

## Explanations of the spectral splittings of $\text{CsFeCl}_3$ and $\text{CsMnBr}_3$

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1989 J. Phys.: Condens. Matter 1 2327

(<http://iopscience.iop.org/0953-8984/1/13/005>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.90

The article was downloaded on 10/05/2010 at 18:03

Please note that [terms and conditions apply](#).

# Explanations of the spectral splittings of CsFeCl<sub>3</sub> and CsMnBr<sub>3</sub>

Yuanwu Qiu<sup>†</sup> and Ji-kang Zhu<sup>‡</sup>

<sup>†</sup> Department of Physics, Tongji University, Shanghai, People's Republic of China

<sup>‡</sup> Shanghai Software Centre, Shanghai, People's Republic of China

Received 8 August 1988, in final form 10 October 1988

**Abstract.** The electronic structures of the clusters (FeCl<sub>6</sub>)<sup>4-</sup> and (MnBr<sub>6</sub>)<sup>4-</sup> were calculated with the spin-polarised MS-X<sub>α</sub> method under the actual lower-symmetry (D<sub>3d</sub>) crystal field of CsFeCl<sub>3</sub> and CsMnBr<sub>3</sub>. The calculations enable some of the splittings in the absorption spectra of the crystals to be theoretically explained.

## 1. Introduction

The electronic structures of divalent first-row transition-metal ions are dominated by spin- and parity-forbidden transitions. The strong enhancement of the forbidden absorptions in the spectra of type ABX<sub>3</sub> (A ≡ monovalent alkali-metal or alkylammonium cation; B ≡ divalent first-row transition metal ion; X<sup>-</sup> ≡ Cl<sup>-</sup>, Br<sup>-</sup> or I<sup>-</sup>) crystals facilitates assignment of these states, and comparison of the spectra provides a useful empirical characterisation of the mechanism of enhancement. The unusual spectral and magnetic properties of the crystals derive from their unique structures. Studies of CsFeCl<sub>3</sub> and CsMnBr<sub>3</sub> are of significance for studies of type ABX<sub>3</sub> crystals.

All previous X<sub>α</sub> calculations of transition-metal ion clusters were under O<sub>h</sub> site symmetry. Only the value of 10Dq can be obtained. Owing to the restriction of the statistical average approximation of the exchange energy in X<sub>α</sub> calculations, the energies of the spectral terms involving the two-electron operator cannot be obtained in general. However, in [1] it was suggested that the one-electron model is adequate for explaining the spectral splittings for some molecules and clusters. In [2] the suggestion was extended to the DV-X<sub>α</sub> framework. The restriction of the statistical average approximation in X<sub>α</sub> calculations can be solved in some special cases by using lower site symmetries.

We completed a series of calculations for (NiF<sub>6</sub>)<sup>4-</sup> [3] (d<sup>8</sup> electron configuration of the free central ion), (CoF<sub>6</sub>)<sup>4-</sup> [4] (d<sup>7</sup>) and (VF<sub>6</sub>)<sup>4-</sup> [5] (d<sup>3</sup>) clusters. In this paper, we calculate the electronic structures of the (FeCl<sub>6</sub>)<sup>4-</sup> (d<sup>6</sup>) and (MnBr<sub>6</sub>)<sup>4-</sup> (d<sup>5</sup>) clusters with the spin-polarised MS-X<sub>α</sub> method under the actual lower-symmetry (D<sub>3d</sub>) crystal field of CsFeCl<sub>3</sub> and CsMnBr<sub>3</sub>. The calculations enable some of the splittings in the absorption spectra of the crystals to be theoretically explained.

## 2. Details of calculations

The optical properties of the CsFeCl<sub>3</sub> and CsMnBr<sub>3</sub> crystals can be obtained by calculations on (FeCl<sub>6</sub>)<sup>4-</sup> and (MnBr<sub>6</sub>)<sup>4-</sup> clusters which are formed with central ions

**Table 1.** The atomic coordinates of the  $(\text{FeCl}_6)^{4-}$  cluster.

	x (au)	y (au)	z (au)
Fe	0	0	0
Cl(1)	3.7414	0	2.8580
Cl(2)	-1.8707	3.2402	2.8580
Cl(3)	-1.8707	-3.2402	2.8580
Cl(4)	-3.7414	0	-2.8580
Cl(5)	1.8707	-3.2402	-2.8580
Cl(6)	1.8707	3.2402	-2.8580

**Table 2.** The atomic coordinates of the  $(\text{MnBr}_6)^{4-}$  cluster.

	x (au)	y (au)	z (au)
Mn	0	0	0
Br(1)	4.0269	0	3.0801
Br(2)	-2.0134	3.4875	3.0801
Br(3)	-2.0134	-3.4875	3.0801
Br(4)	-4.0269	0	-3.0801
Br(5)	2.0134	-3.4875	-3.0801
Br(6)	2.0134	3.4875	-3.0801

**Table 3.** One-electron eigenvalues and eigenfunctions of  $(\text{FeCl}_6)^{4-}$ .

$O_h$	$D_{3d}$	$-E$ (eV)	Charge distribution
$e_g \downarrow$	$2e_g \downarrow$	0.868	0.803Fe + 0.020Cl
$t_{2g} \downarrow$	$a_{1g} \downarrow$	1.804	0.915Fe + 0.005Cl
$t_{2g} \downarrow$	$1e_g \downarrow$	1.828	0.919Fe + 0.005Cl
$e_g \uparrow$	$2e_g \uparrow$	3.886	0.459Fe + 0.078Cl
$t_{2g} \uparrow$	$a_{1g} \uparrow$	5.448	0.645Fe + 0.047Cl
$t_{2g} \uparrow$	$1e_g \uparrow$	5.461	0.629Fe + 0.049Cl

$\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  and six innermost ligand ions  $\text{Cl}^-$  and  $\text{Br}^-$ , respectively. The atomic coordinates of the  $(\text{FeCl}_6)^{4-}$  and  $(\text{MnBr}_6)^{4-}$  clusters are listed in table 1 [6] and table 2 [7], respectively. The site symmetry of  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  is  $D_{3d}$ .

The exchange scaling parameters  $\alpha$  are taken from the table in [8], and those in the inner-sphere and in the outer-sphere regions are chosen as weighted averages according to the number of valence electrons of the various atoms. The radii of atomic spheres are according to [9] with a reduction factor of 0.88 [10, 11]. There is a little overlap between neighbouring atomic spheres. The overlap between the outermost atomic spheres and the outer sphere is 0.15 au. The effects of the atoms outside the cluster is simulated by a Watson sphere. In the atomic region, the  $L_{\text{max}}$  of the spherical harmonic parts of the wavefunctions are chosen as 2 for the central ions and 1 for the ligand ions. In the outer sphere,  $L_{\text{max}}$  is 4.

The computer program used for our calculations was  $X_\alpha$ -VAXIBM. All calculations were performed on the Siemens 7.570-C computer in Tongji University.

### 3. Results and discussion

#### 3.1. $\text{CsFeCl}_3$

The calculated one-electron eigenvalues and eigenfunctions of the  $(\text{FeCl}_6)^{4-}$  clusters are listed in table 3. From the charge distributions, it can be seen that mixing occurs between ligand components and crystal-field orbitals, especially for spin-up orbitals.

The electron configuration of the free ion  $\text{Fe}^{2+}$  is  $d^6$ . Under  $O_h$  site symmetry the ground state is  ${}^5T_{2g}(t_{2g}^4 e_g^2)$ , and the lowest excited state is  ${}^5E_g(t_{2g}^3 e_g^3)$ . The energy difference between these two states is  $10Dq$  [12] and can be obtained by the calculation of the transition energy of  $1e_g \downarrow - 2e_g \downarrow$  with the transition state theory. The calculated result is  $7884 \text{ cm}^{-1}$  which is in good agreement with the experimental result of  $7350 \text{ cm}^{-1}$  [13].

**Table 4.** Energies of some terms of  $(\text{FeCl}_6)^{4-}$ .

Configuration	$O_h$	$D_{3d}$	Electron transition	Energy difference ( $\text{cm}^{-1}$ )	
				Calculated	Experiment
$t_{2g}^3 e_g^3$	${}^5E_g$	${}^5E_g$	$1e_g \downarrow -2e_g \downarrow$	7 884	7 350
$t_{2g}^3 e_g^3$	${}^3T_{1g}$	${}^3E_g$	$2e_g \uparrow -1e_g \downarrow$	13 096	12 658
$t_{2g}^2 e_g^4$	${}^3T_{1g}$	${}^3A_{2g}$	$2e_g \uparrow -a_{1g} \downarrow$	13 276	
$t_{2g}^2 e_g^4$	${}^3T_{2g}$	${}^3E_g$	$2e_g \uparrow -2e_g \downarrow$	21 078	21 169, 21 810
$t_{2g}^4 e_g^2$	${}^3T_{2g}$	${}^3A_{1g}$	$2e_g \uparrow -2e_g \downarrow, 1e_g \downarrow -a_{1g} \downarrow$	21 273	
$t_{2g}^4 e_g^2$	${}^3E_g$	${}^3E_g$	$1e_g \uparrow -1e_g \downarrow$	22 809	22 700
$t_{2g}^3 e_g^3$	${}^3T_{1g}$	${}^3E_g$	$a_{1g} \uparrow -a_{1g} \downarrow$	22 813	23 288, 23 379
$t_{2g}^4 e_g^2$	${}^3T_{1g}$	${}^3A_{2g}$	$1e_g \uparrow -a_{1g} \downarrow$	23 015	

**Table 5.** One-electron eigenvalues and eigenfunctions of  $(\text{MnBr}_6)^{4-}$ .

$O_h$	$D_{3d}$	$-E$ (eV)	Charge distribution
$e_g \downarrow$	$2e_g \downarrow$	0.824	$0.782\text{Mn} + 0.015\text{Br}$
$t_{2g} \downarrow$	$a_{1g} \downarrow$	1.613	$0.901\text{Mn} + 0.003\text{Br}$
$t_{2g} \downarrow$	$1e_g \downarrow$	1.620	$0.912\text{Mn} + 0.003\text{Br}$
$e_g \uparrow$	$2e_g \uparrow$	4.411	$0.363\text{Mn} + 0.092\text{Br}$
$t_{2g} \uparrow$	$1e_g \uparrow$	5.998	$0.434\text{Mn} + 0.076\text{Br}$
$t_{2g} \uparrow$	$a_{1g} \uparrow$	6.017	$0.467\text{Mn} + 0.072\text{Br}$

The energies for some of the triplet terms of the electron configurations  $t_{2g}^5 e_g$  and  $t_{2g}^4 e_g^2$  were also calculated with the transition state theory. The calculated results together with the experimental results of [13] are listed in table 4. According to the calculated results, we assign the bands near  $23\,000\text{ cm}^{-1}$ , which were not assigned in [13], to the transition  ${}^3T_{1g}(t_{2g}^4 e_g^2) \rightarrow {}^5T_{2g}$ , and explain the bands of  $21\,169$  and  $21\,810\text{ cm}^{-1}$  and  $23\,288$  and  $23\,379\text{ cm}^{-1}$  to be splittings of the state  ${}^3T_{2g}(t_{2g}^4 e_g^2)$  and  ${}^3T_{1g}(t_{2g}^4 e_g^2)$ , respectively, under the lower-symmetry ( $D_{3d}$ ) crystal field.

### 3.2. $\text{CsMnBr}_3$

The calculated one-electron eigenvalues and eigenfunctions of the cluster  $(\text{MnBr}_6)^{4-}$  are listed in table 5. The electron configuration of the free ion  $\text{Mn}^{2+}$  is  $d^5$ . Under  $O_h$  site symmetry the ground state is  ${}^6A_{1g}(t_{2g}^3 e_g^2)$ . The energy difference between  ${}^4T_{2g}(t_{2g}^4 e_g)$  and  ${}^4T_{2g}(t_{2g}^2 e_g^3)$  or  ${}^4T_{1g}(t_{2g}^4 e_g)$  and  ${}^4T_{1g}(t_{2g}^2 e_g^3)$  equals twice  $10Dq$  [12]. However, even if the lower symmetry is considered, the  $X_\alpha$  calculation still cannot resolve enough energies in the spectral terms to derive the value of  $10Dq$ . It seems reasonable to take the orbital energy difference of  $t_{2g} \downarrow$  and  $e_g \downarrow$  as the value of  $10Dq$ . The calculated value of  $10Dq$  is thus  $6236\text{ cm}^{-1}$  which agrees with the fitted experimental value of  $7000\text{ cm}^{-1}$  [14].

The energies for some of the quartet terms of electron configurations  $t_{2g}^4 e_g^2$ ,  $t_{2g}^3 e_g^2$  and  $t_{2g}^2 e_g^3$  were calculated with the transition state theory. The calculated results together with the experimental results in [15] are listed in table 6. According to the calculated results, we explain the bands  $29\,665$  and  $29\,980\text{ cm}^{-1}$  to be the splitting of the state  ${}^4T_{1g}(t_{2g}^3 e_g^2)$  under the lower-symmetry ( $D_{3d}$ ) crystal field.

The fine structures of the absorption spectrum of  $\text{CsMnBr}_3$  given in [15] are due to spin-orbit coupling and molecular vibration. The spin-orbit coupling energies of the terms  ${}^4A_{1g}({}^4A_{1g})$ ,  ${}^4E_g({}^4E_g)$ ,  ${}^4A_{1g}({}^4T_{2g})$  and  ${}^4A_{2g}({}^4T_{1g})$  equal zero. The two manifolds

**Table 6.** Energies of some terms of  $(\text{MnBr}_6)^{4-}$ .

Configuration	$O_h$	$D_{3d}$	Transition	Energy difference ( $\text{cm}^{-1}$ )	
				Calculated	Experiment
$t_{2g}^4 e_g$	${}^4T_{2g}$	${}^4A_{1g}$	$2e_g \uparrow -1e_g \downarrow$	20 894	
$t_{2g}^4 e_g$	${}^4T_{2g}$	${}^4E_g$	$2e_g \uparrow -a_{1g} \downarrow$	21 463	21 505
$t_{2g}^3 e_g^2$	${}^4E_g$	${}^4E_g$	$2e_g \uparrow -2e_g \downarrow$	26 611	27 350, 27 480, 27 630
$t_{2g}^3 e_g^2$	${}^4T_{1g}$	${}^4E_g$	$a_{1g} \uparrow -1e_g \downarrow$	30 633	29 525, 29 610, 29 665
$t_{2g}^3 e_g^2$	${}^4T_{1g}$	${}^4A_{2g}$	$1e_g \uparrow -1e_g \downarrow$	30 764	29 980
$t_{2g}^3 e_g^2$	${}^4T_{1g}$	${}^4E_g$	$a_{1g} \uparrow -2e_g \downarrow$	37 302	34 540
$t_{2g}^3 e_g^2$	${}^4T_{1g}$	${}^4A_{2g}$	$1e_g \uparrow -2e_g \downarrow$	37 376	

**Table 7.** The spin-orbit splittings of  ${}^4E_g$  ( ${}^4T_{2g}$ ) and  ${}^4E_g$  ( ${}^4T_{1g}$ ) of  $\text{CsMnBr}_3$ .

	$E'$ ( $\text{cm}^{-1}$ )	$E'$ ( $\text{cm}^{-1}$ )	$E''$ ( $\text{cm}^{-1}$ )	$E''$ ( $\text{cm}^{-1}$ )	Experimental value
${}^4E_g$ ( ${}^4T_{2g}$ )	26 388	26 434	26 495	26 603	26 350, 26 480, 26 550
${}^4E_g$ ( ${}^4T_{1g}$ )	29 518	29 564	29 625	29 733	29 525, 29 610, 29 665

of  ${}^4E_g$  ( ${}^4T_{2g}$ ) ( $26\,350$ – $26\,550\text{ cm}^{-1}$ ) and  ${}^4E_g$  ( ${}^4T_{1g}$ ) ( $29\,525$ – $29\,665\text{ cm}^{-1}$ ) should contain spin-orbit coupling contributions. The expanded one-electron wavefunctions including the effect of the charges in the inter-sphere were obtained by using the charge partition approximation from [16]. The average value of  $r^{-3}$  is calculated with the expanded one-electron eigenfunctions, and the spin-orbit coupling constant  $\xi$  was calculated using the following expression:

$$\xi = - (Z' e^2 \hbar^2 / 2m^2 c^2) \langle r^{-3} \rangle_{3d}$$

where  $Z'$  is the effective number of charge. The calculated spin-orbit coupling constant  $\xi$  of  $\text{Mn}^{2+}$  is  $369\text{ cm}^{-1}$ , and the spin-orbit splittings of  ${}^4E_g$  ( ${}^4T_{2g}$ ) and  ${}^4E_g$  ( ${}^4T_{1g}$ ) are listed in table 7 together with the experimental results from [15].  $E'$  and  $E''$  are the double-valued representations of group  $D_{3d}$ . The agreement between calculations and experiments is fairly good.

## References

- [1] Bagus P S and Bennett B I 1975 *Int. J. Quantum Chem.* **9** 143
- [2] Ziegler T, Rand A and Baerends E J 1977 *Theor. Chim. Acta* **43** 261
- [3] Zhu J K, Zhang B and Liu S H 1985 *Chem. Phys. Lett.* **119** 141
- [4] Zhu J K, Chen J F and Liu S H 1987 *Sci. Sinica A* **30** 1226
- [5] Qiu Y and Zhu J K 1988 *Technical Digest of the 16th International Quantum Electronics Conf. (Tokyo)* (Tokyo: Japan Society of Applied Physics) p 70
- [6] Seifert H J and Klatyk K 1966 *Z. Anorg. Allg. Chem.* **42** 1
- [7] Goodyear J and Kennedy D J 1972 *Acta Crystallogr. B* **28** 1640
- [8] Schwarz K 1972 *Phys. Rev. B* **5** 2466
- [9] Norman J G Jr 1976 *Mol. Phys.* **31** 1191
- [10] Zhu J K, Li D, Li J and Pan Y K 1985 *Sci. Sinica B* **28** 1243
- [11] Zhu J K, Li D, Li J and Pan Y K 1983 *Theor. Chim. Acta* **63** 223
- [12] Griffith J S 1961 *The Theory of Transition-Metal Ions* (Cambridge: CUP) p 412
- [13] Putnik C F, Mattney Cole G Jr, Garrett B B and Holt S L 1976 *Inorg. Chem.* **15** 826
- [14] Pappalardo R 1959 *J. Chem. Phys.* **31** 1051
- [15] Mattney Cole G Jr, Putnik C P and Holt S L 1975 *Inorg. Chem.* **14** 2219
- [16] Case D A and Karplus M 1976 *Chem. Phys. Lett.* **39** 33