Investigation of the Zero-Field Splitting of d^8 Ions in Pseudo-tetragonal Ni(II) Compounds

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This paper presents a cluster approach to the zero-field splitting (ZFS) of the ground state $^3A_2(F)$ of d^8 ions with tetragonal symmetry, in which not only the spin-orbit coupling of the central transition-metal-ion but also that of ligands contributes. For some pseudo-tetragonal Ni(II) compounds the calculated values of the ZFS parameter follow the order $Cl^- > Br^- > I^-$. This agrees with the experimental finding, while the pure crystal field approach considering only the coupling of central metal ion yields the opposite trend.

I. Introduction

The role of covalence in explaining the EPR parameters of transition-metal-ions is a complex problem [1–4]. In [5–8] we have treated and discussed the covalence problem of the g-factor of d^8- and d^3-clusters with octahedral symmetry, using the two s.o. coupling parameter model. The results show that the contribution of s.o. coupling of ligand ions to the g factor of d^n clusters in covalent crystals is important and can not be neglected when the ligand ions have large s.o. coupling parameters or the complex is strongly covalent.

In this paper we investigate the zero-field splitting (ZFS) of the ground state $^3A_2(F)$ of d^8 ions in clusters with tetragonal symmetry by means of the two s.o. coupling parameter models and the high-order perturbation loop method [9], and discuss the ligand contribution to the ZFS parameter in case of some pseudo-tetragonal Ni(II) compounds.

II. Two Spin-orbit Coupling Parameters for ZFS

The Ni(II) ion has a $3d^8$ electron configuration and possesses a $^3A_2(F)$ ground state in octahedral symmetry. According to the LCAO molecular-orbital-model, the one-electron basis functions in an octahedral field for a $3d^8$ central metal ion can be written as [5]

$$|\gamma\rangle = N_\gamma^{1/2}(|d_\gamma\rangle - \lambda_\gamma |p_\gamma\rangle), \tag{1}$$

where $\gamma = t_{2g}$ and e_g are the irreducible representations of the cubic group, N_γ and λ_γ are the normalization and mixing coefficients of molecular orbitals, d denotes the d-orbit function and p the p-orbit of a ligand. The s.o. coupling interaction Hamiltonian which includes s.o. coupling interaction of the ligand ions can be written equivalently as [10]

$$\hat{H}_{so} = \sum_i \zeta_c(r_{ic})\, \boldsymbol{l}_{ic} \cdot \mathbf{s}_i + \sum_i \zeta_l(r_{il})\, \boldsymbol{l}_{il} \cdot \boldsymbol{s}_i\,, \tag{2}$$

where $\boldsymbol{l}_{ic}$ and $\boldsymbol{l}_{il}$ are the one-electron angular momentum operators relative to the nuclei c and l, and $\zeta_c(r_{ic})$ and $\zeta_l(r_{il})$ are the s.o. functions of the central metal and ligand ions, respectively. The second term in (2) expresses explicitly the influence of the s.o. coupling interaction on the ligands. Using Macfarlanes' method [9], we choose a strong-field cubic basis for the perturbation calculation, the perturbation Hamiltonian appropriate for D_{4h} symmetry being

$$\hat{H}' = \hat{H}_b(B, C) + \hat{H}(V_t) + \hat{H}_{so} + \hat{H}_z\,, \tag{3}$$

where $\hat{H}_b(B, C)$, $\hat{H}(V_t)$, $\hat{H}_{so}$, and $\hat{H}_z$ are the off-diagonal terms of electrostatic Coulomb interaction, the tetragonal part of the crystal field, the spin-orbit Hamiltonian, and the Zeeman term, respectively. Since the contributions of the spin-orbit coupling interaction

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of the central ion and the ligand ions to the ZFS parameter have been studied in this work, the LCAO molecular orbit basis could been chosen as the zeroth-order wave function in an octahedral field for a $3d^8$ central metal ion. The analytical perturbation expression of the ZFS parameter in tetragonal symmetry for the ground state $^3A_2(F)$ of d^8 ions and the first- and fourth-order has been derived. In this process, only the one-electron matrix elements of both the central metal ion and the ligand ions are retained; the others are neglected as very small [5, 7]. The expressions can be written as

$$D = D(\zeta_d) + D(\zeta_p) + D(\zeta_d, \zeta_p)\,, \tag{4.1}$$

$$\begin{aligned} D(\zeta_d) = & -35(\zeta_d^{te})^2 D_t(1/D_4^2 - 1/D_2^2)/4 \\ & + 9(\zeta_d^{te})^2 \zeta_d^t (D_s - 5D_t/4)(1/D_4 - 1/D_2)/2D_1D_2 \\ & - 35(\zeta_d^{te})^2 \zeta_d^t D_t/8D_2^3 \\ & - 76\tfrac{9}{16}(\zeta_d^{te})^2 D_t^2(1/D_4^3 - 1/D_2^3) \\ & + 3(\zeta_d^{te})^2(D_s - 5D_t/4)^2(1/D_1D_2^2 - 1/D_3D_4^2) \\ & - 35(\zeta_d^{te})^2 \zeta_d^t D_t(2/D_4 - 1/D_2)/8D_2D_4\,, \end{aligned} \tag{4.2}$$

$$\begin{aligned} D(\zeta_p) = & -35(\zeta_p^{te})^2 D_t(1/D_4^2 - 1/D_2^2)/4 \\ & + 9(\zeta_p^{te})^2 \zeta_p^t (D_s - 5D_t/4)(1/D_4 - 1/D_2)/2D_1D_2 \\ & - 35(\zeta_p^{te})^2 \zeta_p^t D_t/8D_2^3 \\ & - 76\tfrac{9}{16}(\zeta_p^{te})^2 D_t^2(1/D_4^3 - 1/D_2^3) \\ & + 3(\zeta_p^{te})^2(D_s - 5D_t/4)^2(1/D_1D_2^2 - 1/D_3D_4^2) \\ & - 35(\zeta_p^{te})^2 \zeta_p^t D_t(2/D_4 - 1/D_2)/8D_2D_4\,, \end{aligned} \tag{4.3}$$

$$\begin{aligned} D(\zeta_d, \zeta_p) = & \; 35\zeta_d^{te}\zeta_p^{te} D_t(1/D_4^2 - 1/D_2^2)/2 \\ & - 76\tfrac{9}{8}\zeta_d^{te}\zeta_p^{te} D_t^2(1/D_4^3 - 1/D_2^3) \\ & + [-2\zeta_d^{te}\zeta_p^{te}\zeta_d^t + (\zeta_p^{te})^2\zeta_d^t + (\zeta_d^{te})^2\zeta_p^t - 2\zeta_d^{te}\zeta_p^{te}\zeta_p^t] \\ & \cdot [9(D_s - 5D_t/4)(1/D_4 - 1/D_2)/2D_1D_2 \\ & \quad - 35D_t/8D_2^3 - 35D_t(2/D_4 - 1/D_2)/8D_2D_4] \\ & - 6\zeta_d^{te}\zeta_p^{te}(D_s - 5D_t/4)^2(1/D_1D_2^2 - 1/D_3D_4^2)\,, \end{aligned} \tag{4.4}$$

where

$$\zeta_d^{te} = (N_t N_e)^{1/2}\,\zeta_d^0\,, \qquad \zeta_d^t = N_t\,\zeta_d^0\,,$$

$$\zeta_p^{te} = (N_t N_e)^{1/2}\,\lambda_t\,\lambda_e\,\zeta_p^0/2\,, \quad \zeta_p^t = N_t\,\lambda_t^2\,\zeta_p^0/2\,. \tag{5}$$

$D(\zeta_d)$, $D(\zeta_p)$ and $D(\zeta_d, \zeta_p)$ are the contributions from the central metal ion, the ligand ion and both to the ZFS parameter, respectively. ζ_d^0 and ζ_p^0 are the spin-orbit coupling parameters of the central ion and the ligand ions, respectively. The zero-order energy separations are

$$\begin{aligned} D_1 &= \Delta E(^3T_1^b) = 12B + 10D_q\,, \\ D_2 &= \Delta E(^3T_2) = 10D_q\,, \\ D_3 &= \Delta E(^1T_1) = 12B + 2C + 10D_q\,, \\ D_4 &= \Delta E(^1T_2^b) = 8B + 2C + 10D_q\,, \end{aligned} \tag{6}$$

where the crystal field parameters D_t, D_s and D_q in (4) to (6) have their usual meaning [11, 12].

III. Application

The optical spectra and EPR parameters of the compounds Ni(5-methyl pyrazole)$_4$X$_2$[Ni(mpz)$_4$X$_2$] and Ni(pyrazole)$_4$X$_2$[Ni(pz)$_4$X$_2$] (X=Cl, Br, I) have been obtained by Vermass, Groeneveld and Reedÿk [12]. These experimental results show that the g-shifts and ZFS parameters D are in the order Ni(pz)$_4$Cl$_2$ > Ni(pz)$_4$Br$_2$ and Ni(mpz)$_4$Cl$_2$ > Ni(mpz)$_4$Br$_2$ >

Table 1. The experimental parameters* (in cm^{-1}) of Ni(II) compounds.

	B	C	ζ_d	D_q	D_s	D_t
free Ni^{2+} **	1084	4831	649			
Ni(pz)$_4$Cl$_2$	940	3400		1095	1040	285
Ni(pz)$_4$Br$_2$	920	3400		1090	1250	345
Ni(mpz)$_4$Cl$_2$	900	3450		1100	950	300
Ni(mpz)$_4$Br$_2$	890	3400		1080	1250	320
Ni(mpz)$_4$I$_2$	900	3400		1090	1400	440

* [12], at room temperature. – ** [16].

Compound	f_γ	R (nm) [7, 12]	$S_{dp}(e_g)$	$S_{dp}(t_{2g})$	N_t	N_e	λ_t	λ_e
Ni(pz)$_4$Cl$_2$	.7855	.2507	.0231	.00684	.9344	.9387	.2720	.2797
Ni(pz)$_4$Br$_2$	.7762	.2682	.0205	.00561	.9289	.9330	.2822	.2892
Ni(mpz)$_4$Cl$_2$	.7722	.257	.0198	.00562	.9271	.9310	.2861	.2927
Ni(mpz)$_4$Br$_2$	.7624	.273	.0182	.00483	.9210	.9248	.2977	.3039
Ni(mpz)$_4$I$_2$	.7670	.297	.0161	.00413	.9234	.9267	.2922	.2977

Table 2. The group overlap integrals and the molecular orbital coefficients of Ni(II) compounds.

Table 3. Comparison between calculated and observed ZFS parameters of Ni(II) compounds (in cm^{-1}).

Compound	Calculated values				Observed values [12]
	$D(\zeta_d)$	$D(\zeta_p)$	$D(\zeta_d, \zeta_p)$	D	D
$Ni(pz)_4Cl_2$	7.557	0.0264	−0.8929	6.691	7.2 ± 0.1
$Ni(pz)_4Br_2$	9.513	0.6438	−4.9513	5.205	5.4 ± 0.1
$Ni(mpz)_4Cl_2$	7.698	0.0307	−0.9728	6.756	7.4 ± 0.2
$Ni(mpz)_4Br_2$	8.734	0.6769	−4.8644	4.547	5.3 ± 0.2
$Ni(mpz)_4I_2$	12.59	3.9735	−14.15	2.417	2.5 ± 0.3

$Ni(mpz)_4I_2$. But the calculated results from the classical crystal field approach show the opposite trend. The problem of g-shift has been explained in our previous work [7], but few theoretical analyses interpret the experimental results of the ZFS parameter satisfactorily. A high-order perturbation formula of EPR parameters for d^2 (d^8) ions in low symmetry [13] has been obtained by us, but only the contribution of the spin-orbit coupling of the central metal ion to the EPR parameters was included. Now the two spin-orbit coupling parameter model has been employed to calculate the ZFS parameter. The symmetry of these Ni(II) compounds is approximately tetragonal (D_{4h}) [7, 12].

In order to determined the LCAO coefficients N_γ and λ_γ, a semiempirical method [4, 5] was employed. We used the approximate relationship

$$f_\gamma = N_\gamma^2 [1 - 2\lambda_\gamma S_{dp}(\gamma) + \lambda_\gamma^2 S_{dp}^2(\gamma)] \tag{7}$$

and the normalization correlation

$$N_\gamma [1 - 2\lambda_\gamma S_{dp}(\gamma) + \lambda_\gamma^2] = 1\,, \tag{8}$$

where [5]

$$f_\gamma = f = (B/B_0 + C/C_0)/2\,. \tag{9}$$

The electrical spectra of Ni(II) compounds were reported in [12]. The values of Racah and the crystal field parameters, B, C, D_q, D_s, and D_t calculated by means of the ligand field method from these experimental findings are listed in Table 1. The calculated overlap integrals and MO coefficients, obtained by using a semiempirical method, are presented in Table 2. The s.o. coupling parameters of the ligands Cl^-, Br^-, I^- and N^- are 587, 2460, 5060, and 75 cm^{-1}, respectively [14, 15]. As the s.o. coupling parameter of N^- is very small, its contribution can be neglected. Thus, we have calculated the ZFS parameters of the ground state $^3A_2(F)$ for Ni(II) compounds without any adjusted parameters; these are listed in Table 3.

Table 3 shows explicitly that the contribution to the ZFS of the s.o. coupling of the ligand ions, the positive term $D(\zeta_p)$, is smaller than the negative contribution $D(\zeta_d, \zeta_p)$ from the combined interaction of the central and ligand ion. The combined term $D(\zeta_d, \zeta_p)$ becomes larger with increasing spin-orbit coupling parameters of the ligand atoms. This result is different from that for the g-factor, where the combined contribution term $g(\zeta_d, \zeta_p)$ is always very small and has been neglected [7].

IV. Conclusion

When the contribution of the s.o. coupling of ligand ions is included in the calculation of the ZFS parameter, the obtained values have the same order as the observed one. Evidently the two s.o. coupling parameters model is necessary for explaining the EPR parameter values of these Ni(II) compounds.

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