Effects of the electrostatically correlated crystal field in S ground-state splitting of Mn^{2+}

LETTER TO THE EDITOR

Effects of the electrostatically correlated crystal field in S ground-state splitting of Mn^{2+}

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Abstract. Estimates of the contributions of the electrostatically correlated crystal field (ECCF) to the S ground-state splitting of Mn^{2+} are made based on an overlap model. It is shown that the ECCF contributes oppositely to the dominant contributions due to the relativistic crystal field and is a significant cancellation mechanism.

The study of ground-state splitting of S-state ions reveals many mechanisms that are usually obscured by the overwhelming ordinary crystal field and provides a picture of mutually competing effects to explain qualitatively several features of the experimental results (Siu and Newman 1982). On the one hand, the dominant contributions to the zero-field splitting (ZFS) of Gd^{3+} with a Cl$^-$ ligand and Mn^{2+} with an F$^-$ ligand are all negative, which leads to the negative sign of their $\bar{b}_2$ (Siu 1988a). On the other hand, in order to obtain quantitative agreement between theory and experiment, contributions opposite in sign to the dominant ones are indispensible (Newman and Urban 1975). In the case of Gd^{3+}, it has been argued that the electrostatically correlated crystal field (ECCF) is one of these cancellation mechanisms (Siu 1987). However, no complete calculation is provided to estimate any of these important cancellation effects, due to the lack of results of detailed numerical computation. This work aims at providing a complete calculation for ECCF contributions to the ZFS of Mn^{2+} with an F$^-$ ligand. Our approach will be, first, to obtain a tensor operator form of the mechanism. The contributions to ZFS are then estimated by obtaining the corresponding parameters for the F$^-$ ligand. This will show that ECCF in the case of Mn^{2+} is a significant cancellation mechanism. Hence, it follows that the balance between dominant contributions and those that cause cancellation determines not only the magnitude of the spin-Hamiltonian parameters but also their signs, which is essential for understanding the sign change of $\bar{b}_2$ for Mn^{2+} from negative for F$^-$ and O^{2-} as ligands to positive for octahedral chloro-complexes (Heming *et al* 1983, 1984).

ECCF has been proposed by Rajnak and Wybourne (1964) and applied to the S ground-state splitting of Gd^{3+} by Wybourne (1966) but only insignificant contributions are obtained using the electrostatic model. Newman and Bishton (1968) extended the ECCF to a correlation crystal field (CCF) parametrisation scheme and Judd (1977, 1979, 1980) studied various physical mechanisms of CCF for rare earths and actinides. CCF was also applied to 3d^n systems as a linear parametrisation scheme (Newman *et al* 1984) and some models were proposed. Hence, the study of the ZFS contributions of the ECCF

mechanism cannot only help to elucidate the ZFS problem, but also provide a clue to its importance in CCF.

The ECCF may be schematically represented as

$$\langle l^N SL|V_E|l^{N-1}(S_2L_2)l'; SL_1\rangle\langle l^{N-1}(S_2L_2)l'; SL_1|V_{CF}|l^N SL_3\rangle \tag{1}$$

where V_E is the electrostatic Coulomb interaction given by

$$V_E = \sum_{i>j} \frac{e^2}{r_{ij}}.$$

ECCF gives an effective interaction V_{eff} for the γSL and $\gamma_3 SL_3$ states of l^N configuration

$$\langle l^N \gamma SLM_L|V_{eff}|l^N \gamma_3 SL_3M_{L3}\rangle$$

$$= \sum_{kq} (-1)^{L-M_L} \begin{pmatrix} L & k & L_3 \\ -M_L & q & M_{L3} \end{pmatrix} \sum_{k_1k_2} \frac{-2B_q^k}{\Delta E_{n'l'}} \frac{\langle nl|r^k|n'l'\rangle}{\langle nl|r^k|nl\rangle}$$

$$\times \frac{(2k_2+1)}{(2k+1)^{1/2}} \begin{Bmatrix} k_1 & k_2 & k \\ l & l' & l \end{Bmatrix} R^{(k_1)}(llll')\langle l| |\mathbf{C}^{(k)}| |l'\rangle\langle l| |\mathbf{C}^{(k_1)}| |l\rangle$$

$$\times \langle l| |\mathbf{C}^{(k_1)}| |l'\rangle\langle l^N\gamma SL| |(\mathbf{U}^{(k_1)}\mathbf{U}^{(k_2)})^k| |l^N\gamma_3 S_3 L_3\rangle \tag{2}$$

where $R^{(k_1)}(llll')$ is the Slater radial integral for $nl \to n'l'$ excitation, $\Delta E_{n'l'}$ is the $nl \to n'l'$ excitation energy and B_q^k is the crystal field parameter according to Wybourne's normalisation, in terms of which the intrinsic paramenter $\bar{B}_k = B_0^k$ for one ligand is defined. We may express the ECCF as

$$V(\text{ECCF}) = \sum_{\substack{k,q \\ k_1k_2}} B_q^k(k_1k_2)(\mathbf{U}^{(k_1)}\mathbf{U}^{(k_2)})_q^{(k)} \tag{3}$$

and calculate the contributions of the ECCF to the ground S-state splitting parameters $\bar{b}_2$ and $\bar{b}_4$ and derive them as follows:

$$\bar{b}_2(\text{ECCF}) = -\tfrac{1}{100}\sqrt{\tfrac{7}{2}}p^2[\tfrac{3}{5}\bar{B}_2(22) + (\sqrt{22}/3)\bar{B}_2(44)] \tag{4}$$

$$\bar{b}_4(\text{ECCF}) = \tfrac{1}{315}\sqrt{\tfrac{11}{70}}\{(36/\sqrt{11})\bar{B}_4(22)[\tfrac{52}{49}d^2 + (6/\sqrt{14})pf$$

$$-\tfrac{1}{6}(5d_1^2 + 13d_3^2 - 44\sqrt{\tfrac{2}{7}}d_1d_3)] - 15\sqrt{2}\bar{B}_4(24)[\tfrac{32}{49}d^2 + (9/2\sqrt{14})pf$$

$$+ \tfrac{1}{42}(35d_1^2 - 2d_3^2 - 8\sqrt{\tfrac{2}{7}}d_1d_3)] + 5\sqrt{65}\bar{B}_4(44)[\tfrac{16}{49}d^2 - (3/\sqrt{14})pf$$

$$-\tfrac{1}{3}(\tfrac{1}{2}d_1^2 + \tfrac{4}{7}d_3^2 + 4\sqrt{\tfrac{2}{7}}d_1d_3)]\}. \tag{5}$$

The ECCF contributions to the d^5 ground-state splitting parameters can now be obtained by calculating direct ECCF contributions to the $\bar{B}_k(k_1k_2)$:

$$\bar{B}_k(k_1k_2) = -2\sum_{l'} \frac{\bar{B}_k\langle nl|r^k|n'l'\rangle}{\Delta E_{n'l'}\langle nl|r^k|nl\rangle} \frac{(2k_2+1)}{(2k+1)^{1/2}} \begin{Bmatrix} k_1 & k_2 & k \\ l & l' & l \end{Bmatrix}$$

$$\times R^{(k_1)}(llll')\langle l| |\mathbf{C}^{(k)}| |l'\rangle\langle l| |\mathbf{C}^{(k_1)}| |l\rangle\langle l| |\mathbf{C}^{(k_1)}| |l'\rangle$$

$$+ \text{ a similar term with } k_1 \text{ and } k_2 \text{ interchanged.} \tag{6}$$

Table 1 gives the ECCF contributions to $\bar{B}_k(k_1k_2)$ in the case of 3d electron. Combining equations (4), (5) and (6), we obtain expressions for the contributions to $\bar{b}_2$ and $\bar{b}_4$ as

Table 1. The ECCF contributions to $\bar{B}_k(k_1k_2)$. $\bar{B}_k(n'l')$ is defined by (9) and $R^{(k)}(nl) = R^{(k)}(3d, 3d, 3d, nl)$.

$\bar{B}_k(k_1k_2)$	$3d \to ns(-2\bar{B}_k(ns)/\Delta E_{ns})$	$3d \to nd(-2\bar{B}_k(nd)/\Delta E_{nd})$	$3d \to ng(-2\bar{B}_k(ng)/\Delta E_{ng})$
$\bar{B}_2(22)$	$-\sqrt{\tfrac{2}{7}}R^{(2)}(ns)$	$\tfrac{15}{49}\sqrt{\tfrac{2}{7}}R^{(2)}(nd)$	$-\tfrac{36}{49}\sqrt{\tfrac{2}{7}}R^{(2)}(ng)$
$\bar{B}_2(24)$	$-\tfrac{9}{5}\sqrt{\tfrac{2}{7}}R^{(2)}(ns)$	$-\tfrac{4}{49}\sqrt{\tfrac{2}{7}}(9R^{(2)}(nd) - 5R^{(4)}(nd))$	$-\tfrac{1}{49}\sqrt{\tfrac{2}{7}}(\tfrac{9}{5}R^{(2)}(ng) + 50R^{(4)}(ng))$
$\bar{B}_2(44)$	0	$-\tfrac{30}{49}\sqrt{\tfrac{11}{7}}R^{(4)}(nd)$	$-\tfrac{90}{49}\sqrt{\tfrac{11}{77}}R^{(4)}(ng)$
$\bar{B}_4(22)$	0	$\tfrac{20}{147}\sqrt{\tfrac{10}{7}}R^{(2)}(nd)$	$\tfrac{50}{147}\sqrt{\tfrac{10}{7}}R^{(2)}(ng)$
$\bar{B}_4(24)$	0	$\tfrac{10}{49}\sqrt{\tfrac{5}{77}}(R^{(2)}(nd) + \tfrac{3}{9}R^{(4)}(nd))$	$\tfrac{10}{49}\sqrt{\tfrac{5}{77}}(3R^{(2)}(ng) - \tfrac{325}{99}R^{(4)}(ng))$
$\bar{B}_4(44)$	0	$\tfrac{5}{147}\sqrt{\tfrac{286}{7}}R^{(4)}(nd)$	$\tfrac{300}{539}\sqrt{\tfrac{286}{77}}R^{(4)}(ng)$

Table 2. The matrix elements $\langle 3d|V|nd\rangle$ and corresponding parameters $\bar{B}_k(nd)$.

n	$\langle 3d,0|V|nd,0\rangle$	$\langle 3d,1|V|nd,1\rangle$	$\bar{B}_2(nd)$ (cm^{-1})	$\bar{B}_4(nd)$ (cm^{-1})	E_{nd} (Hartree)
3	6539.0	2867.0	9406.0	4888.0	-1.0197
4	$-15\,981.0$	$-14\,963.0$	$-30\,944.0$	7144.2	$-0.425\,10$
5	$-13\,997.0$	-1366.0	$-15\,363.0$	$-21\,915.0$	$-0.223\,69$
6	-8422.9	1699.7	-6723.2	$-19\,241.0$	$-0.004\,352$
7	20.60	3162.1	3182.7	-7551.9	0.302\,215
8	6316.7	2465.0	8781.7	5453.9	0.692\,20
9	7103.4	834.03	7937.4	10\,784.0	1.1618
10	3646.3	-531.78	3114.5	7839.6	1.708\,75
11	-782.24	-846.82	-1629.1	624.34	2.331\,85
12	-3016.4	-456.82	-3473.2	-4333.1	3.030\,65
13	-2510.0	115.27	-2394.7	-4794.7	3.8052
14	-440.59	324.39	-116.21	-1571.6	4.6557
15	1203.7	223.61	1427.3	1629.9	5.5822
16	1516.9	-28.93	1487.9	2799.8	6.5845
17	612.16	-133.81	478.35	1423.0	7.6615
18	-441.93	-108.10	-550.04	-536.03	8.8135
19	-897.12	15.47	-881.66	-1651.9	10.040
20	-509.83	64.10	-445.72	-1071.5	11.3405

follows:

$$
\bar{b}_2(\text{ECCF}) = \sum_{n\geq 4}\frac{p^2}{2450}\left(-\frac{147}{5}\frac{\bar{B}_2(ns)}{\Delta E_{ns}}R^{(2)}(ns)+9\frac{\bar{B}_2(nd)}{nd}R^{(2)}(nd)-110\frac{\bar{B}_2(nd)}{\Delta E_{nd}}\right.
$$

$$
\left.\times R^{(4)}(nd)-\frac{108}{5}\frac{\bar{B}_2(ng)}{\Delta E_{ng}}R^{(2)}(ng)-30\frac{\bar{B}_2(ng)}{\Delta E_{ng}}R^{(4)}(ng)\right) \tag{7}
$$

$$
\bar{b}_4(\text{ECCF}) = \sum_{n\geq 4}-\frac{20}{7203}\left\{\left(\frac{8}{5}\frac{\bar{B}_4(nd)}{\Delta E_{nd}}R^{(2)}(nd)+4\frac{\bar{B}_4(ng)}{\Delta E_{ng}}R^{(2)}(ng)\right)\right.
$$

$$
\times\left[\frac{52}{49}d^2+\frac{6}{\sqrt{14}}pf-\frac{1}{6}\left(5d_1^2+13d_3^2-44\sqrt{\frac{2}{7}}d_1d_3\right)\right]
$$

$$
-\left(11\frac{\bar{B}_4(nd)}{\Delta E_{nd}}(9R^{(2)}(nd)+5R^{(4)}(nd))\right.
$$

$$
\left.+\frac{\bar{B}_4(ng)}{\Delta E_{ng}}(3R^{(2)}(ng)-\tfrac{325}{99}R^{(4)}(ng))\right)
$$

$$
\times\left[\frac{32}{49}d^2+\frac{9}{2\sqrt{14}}pf+\frac{1}{42}\left(35d_1^2-2d_3^2-8\sqrt{\frac{2}{7}}d_1d_3\right)\right]
$$

$$
+\left(\frac{143\bar{B}_4(nd)}{18\Delta E_{nd}}R^{(4)}(nd)+\frac{130\bar{B}_4(ng)}{11\Delta E_{ng}}R^{(4)}(ng)\right)
$$

$$
\left.\times\left[\frac{16}{49}d^2-\frac{3}{\sqrt{14}}pf-\frac{1}{3}\left(\frac{1}{2}d_1^2+\frac{4}{7}d_3^2+4\sqrt{\frac{2}{7}}d_1d_3\right)\right]\right\} \tag{8}
$$

Table 3. Overlap integrals involving excited ns states of Mn^{2+} and the occupied 3s and 3p states of F^- at a distance of 4.0454 au; parameters $\bar{B}_2(ns)$; Slater integrals $R^{(2)}$ (3d 3d; 3d ns) and orbital energies of ns.

n	$\langle ns|s\rangle$	$\langle ns|p\rangle$	$\bar{B}(ns)$ (cm^{-1})	$R^{(2)}(ns)$ ($1/a_0$)	$E(ns)$ (Hartree)
4	−0.172 38	0.218 11	2475.4	−0.015 099	−0.867 55
5	0.130 16	0.0971 185	10 115.0	−0.005 3333	−0.413 29
6	0.093 976	−0.024 623	2965.0	−0.004 0700	−0.196 15
7	0.063 886	−0.074 043	−606.78	−0.003 9275	0.073 26
8	0.016 733	−0.091 778	−3471.5	−0.003 4459	0.437 79
9	−0.017 365	−0.063 089	−3643.3	−0.002 8783	0.891 10
10	−0.025 012	−0.012 904	−1679.6	−0.002 3731	1.4294
11	−0.014 165	0.028 551	689.83	−0.001 9879	2.0504
12	−0.001 0950	0.038 008	1691.7	−0.001 7312	2.7529
13	0.004 2110	0.021 295	1157.9	−0.001 5880	3.5359
14	0.002 5880	−0.004 1410	−76.821	−0.001 5336	4.3985
15	0.000 0620	−0.017 408	−793.95	−0.001 5421	5.3402
16	0.000 1830	−0.014 413	−651.62	−0.001 5903	6.3602
17	0.001 6850	−0.001 2965	14.033	−0.001 6590	7.4579
18	0.001 6641	0.008 3068	452.60	−0.001 7335	8.6327
19	−0.000 4719	0.009 1442	397.93	−0.001 8029	9.8843
20	−0.002 5351	0.002 3054	−4.8814	−0.001 8602	11.212
21	−0.002 2592	−0.003 9473	−279.01	−0.001 9015	12.617
22	0.000 1476	−0.005 5768	−248.78	−0.001 9255	14.097
23	0.002 3171	−0.001 9008	13.904	−0.001 9329	15.654
24	0.002 2071	0.002 0428	189.59	−0.001 9252	17.287
25	0.000 0949	0.003 5500	166.59	−0.001 9046	18.996
26	−0.001 8884	0.001 4546	−15.657	−0.001 8731	20.780
27	−0.001 9307	−0.001 0601	−132.58	−0.001 8325	22.639
28	−0.000 2146	−0.002 2758	−113.49	−0.001 7845	24.573
29	0.001 4790	−0.001 0175	17.837	−0.001 7305	26.583
30	0.001 5977	0.000 5973	96.900	−0.001 6720	28.667

To calculate (7) and (8), we have to obtain the parameters $\bar{B}_k(n'l')$, which are defined as follows (Siu 1987):

$$\bar{B}_k(n'l') = \bar{B}_k\langle nl|r^k|n'l'\rangle/\langle nl|r^k|nl\rangle. \tag{9}$$

It has been proposed (Siu 1987) that the $\bar{B}_k(n'l')$ should be obtained from the identity

$$\langle nl|V|n'l'\rangle = \langle nl|\hat{O}|n'l'\rangle \tag{10}$$

where V is the conventional crystal field in parametrisation form and $\hat{O}$ is defined as

$$\hat{O} = \sum_\tau \varepsilon_\tau |\chi_\tau\rangle\langle\chi_\tau|$$

where the suffix τ distinguishes the outer-shell ligand states p_σ, p_π and s, and ε_τ are coefficients so chosen that

$$\langle nl|V|nl\rangle = \langle nl|\hat{O}|nl\rangle$$

(the overlap model, see Siu (1988a)). Once the equations (10) are calculated $\bar{B}_k(n'l')$ may be obtained from a relationship between the V matrix elements and their parameters. Let E_0, E_1 be the matrix elements for orbital magnetic quantum number $m = 0$ and 1 respectively. We have, for a d electron,

$$\bar{B}_2 = E_0 + E_1 \qquad \bar{B}_4 = \tfrac{3}{5}(3E_0 - 4E_1) \tag{11}$$

Table 4. ECCF contributions to the intrinsic spin-Hamiltonian parameter $\bar{b}_k$ (in units of 10^{-4} cm^{-1}).

n	$\bar{b}_2(3d \rightarrow nd)$	$\bar{b}_2(3d \rightarrow ns)$	$\bar{b}_4(3d \rightarrow nd)$
4	470.83	14.57	1.20
5	121.75	5.28	-1.91
6	42.45	0.87	-1.33
7	-14.26	-0.13	-0.37
8	-25.73	-0.49	0.18
9	-14.31	-0.33	0.22
10	-3.21	-0.10	0.09
11	0.84	0.03	0.00
12	0.65	0.05	-0.01
13	-0.04	0.02	0.00
14	-0.02	0.00	0.00
15	0.29	-0.01	0.00
16	0.35	-0.01	0.00
17	0.12	0.00	0.00
18	-0.13	0.01	0.00
19	-0.20	0.00	0.00
20	-0.09	0.00	0.00
Total	579.29	19.75	-1.92

(Siu 1988a). Table 2 shows the values of $\langle 3d|V|nd \rangle$ and corresponding parameters $\bar{B}_k(nd)$ based on the overlap integrals calculated by Poon, which have been presented in table 1 of Siu (1988a). Table 3 gives the overlap integrals $\langle ns|s \rangle$ and $\langle ns|p \rangle$ ($n \geqslant 4$) calculated using Clementi's F$^-$ wavefunctions (Clementi 1965) and a potential well with a width of 11.61 au confining the ionic wavefunctions of Mn^{2+}, $R^{(2)}(3d, 3d, 3d, ns)$, $\bar{B}_2(ns)$ and $E(ns)$. The admixture coefficients representing the spin–orbit coupling effect in the expressions for the ground state in terms of LS-coupled states with $J = \frac{5}{2}$:

$$|\mathscr{S}\rangle = s|^6S_{5/2}\rangle + p|^4P_{5/2}\rangle + d|^4D_{5/2}\rangle + f|^4F_{5/2}\rangle + g|^4G_{5/2}\rangle$$
$$+ d_1|^2D1_{5/2}\rangle + d_2|^2D2_{5/2}\rangle + d_3|^2D3_{5/2}\rangle \tag{12}$$

with $s = 0.99975$, $p = 2.2230 \times 10^{-2}$, $d = -4.1405 \times 10^{-4}$, $f = 7.632 \times 10^{-6}$, $g = -2.220 \times 10^{-7}$, $d_1 = 2.5439 \times 10^{-4}$, $d_2 = -4.639 \times 10^{-6}$ and $d_3 = -3.950 \times 10^{-4}$ have already been obtained (Siu 1988b), and the Slater radial integrals for $3d \rightarrow nd$ excitation are given in table 1 of Siu and Poon (1988). Hence, we obtain the ECCF contributions and table 4 gives the results of $\bar{b}_k(3d \rightarrow nd, n \geqslant 4)$ and $\bar{b}_2(3d \rightarrow ns, n \geqslant 4)$. The total ECCF contributions are

$$\bar{b}_2(\text{ECCF}, d \rightarrow d) = 579.29 \times 10^{-4} \text{ cm}^{-1}$$
$$\bar{b}_2(\text{ECCF}, d \rightarrow s) = 19.75 \times 10^{-4} \text{ cm}^{-1} \tag{13}$$
$$\bar{b}_4(\text{ECCF}) = -1.92 \times 10^{-4} \text{ cm}^{-1}.$$

The total rank-2 contribution of the ECCF is 599.04×10^{-4} cm^{-1}, which is much larger than spin correlated crystal fields and can be compared with the relativistic crystal field contribution (-0.2201 cm^{-1}). Hence, it shows that ECCF is a significant cancellation mechanism.

It should be noted that an effective screening of the Coulomb matrix element (Newman 1977) tends to reduce the calculated values of the Slater radial integrals we

used, although it is not more than 10% for the f-function integrals. Further study will make our estimate more precise but we expect that a 10% reduction of the contributions in (13) would not affect the relative importance of the ECCF. Besides, it can be seen that the rank-2 contribution of the $3d \rightarrow ns$ excitations is of the same order of magnitude as the uncertainty in that of the $3d \rightarrow nd$ excitations. Hence it can in fact be neglected. The contributions of the excitations $3d \rightarrow ng$ are expected to be smaller than that of the $3d \rightarrow ns$ excitations due to the decrease of both the overlap integrals and the Slater integrals, and the increase of the energy $E(ng)$. Hence, it is quite safe here to neglect the contributions of the excitations $3d \rightarrow ng$.

Following the discussion of Siu (1987), the magnetically correlated CF will contribute to the ZFS of Gd^{3+} with similar magnitude to the ECCFs. If it is also the case for Mn^{2+}, we may explain the small experimental value for Mn^{2+} with an F^- ligand (-0.03 cm^{-1}, Heming *et al* 1986). Calculations based on an overlap model to estimate the contributions of the magnetically correlated CF are presently being carried out.

In summary, we have shown that the ECCF does make opposite contributions, relative to those from the RCF, to the ground S-state splitting of Mn^{2+}. These contributions from the ECCF are quite significant. This clarifies the long-held doubt as to whether significant cancellations can be determined, and shows that the experimental facts might be explained by a suitable balance between the dominant contribution and cancellation ones.

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