12)$ [a]

	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	Γ_6
$\Gamma_1 = A_1$	Γ_1	.	.	.	.	.
$\Gamma_2 = A_2$	Γ_2	Γ_1	.	.	.	.
$\Gamma_3 = E_1$	Γ_3	Γ_3	$\Gamma_1,\Gamma_3,(\Gamma_2)$	.	.	.
$\Gamma_4 = E_{1/2}$	Γ_4	Γ_4	Γ_4,Γ_5	$\Gamma_2,\Gamma_3,(\Gamma_1)$	.	.
$\Gamma_5(1) = E_{3/2}(2)$	Γ_5	Γ_6	Γ_4	Γ_3	Γ_2	.
$\Gamma_6(1) = E_{3/2}$	Γ_6	Γ_5	Γ_4	Γ_3	Γ_1	Γ_2

[a] Double degenerate representation $E_{3/2}$ is split into a complex conjugate pair $\{\Gamma_5+\Gamma_6\}$.

b) group C_{4v}' $(h = 16)$

	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	Γ_6	Γ_7
$\Gamma_1 = A_1$	Γ_1	.	.	.	.	.	.
$\Gamma_2 = A_2$	Γ_2	Γ_1	.	.	.	.	.
$\Gamma_3 = B_1$	Γ_3	Γ_4	Γ_1	.	.	.	.
$\Gamma_4 = B_2$	Γ_4	Γ_3	Γ_2	Γ_1	.	.	.
$\Gamma_5 = E_1$	Γ_5	Γ_5	Γ_5	Γ_5	$\Gamma_1,\Gamma_3,\Gamma_4,(\Gamma_2)$	.	.
$\Gamma_6 = E_{1/2}(2)$	Γ_6	Γ_6	Γ_7	Γ_7	Γ_6,Γ_7	$\Gamma_2,\Gamma_5,(\Gamma_1)$	.
$\Gamma_7 = E_{3/2}(2)$	Γ_7	Γ_7	Γ_6	Γ_6	Γ_6,Γ_7	$\Gamma_3,\Gamma_4,\Gamma_5$	$\Gamma_2,\Gamma_5,(\Gamma_1)$

New IRs in the double groups are typed on a grey background; $\Gamma_i \otimes \Gamma_j = \Gamma_j \otimes \Gamma_i$.

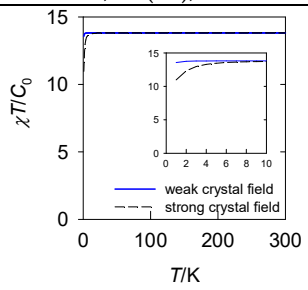
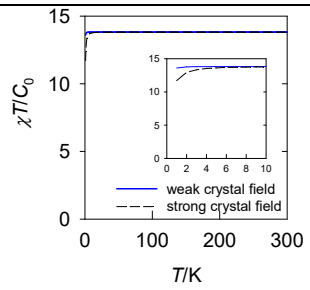
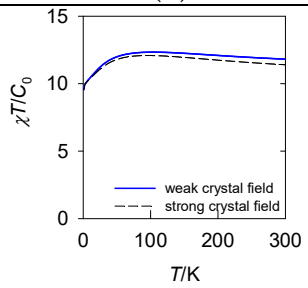
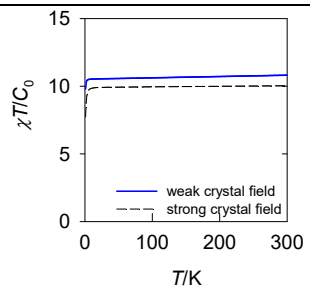
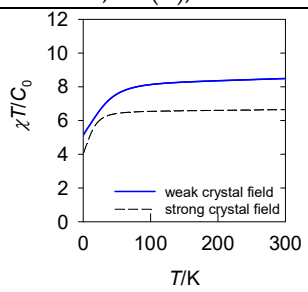
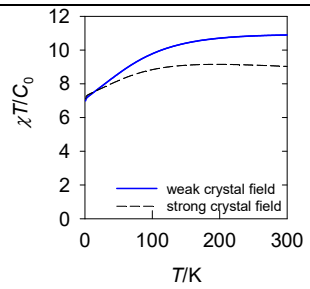
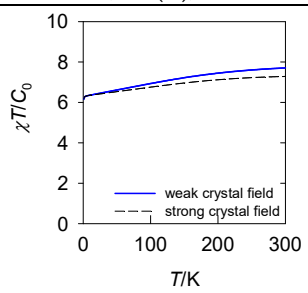
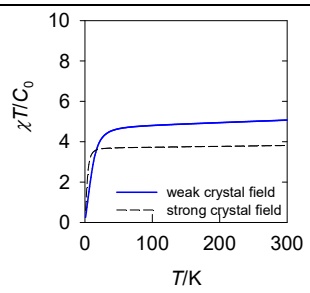
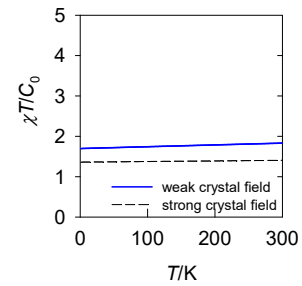
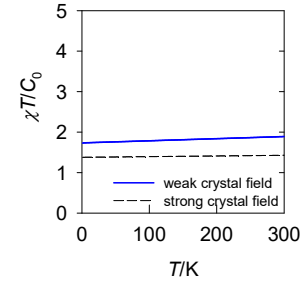
D_{3h}, trigonal bipyramid	**C_{4v}**, square pyramid
d^5, Fe(III), $^6A_1'$	$^6A_1$
	
d^6, Fe(II), $^5E''$	$^5B_2$
	
d^7, Co(II), $^4A_2''$	^4E
	
d^8, Ni(II), $^3E''$	$^3B_2$
	
d^9, Cu(II), $^2A_1'$	$^2B_1$
	

Figure S1. DC susceptibility at $B = 0.1$ T converted to the product function as calculated by GCFT for weak (strong) crystal field with $F_4 = 5000$ (15000) cm^{-1}. Data presented as $\chi T/C_0$ *vs* T [dimensionless]; reduced Curie constant $C_0 = N_A \mu_0 \mu_B^2 / k_B$ = 4.714 x 10^{-6} m^3 K mol^{-1} [SI].

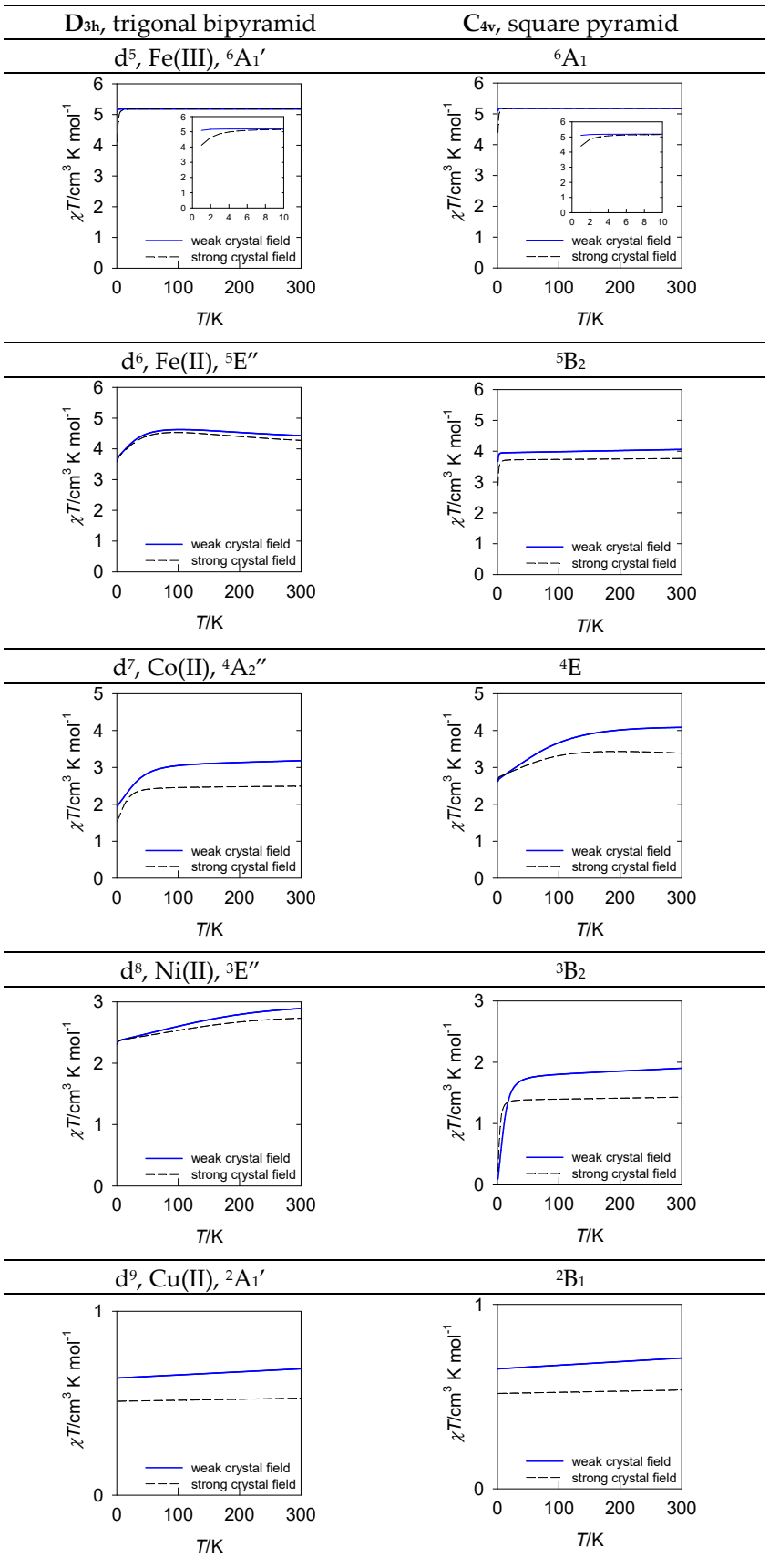


Figure S2. DC susceptibility at $B = 0.1$ T converted to the product function as calculated by GCFT for weak (strong) crystal field with $F_4 = 5000$ (15000) cm^{-1}. Data presented as χT *vs* T in cm^3 K mol^{-1} [cgs&emu].

Table 2.1 Values of $(4/g^2)\chi T$ as a Function of the Spin S

S	$(4/g^2)\chi T$ (cm^3 K mol^{-1})
1/2	0.375
1	1.000
3/2	1.876
2	3.001
5/2	4.377
3	6.002
7/2	7.878