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Theoretical investigations of the microscopic spin Hamiltonian parameters including the spin–spin and spin–other-orbit interactions for $Ni^{2+}(3d^8)$ ions in trigonal crystal fields

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Abstract

The microscopic origin of the spin Hamiltonian (SH) parameters for $Ni^{2+}(3d^8)$ ions in a trigonal type I symmetry (C_{3v}, D_{3d}, D_3) crystal field (CF) is studied. In addition to the spin–orbit (SO) interaction, we consider also the spin–spin (SS) and spin–other-orbit (SOO) interactions. The relative importance of the four (SO, SS, SOO, and combined SO–SS–SOO) contributions to the SH parameters is investigated using the CFA/MSH package and the complete diagonalization method (CDM). The SO mechanism is dominant for all CF parameter (CFP) ranges studied, except where the contributions D_{SO} to the zero-field splitting (ZFS) parameter D change sign. For the trigonal CFP, $v_c \approx 1200\ cm^{-1}$ D due to the other three mechanisms exceeds D_{SO}. Although $|D_{SOO}|$ is quite small, the combined $|D_{SO-SOO}|$ is appreciable. The SO-based perturbation theory (PT) works generally well for the g-factors: $g_\parallel$ and $g_\perp$, while it fails for D in the vicinity of v_c and for large $|v'|$ and $v > 0$. The high percentage discrepancy ratio $\delta_D = 2020\%$ for v_c indicates unreliability of D_{SO} (in PT). Applications to Ni^{2+} ions at trigonal symmetry sites in $LiNbO_3$, α-$LiIO_3$, and Al_2O_3, are provided. The theoretical SH parameters are in good agreement with the experimental data. The low symmetry (C_3) effects induced by the angle φ are tentatively studied, but appear to be quite small.

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1. Introduction

As is well known, the spin Hamiltonian (SH) parameters and the crystal field (CF) ones for the transition metal (TM) ions in crystals are very sensitive to subtle changes of the crystal structure [1–4]. Hence, studies of these parameters using EMR (electron magnetic resonance) and optical spectroscopy, respectively, can provide a great deal of microscopic insight concerning the crystal structure, structural disorder, phase transitions, pressure behaviour as well as the observed magnetic and spectroscopic properties [5–9]. Two major approaches (see, e.g., [3]) to the microscopic derivation of the SH parameters exist, namely, the complete diagonalization method (CDM) and the perturbation theory method (PTM). The PTM takes into account the contributions to the SH parameters from some $3d^N$ excited states within the ligand field framework [10, 11]. Advances in the computational techniques in the last few decades have enabled development of the CDM by various authors [5, 8, 9, 12]. The CDM takes into account the contributions from all $3d^N$ excited states and hence can provide a more accurate determination of the SH parameters. Both PTM and CDM have been extensively used to investigate the SH parameters for $3d^N$ ions with the ground orbital singlet state at axial symmetry sites [4–6, 10–14]. These studies include, e.g., the 'quasi-fourth-order' perturbation formulae for the SH parameters D, $g_\parallel$, and $g_\perp$ for $3d^8$ ions in a trigonal symmetry CF derived by Petrosyan and Mirzakhanyan (P&M) [11] and the CDM using the strong CF scheme for calculation of the SH parameters for $3d^2$ and $3d^8$ ions in a trigonal symmetry CF developed by Ma *et al* [8, 15]. A comparative study of various applications of both methods for $3d^8$ and $3d^2$ ions at trigonal type I (C_{3v}, D_3, D_{3d}) symmetry sites in crystals has recently been carried out by us [14] taking into account only the spin–orbit (SO) coupling mechanism dealt with in earlier papers [8, 16, 17]. The CDM using the intermediate CF scheme developed by us [14] has been incorporated into a separate CFA/MSH computer package for calculation of the SH parameters for $3d^8(3d^2)$ ions at trigonal type I symmetry sites.

As an extension, the magnetic interactions [18, 19] for atoms with a single unfilled shell of outer electrons and a number of closed shells have been incorporated into the CFA/MSH package, in addition to the SO coupling. This includes the SS and SOO interactions, which have been omitted in previous studies [8, 11, 14–17]. The Hamiltonians H_{SOO} and H_{SS} represent the mutual interactions between the dipole moment of one electron and the orbital motion of another electron and between the magnetic dipole moments of the electrons in the unfilled shell, respectively. The extension has been motivated, among other things, by the results of studies indicating that the effects of the SS interaction are appreciable for $3d^5$ [20] and $3d^3$ ions [21]. In order to investigate more accurately the contributions to the SH parameters and the optical spectra for $3d^2(3d^8)$ ions at trigonal type I (C_{3v}, D_3, D_{3d}) and type II (C_3, C_{3i}) symmetry sites, a new module including for the first time the SS and SOO interactions has been developed within the CFA/MSH computer package [22, 23] based on the early CFA package [24]. Utilizing the extended CFA/MSH package, the optical spectra and SH parameters for $V^{3+}(3d^2)$ ions at C_3 symmetry sites in α-Al_2O_3 have been successfully investigated [22]. The study [14] has revealed that for $3d^2(3d^8)$ ions at trigonal sites the zero-field splitting (ZFS) parameter D_{SO} due to the SO interaction changes sign with the strength of some CF parameters (CFPs). Hence, it is of importance to consider the relevant contributions to the SH parameters due to the SS and SOO interactions. In the present paper, using the CFA/MSH package [22], we systematically investigate the SH parameter contributions in question for $Ni^{2+}(3d^8)$ ions at trigonal sites over a wide range of the CFPs. Additionally, the CDM results are analysed to provide insight into the limits of validity of the PT expressions [11].

2. Microscopic SH parameters for $3d^8$ ions at trigonal symmetry sites

Since the background theory has been presented earlier [14, 22] we provide here only the basic definitions and notation pertinent for the present considerations. The total Hamiltonian for $3d^8$ ions in a trigonal CF is taken as [14, 22, 24]

$$H = H_{ee}(B, C) + H_{Trees}(\alpha) + H_{SO}(\zeta) + H_{CF}(B_{kq}) + H_{SS}(M^k_{SS}) + H_{SOO}(M^k_{SOO}) \quad (1)$$

where the terms denote the electrostatic, Trees correction, SO, CF, SS, and SOO Hamiltonians, respectively. Although the physical origins of the parameters corresponding to the SS and SOO couplings in the effective Hamiltonian are different, since the operators are the same, for $3d^N$ ions the following relation holds: $M^k_{SS} = M^k_{SOO} = M^k$, and the rank $k = 0, 2$ [25]. Explicit expressions for the SS and SOO interactions for $3d^N$ ions can be found in [22]. Since the computed eigenvalues do not depend on the choice of the basis, one can use the LS basis [24] $|\alpha SLM_L M_S\rangle$ and decompose the matrix elements of each term defined in equation (1) into sums and products of the $3j$ symbols and the reduced matrix elements of double- and unit-tensor operators tabulated in, e.g., [26] and [27]. Details concerning the choice of the basis and calculation of the matrix elements for H_{ee}, H_{CF}, and H_{SO} have been provided in [24], whereas those for H_{SS} and H_{SOO} are in [22].

For $3d^8(Ni^{2+})$ ions in a trigonal CF the effective SH (see, e.g., [3]) taking into account the ZFS and Zeeman terms is given as

$$H_S = D(S_z^2 - \tfrac{1}{3}S(S+1)) + \mu_B g_\parallel B_z S_z + \mu_B g_\perp (B_x S_x + B_y S_y). \quad (2)$$

The CDM [14, 22] yields the ZFS parameter D in equation (2) as the difference between the energies of the ground states $|E(^3F\downarrow {}^3A_{2g}\downarrow {}^3A_2)\rangle$ and $|A_1(^3F\downarrow {}^3A_{2g}\downarrow {}^3A_2)\rangle$ obtained by the diagonalization of complete energy matrices:

$$D = \varepsilon(|E(^3F\downarrow {}^3A_{2g}\downarrow {}^3A_2)\rangle) - \varepsilon(|A_1(^3F\downarrow {}^3A_{2g}\downarrow {}^3A_2)\rangle). \quad (3)$$

Here, we use the notation [14] $|\Gamma_{C^*_{3v}}(^{2S+1}L\downarrow {}^{2S+1}\Gamma_{O_h}\downarrow {}^{2S+1}\Gamma_{C_{3v}})\rangle$ to label the final CF states arising from the $3d^8(3d^2)$ configuration.

Using the microscopic SH (MSH) theory [3, 14, 22], the general expressions for the Zeeman g-factors: $g_\parallel$ and $g_\perp$ are obtained as given in [14]. In the present paper, unlike in [14], the MSH calculations are carried out using the extended CFA/MSH computer package [22, 23] including the SS and SOO interactions. The energy levels and MSH parameters are obtained as functions of the Racah electrostatic parameters B and C, the CFPs B_{20}, B_{40}, and B_{43}, the Trees correction α, the SO coupling constant ξ_d, the SS and SOO parameters M^0 and M^2, and the orbital reduction factor k for the orbital momentum operator used in the g-factor calculations [14].

The perturbation expressions of the SH parameters D, $g_\parallel$, and $g_\perp$ for $3d^8$ ions in trigonal type I (C_{3v}, D_3, D_{3d}) symmetry have been obtained by P&M [11] in terms of the conventional CFPs Dq, v, and v', which are related to those in the Wybourne notation [9, 24, 28] as

$$B_{20} = v - 2\sqrt{2}v', \qquad B_{40} = -14Dq + 2w/3, \qquad B_{43} = -\sqrt{7/10}(20Dq + w/3) \quad (4)$$

where $w = 2v + 3\sqrt{2}v'$, Dq is the cubic CF parameter, whereas v and v' measure the non-cubic trigonal CF components and vanish identically in cubic symmetry [9, 28]. Equivalently, in the Wybourne notation for trigonal symmetry the CF cubic component (B^{cubic}_{kq}) and the non-cubic one (B'_{kq}) are defined as [24]

$$H_{CF} = B^{cubic}_{40}[C^{(4)}_0 + \sqrt{10/7}(C^{(4)}_3 + C^{(4)}_{-3})] + B'_{20}C^{(2)}_0 + B'_{40}[C^{(4)}_0 - \sqrt{7/40}(C^{(4)}_3 + C^{(4)}_{-3})], \quad (5)$$

and the following relationships hold [24]:

$$B_{kq} = B^{cubic}_{kq} + B'_{kq}, \qquad B^{cubic}_{40} = -14Dq, \qquad B'_{20} = B_{20} = v - 2\sqrt{2}v',$$
$$B'_{40} = (4/3)(v + 3v'/\sqrt{2}). \quad (6)$$

In order to show the departure of $g_\parallel$ and $g_\perp$ from the free-ion value $g_e = 2.0023$, it is convenient to define $\Delta g_\parallel = g_e - g_\parallel$, $\Delta g_\perp = g_e - g_\perp$. To study the individual contributions for $Ni^{2+}(3d^8)$ ions arising from the SO, SS, and SOO interactions, the variations of the SH parameters D, $\Delta g_\parallel$, and $\Delta g_\perp$ with the CFPs Dq, v, and v' are calculated. To enable direct comparison with the PT results [11], we take $B = 816\,cm^{-1}$, $C = 3224\,cm^{-1}$, $\xi_d = 540\,cm^{-1}$, and the orbital reduction factor $k = 0.83$ as for $LiNbO_3$:Ni^{2+} [11]. Another reasonable choice of the parameters would not change the conclusions drawn here. The SS (SOO) parameters and Trees correction for free $Ni^{2+}(3d^8)$ ions are taken as $M^0 = 2.3674\,cm^{-1}$ and $M^2 = 1.2918\,cm^{-1}$ [29] (comparable with $M^0 = 2.375\,cm^{-1}$ and $M^2 = 1.295\,cm^{-1}$ [18]), and $\alpha = 43.48\,cm^{-1}$ [28], respectively. It should be noted that limited data are available in the literature: $v = -550\,cm^{-1}$ for Ni^{2+}:α-$LiIO_3$ [11, 14], $Dq = 792\,cm^{-1}$ for Ni^{2+}:$LiNbO_3$ [8, 11, 14]. In order to cover a wide range of the CFP values, the range of the CFPs v and v' is chosen from -2000 to $2000\,cm^{-1}$, while that of Dq is from 400 to $2000\,cm^{-1}$, and the calculations were performed with the step $200\,cm^{-1}$. The results obtained by the CDM [22, 23] and PTM [11] are presented in figures 1 and 2, whereas in order to reduce the size of tables only the major data points are listed in tables 1–3. Below we analyse these results.

2.1. Validity of the PTM

The results in figures 1 and 2 and tables 1–3 enable a quantitative comparison between the CDM and PTM results. While the PTM deals with the SO contributions to the SH parameters within a limited number of $CF(3d^8)$ states, the CDM considers the three mechanisms (SO, SS, and SOO) within all 45 CF states. In order to illustrate the relative validity of the PTM, it is convenient to define the percentage differences:

$$\delta_\chi = \frac{|\chi_{SO(CDM)} - \chi_{SO(PTM)}|}{|\chi_{SO(CDM)}|} \times 100\% \tag{7}$$

where $\chi = D$, $\Delta g_\parallel$, or $\Delta g_\perp$. The results for D, $\Delta g_\parallel$, and $\Delta g_\perp$ as a function of a given CFP in tables 1–3 yield the following percentage limits in the CFP ranges considered: $9.4 \leqslant \delta_D \leqslant 14$, $0.2 \leqslant \delta_{\Delta g_\parallel} \leqslant 3.6, 0.2 \leqslant \delta_{\Delta g_\perp} \leqslant 4.3$ for Dq (see table 1); $2.5 \leqslant \delta_D \leqslant 2020, 0.1 \leqslant \delta_{\Delta g_\parallel} \leqslant 2.9$, $0.21 \leqslant \delta_{\Delta g_\perp} \leqslant 1.3$ for v (see table 2); $0.7 \leqslant \delta_D \leqslant 104, 0.4 \leqslant \delta_{\Delta g_\parallel} \leqslant 27, 0.5 \leqslant \delta_{\Delta g_\perp} \leqslant 2.1$ for v' (see table 3). These data indicate that the approximate PTM formulae [11] work well for $g_\parallel$ and $g_\perp$, except for large $|v'|$ (i.e. $-2000\,cm^{-1} \leqslant v' \leqslant -800\,cm^{-1}$ and $1400\,cm^{-1} \leqslant v' \leqslant 2000\,cm^{-1}$; see table 3), whereas they fail for D with δ_D exceeding 10% in most of the CFP ranges. Importantly, the maximum $\delta_D = 2020\%$ for $v_c = 1200\,cm^{-1}$ (see table 2) indicates that the approximate PTM formula [11] for D is not convergent in the vicinity of v_c. The trends in variation of the discrepancy between the PTM and CDM results for the ZFS parameter D can be assessed conveniently by means of their absolute values:

$$|\Delta D| = |D_{SO(CDM)} - D_{SO(PTM)}|. \tag{8}$$

$|\Delta D|$ increases with v increasing from negative to positive values as well as with the absolute values of v', whereas it decreases with Dq increasing. Although $|\Delta D|$ varies with the CFPs, the percentage ratios δ_D are always relatively large. The divergences between the PTM and CDM results arise from the fact that the PTM considers the contributions to the SH parameters due to selected CF states arising from the low lying ^{2S+1}L terms, whereas the CDM considers those due to all 45 states arising within the whole $3d^8$ electronic configuration.

The large values of D obtained for $Dq = 400\,cm^{-1}$ using both the PTM and CDM (table 1) raise doubts as regards whether the MSH approach is still valid in this range. Analysis of the CFA package outputs indicates that the first excited CF state lies $E_1 = 3711\,cm^{-1}$ higher

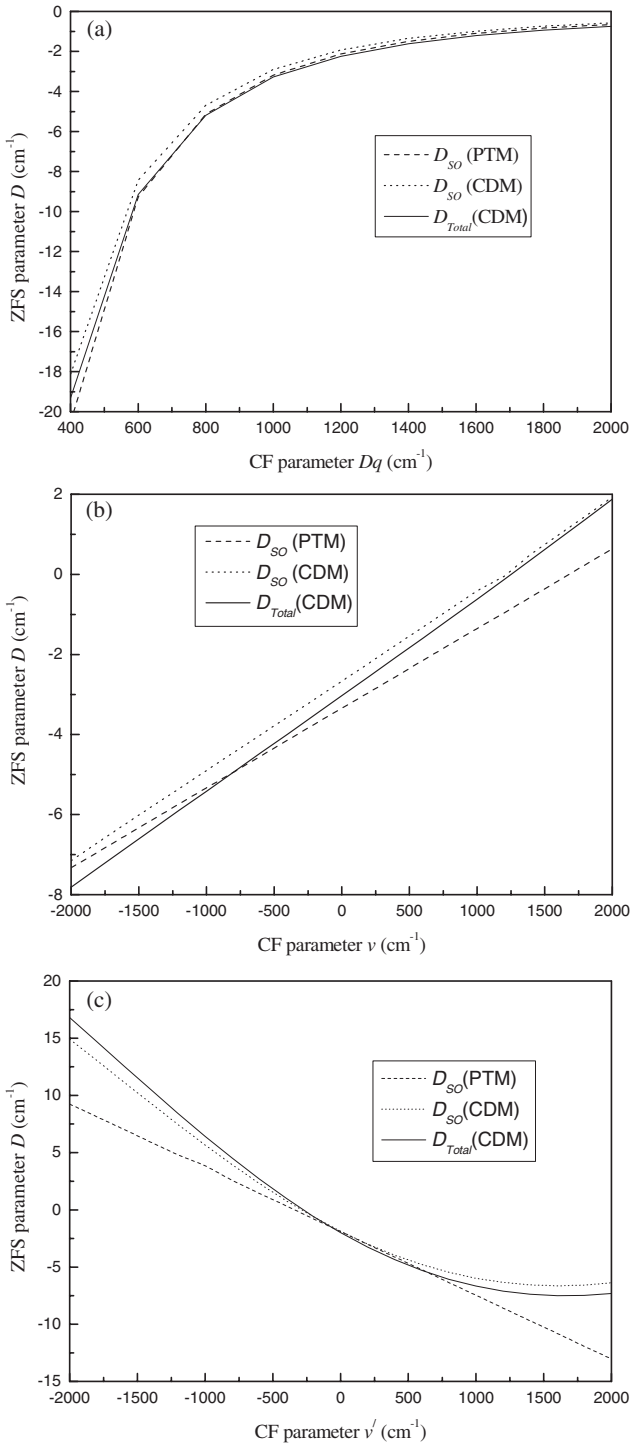

Figure 1. The ZFS parameter D for the $^3A_2$ ground state of Ni^{2+} ions ($B = 816$, $C = 3224$, $\xi_d = 540$, $M^0 = 2.3674$, $M_2 = 1.2918$) in C_{3v} symmetry versus (a) Dq ($v = -950$, $v' = 600$), (b) v ($v' = 600$, $Dq = 792$), and (c) v' ($v = -950$, $Dq = 792$). All values are in cm^{-1}.

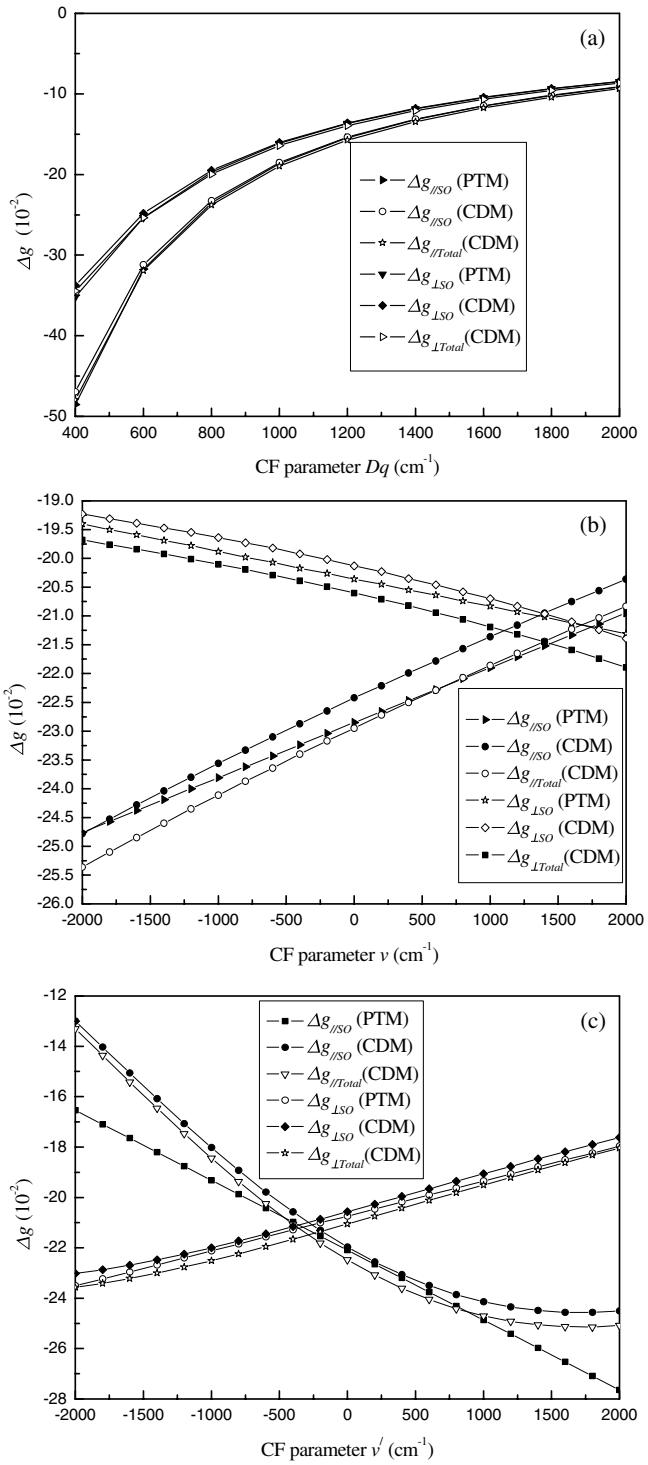

Figure 2. The parameters $\Delta g_{\parallel}$, and $\Delta g_{\perp}$ for the $^3A_2$ ground state of Ni^{2+} ions in C_{3v} symmetry versus (a) Dq, (b) v, and (c) v'. The orbital reduction factor $k = 0.83$; the other parameters are as shown in figure 1.

Table 1. The spin Hamiltonian parameters D (in units of cm^{-1}), $\Delta g_{\parallel}$, and $\Delta g_{\perp}$ for $Ni^{2+}(3d^8)$ ions in a trigonal CF as a function of the cubic CF parameter $Dq(B_{40}^{cubic})$, calculated assuming $B = 816$, $C = 3224$, $\xi_d = 540$, $\nu = -950$, $\nu' = 600$ ($B_{20} = -2647$, $B_{40} = 430$), $k = 0.83$ [11], $\alpha = 43.48$ [28], $M^0 = 2.3674$, and $M^2 = 1.2918$ [29] (in cm^{-1}, except for k). The ratios δ, γ, and μ have been defined in the text. Note that the CDM yields $\Delta g_{\parallel SS} = \Delta g_{\perp SS} = 0.0000$ for all CFP ranges considered.

CFP (cm^{-1})		D (cm^{-1})									$\Delta g_{\parallel} = g_e - g_{\parallel}$ ($g_e = 2.0023$)		$\Delta g_{\perp} = g_e - g_{\perp}$	
Dq	B_{40}^{cubic}	D_{SO}[a]	D_{SO}[b]	D_{SS}[b]	D_{SOO}[b]	D_{Total}[c]	$\lvert\Delta D\rvert$	δ_D (%)	γ_D (%)	μ_D (%)	$\Delta g_{\parallel SOO}$[b]	$\Delta g_{\parallel Total}$[c]	$\Delta g_{\perp SOO}$[b]	$\Delta g_{\perp Total}$[c]
400	−5 600	−20.53	−18.13	−0.392	−0.013	−19.32	2.40	13.2	6.2	4.1	−0.0130	−0.4796	−0.0097	−0.3447
600	−8 400	−9.27	−8.43	−0.282	−0.006	−9.15	0.84	10.0	7.9	4.7	−0.0082	−0.3191	−0.0067	−0.2538
800	−11 200	−5.13	−4.69	−0.224	−0.003	−5.19	0.44	9.4	9.6	5.3	−0.0060	−0.2380	−0.0051	−0.1995
1000	−14 000	−3.18	−2.90	−0.187	−0.002	−3.28	0.28	9.7	11.6	8.9	−0.0047	−0.1895	−0.0041	−0.1640
1200	−16 800	−2.13	−1.93	−0.162	−0.002	−2.24	0.20	10.4	13.8	6.5	−0.0039	−0.1573	−0.0035	−0.1392
1400	−19 600	−1.50	−1.35	−0.143	−0.001	−1.61	0.15	11.1	16.1	7.2	−0.0033	−0.1345	−0.0030	−0.1208
1600	−22 400	−1.10	−0.99	−0.129	−0.001	−1.20	0.11	11.1	17.5	6.7	−0.0029	−0.1174	−0.0026	−0.1067
1800	−25 200	−0.83	−0.74	−0.117	−0.001	−0.93	0.09	12.2	20.4	7.7	−0.0025	−0.1041	−0.0023	−0.0956
2000	−28 000	−0.65	−0.57	−0.107	−0.001	−0.74	0.08	14.0	23.0	8.4	−0.0023	−0.0935	−0.0021	−0.0866

[a] Calculated by us using the PTM of P&M [11].
[b] Present CDM results.
[c] Present CDM results, which simultaneously consider the SO, SS, and SOO interactions.

Table 2. The SH parameters D (in units of cm^{-1}), $\Delta g_{\parallel}$, and $\Delta g_{\perp}$ for $Ni^{2+}(3d^8)$ ions in a trigonal CF as a function of the CF parameter v, calculated assuming $B = 816$, $C = 3224$, $\xi_d = 540$, $Dq = 792$ (the corresponding $B_{40}^{cubic} = -11\,088$), $v' = 600$, $k = 0.83$ [11], $\alpha = 43.48$ [28], $M^0 = 2.3674$, and $M^2 = 1.2918$ [29] (in cm^{-1}, except for k). The ratios δ, γ, and μ have been defined in the text. Note that the CDM yields $\Delta g_{\parallel SS} = \Delta g_{\perp SS} = 0.0000$ for all CFP ranges considered.

CFP (cm^{-1})			D (cm^{-1})									$\Delta g_{\parallel} = g_e - g_{\parallel}$ ($g_e = 2.0023$)		$\Delta g_{\perp} = g_e - g_{\perp}$	
v	B_{20}	B_{40}	D_{SO}[a]	D_{SO}[b]	D_{SS}[b]	D_{SOO}[b]	D_{Total}[c]	$\lvert\Delta D\rvert$	δ_D (%)	γ_D (%)	μ_D (%)	$\Delta g_{\parallel SOO}$[b]	$\Delta g_{\parallel Total}$[c]	$\Delta g_{\perp SOO}$[b]	$\Delta g_{\perp Total}$[c]
−2000	−3697	−970	−7.33	−7.15	−0.234	−0.005	−7.81	0.18	2.5	8.5	5.4	−0.0064	−0.2536	−0.0051	−0.1968
−1600	−3297	−436	−6.53	−6.24	−0.231	−0.004	−6.85	0.29	4.6	8.9	5.5	−0.0063	−0.2485	−0.0051	−0.1984
−1200	−2897	97	−5.73	−5.35	−0.228	−0.004	−5.89	0.38	7.1	9.2	5.2	−0.0061	−0.2435	−0.0051	−0.2001
−800	−2497	630	−4.94	−4.45	−0.224	−0.003	−4.94	0.49	11.0	9.9	5.3	−0.0060	−0.2387	−0.0052	−0.2019
−400	−2097	1164	−4.14	−3.56	−0.222	−0.003	−3.99	0.58	16.3	10.8	5.1	−0.0059	−0.2340	−0.0052	−0.2039
0	−1697	1697	−3.34	−2.67	−0.219	−0.002	−3.03	0.67	25.1	11.9	4.6	−0.0058	0.2295	−0.0052	−0.2060
400	−1297	2230	−2.55	−1.77	−0.216	−0.002	−2.07	0.78	44.1	14.5	4.0	−0.0057	−0.2250	−0.0053	−0.2082
800	−897	2764	−1.75	−0.87	−0.213	−0.001	−1.11	0.88	101.1	21.6	2.3	−0.0056	−0.2207	−0.0053	−0.2106
1000	−697	3030	−1.35	−0.41	−0.212	−0.001	−0.62	0.94	229.3	33.9	0.5	−0.0056	−0.2186	−0.0054	−0.2119
1200	−497	3297	−0.96	0.05	−0.211	−0.001	−0.13	1.01	2020.0	138.5	24.6	−0.0055	−0.2165	−0.0054	−0.2132
1400	−297	3564	−0.56	0.51	−0.209	0.000	0.37	1.07	209.8	37.8	18.6	−0.0055	−0.2144	−0.0054	−0.2145
1600	−97	3830	−0.16	0.98	−0.208	0.000	0.87	1.14	116.3	12.6	11.3	−0.0054	−0.2123	−0.0055	−0.2159
1800	103	4097	0.24	1.45	−0.207	0.000	1.37	1.21	83.4	5.8	9.3	−0.0054	−0.2103	−0.0055	−0.2174
2000	303	4364	0.64	1.93	−0.206	0.001	1.88	1.29	66.8	2.7	8.2	−0.0054	−0.2083	−0.0055	−0.2189

[a] Calculated by us using the PTM of P&M [11].
[b] Present CDM results.
[c] Present CDM results, which simultaneously consider the SO, SS, and SOO interactions.

Table 3. The spin Hamiltonian parameters D (in units of cm^{-1}), $\Delta g_{\parallel}$, and $\Delta g_{\perp}$ for $Ni^{2+}(3d^8)$ as a function of the CF parameter ν', calculated assuming $B = 816$, $C = 3224$, $\xi_d = 540$, $Dq = 792$ ($B_{40}^{cubic} = -11\,088$), $\nu = -950$, $k = 0.83$ [11], $\alpha = 43.48$ [28], $M^0 = 2.3674$, and $M^2 = 1.2918$ [29] (in cm^{-1}, except for k). The ratios δ, γ, and μ have been defined in the text. Note that the CDM yields $\Delta g_{\parallel SS} = \Delta g_{\perp SS} = 0.0000$ for all CFP ranges considered.

CFP (cm^{-1})			D (cm^{-1})									$\Delta g_{\parallel} = g_e - g_{\parallel}$ ($g_e = 2.0023$)		$\Delta g_{\perp} = g_e - g_{\perp}$	
ν'	B_{20}	B_{40}	D_{SO}[a]	D_{SO}[b]	D_{SS}[b]	D_{SOO}[b]	D_{Total}[c]	$\lvert\Delta D\rvert$	δ_D (%)	γ_D (%)	μ_D (%)	$\Delta g_{\parallel SOO}$[b]	$\Delta g_{\parallel Total}$[c]	$\Delta g_{\perp SOO}$[b]	$\Delta g_{\perp Total}$[c]
−2000	4707	−6924	9.25	14.93	1.294	0.011	16.80	5.68	38.0	11.1	3.4	−0.0034	−0.1330	−0.0060	−0.2357
−1600	3757	−5792	7.03	11.18	0.986	0.008	12.59	4.15	37.1	11.2	3.3	−0.0039	−0.1542	−0.0059	−0.2322
−1200	2444	−4661	4.80	7.46	0.695	0.005	8.43	2.66	35.7	11.5	3.2	−0.0045	−0.1747	−0.0058	−0.2277
−800	1313	−3529	2.57	3.94	0.431	0.003	4.51	1.37	34.8	12.6	3.0	−0.0049	−0.1937	−0.0056	−0.2224
−400	181	−2398	0.34	0.79	0.198	0.001	0.99	0.45	57.0	20.2	0.1	−0.0053	−0.2106	−0.0055	−0.2166
0	−950	−1267	−1.89	−1.87	0.000	−0.001	−1.99	0.02	1.1	6.4	6.0	−0.0057	−0.2248	−0.0054	−0.2105
400	−2081	−135	−4.12	−3.97	−0.160	−0.003	−4.36	0.15	3.8	8.9	5.2	−0.0060	−0.2361	−0.0052	−0.2043
800	−3213	996	−6.35	−5.46	−0.282	−0.004	−6.07	0.89	16.3	10.0	5.3	−0.0062	−0.2442	−0.0051	−0.1981
1000	−3778	1562	−7.46	−5.98	−0.329	−0.005	−6.67	1.48	24.7	10.3	5.3	−0.0062	−0.2470	−0.0050	−0.1951
1200	−4344	2127	−8.59	−6.34	−0.366	−0.005	−7.11	2.25	35.3	10.8	5.6	−0.0063	−0.2492	−0.0049	−0.1921
1400	−4910	2693	−9.69	−6.56	−0.395	−0.005	−7.39	3.31	47.7	11.2	5.8	−0.0063	−0.2506	−0.0049	−0.1891
1600	−5475	3259	−10.81	−6.64	−0.415	−0.005	−7.51	4.24	62.8	11.6	6.0	−0.0063	−0.2513	−0.0048	−0.1862
1800	−6041	3825	−11.92	−6.58	−0.426	−0.005	−7.48	5.34	81.1	12.0	6.3	−0.0063	−0.2514	−0.0047	−0.1832
2000	−6607	4390	−13.04	−6.38	−0.428	−0.006	−7.31	6.66	104.4	12.7	6.8	−0.0063	−0.2508	−0.0047	−0.1804

[a] Calculated by us using the PTM of P&M [11].
[b] Present CDM results.
[c] Present CDM results, which simultaneously consider the SO, SS, and SOO interactions.

in energy above the ground level in this case. Since E_1 is considerably larger than the SO coupling constant, the condition for applicability of the MSH approach is satisfied. However, to the best of our knowledge no such large values of D have been reported for $Ni^{2+}(3d^8)$ ions.

2.2. The microscopic origin of the SH parameters

In order to illustrate the relative importance of SS and SOO contributions to the SH parameters with respect to those due to the SO interaction, it is convenient to define the percentage ratios

$$\gamma_\chi = \frac{|\chi_{\text{Total(CDM)}} - \chi_{\text{SO(CDM)}}|}{|\chi_{\text{Total(CDM)}}|} \times 100\% \tag{9}$$

where $\chi = D$, $\Delta g_\parallel$, or $\Delta g_\perp$. Tables 1–3 list the contributions to the SH parameters D, $\Delta g_\parallel$, and $\Delta g_\perp$ from each SO, SS, and SOO interaction separately and the combined ones, as well as the percentage ratios γ_D in equation (9). Tables 1–3 and figures 1 and 2 enable drawing the following conclusions.

(i) The SH parameters originate, as expected, mainly from the SO mechanism. The SO contributions are sensitive to the CFPs Dq, v, and v', whereas those due to the SS and SOO mechanisms are not so sensitive.

(ii) In the CFP (Dq, v, v') ranges considered, the percentage ratios γ_D vary with CFPs and are within the limits: $6.2 \leqslant \gamma_D \leqslant 23$ for Dq (see table 1), $2.7 \leqslant \gamma_D \leqslant 138.5$ for v (see table 2), $3.4 \leqslant \gamma_D \leqslant 20.2$ for v' (see table 3); whereas $\gamma_{\Delta g_\parallel}$ and $\gamma_{\Delta g_\perp}$ are approximately constant—between 2.1% and 2.4%, and hence are not listed in tables 1–3. The SOO contributions to $\Delta g_\parallel$ and $\Delta g_\perp$ are appreciable, whereas those due to the SS interaction $\Delta g_{\parallel\text{SS}}$ and $\Delta g_{\perp\text{SS}}$ are virtually zero for all CFP ranges considered.

(iii) For most of the CFP (Dq, v, v') ranges considered, the following relationships hold:

$$|\Delta g_{\parallel\text{SO}}| \gg |\Delta g_{\parallel\text{SS}}|, \qquad |\Delta g_{\parallel\text{SO}}| \gg |\Delta g_{\parallel\text{SOO}}|, \qquad |\Delta g_{\parallel\text{SS}}| \ll |\Delta g_{\parallel\text{SOO}}|, \tag{10a}$$

$$|\Delta g_{\perp\text{SO}}| \gg |\Delta g_{\perp\text{SS}}|, \qquad |\Delta g_{\perp\text{SO}}| \gg |\Delta g_{\perp\text{SOO}}|, \qquad |\Delta g_{\perp\text{SS}}| \ll |\Delta g_{\perp\text{SOO}}|, \tag{10b}$$

$$|D_{\text{SO}}| \gg |D_{\text{SS}}|, \qquad |D_{\text{SO}}| \gg |D_{\text{SOO}}|, \qquad |D_{\text{SS}}| > |D_{\text{SOO}}|. \tag{10c}$$

Note that the first inequality (10*c*) is not always valid as it fails in the vicinity of v_c.

(iv) The role of the combined SO–SS–SOO mechanism involving mixed transitions between the CF states due to these interactions can be accounted for by the difference

$$D_{\text{SO–SS–SOO}} = D_{\text{Total}} - (D_{\text{SO}} + D_{\text{SS}} + D_{\text{SOO}}). \tag{11}$$

The non-zero value of $D_{\text{SO–SS–SOO}}$ is a measure of the importance of the combined mechanism. Similar differences can be defined for $\Delta g_\parallel$ and $\Delta g_\perp$. We also use the percentage differences defined as

$$\mu_\chi = \frac{|\chi_{\text{Total}} - (\chi_{\text{SO}} + \chi_{\text{SS}} + \chi_{\text{SOO}})|}{|\chi_{\text{Total}}|} \times 100\% \tag{12}$$

where $\chi = D$, $\Delta g_\parallel$, or $\Delta g_\perp$. The results in tables 1–3 yield limits for μ_χ varying for a given CFP: $4.1 \leqslant \mu_D \leqslant 8.9$, $0 \leqslant \mu_{\Delta g_\parallel} \leqslant 0.6$, and $0 \leqslant \mu_{\Delta g_\perp} \leqslant 0.8$ for Dq; $0.5 \leqslant \mu_D \leqslant 24.6$, $0.2 \leqslant \mu_{\Delta g_\parallel} \leqslant 0.3$, and $0.2 \leqslant \mu_{\Delta g_\perp} \leqslant 0.3$ for v; $0.1 \leqslant \mu_D \leqslant 12.8$, $0.2 \leqslant \mu_{\Delta g_\parallel} \leqslant 0.3$, and $0.2 \leqslant \mu_{\Delta g_\perp} \leqslant 0.3$ for v'. These results indicate that for most of the CFP ranges considered the combined SO–SS–SOO contributions are appreciable for D, whereas those for $\Delta g_\parallel$ and $\Delta g_\perp$ are quite small. It is worthwhile to note that using the analytical expressions for the combined SO–SS mechanism for $3d^5(^6S)$ ions in C_3 symmetry, Yu *et al* [20] estimated the ratio $|D_{\text{SO–SS}}|/|D_{\text{Total}}| \approx 6.3\%$ for $Mn(I):Ca(PO_4)_3F$, which is comparable with the above values of μ_D.

Table 4. The spin Hamiltonian parameters D (in units of cm^{-1}), $\Delta g_{\parallel}$, and $\Delta g_{\perp}$ for $Ni^{2+}(3d^8)$ ions in a trigonal CF as a function of the CF parameter v. The parameter values used are the same as in table 2.

CFP (cm^{-1})			D (cm^{-1})								
v	B_{20}	B_{40}	D_{SO}[a]	D_{SO}[b]	D_{SS}[b]	D_{SOO}[b]	D_{Total}[c]	$\lvert\Delta D\rvert$	δ_D (%)	γ_D (%)	μ_D (%)
1050	−647	3097	−1.25	−0.30	−0.212	−0.001	−0.50	0.95	316.7	40.0	2.6
1100	−597	3164	−1.15	−0.18	−0.211	−0.001	−0.37	0.97	538.9	51.4	5.9
1150	−547	3230	−1.05	−0.07	−0.211	−0.001	−0.25	0.98	1400.0	72.0	12.8
1200	−497	3297	−0.96	0.05	−0.211	−0.001	−0.13	1.01	2020.0	138.5	24.6
1250	−447	3364	−0.86	0.16	−0.210	0.000	−0.01	1.02	637.5	106.3	400.0
1300	−397	3430	−0.76	0.28	−0.210	0.000	0.12	1.04	371.4	133.3	41.7
1350	−347	3497	−0.66	0.39	−0.210	0.000	0.24	1.05	269.2	62.5	25.0

[a] Calculated by us using the PTM of P&M [11].
[b] Present CDM results.
[c] Present CDM results, which simultaneously consider the SO, SS, and SOO interactions.

Our results show that while the SO mechanism is dominant for most of the CFP ranges considered, the contributions to D from the other three mechanisms may exceed those from the SO mechanism in the vicinity of some critical points (see table 2), e.g. yielding the maximum $\gamma_D = 138.5\%$ for $v_c = 1200\ cm^{-1}$. This is due to the fact that in this critical range D_{SO} goes through zero. To illustrate more accurately the variation of D_{SO}, we have increased the interval in v and listed the results in table 4. It should be pointed out that each specific mechanism, i.e. SO, SS, SOO, and the combined SO–SS–SOO one, describes in fact the joint effect of the given interaction and the non-cubic trigonal CF for $3d^8$ ions. In general, our numerical calculations show that setting $\xi_d = 0$ and $M^0 = M^2 = 0$ or $v = v' = 0$ results in $D = 0$ and $\Delta g(=g_{\parallel} - g_{\perp}) = 0$, whereas considering simultaneously the magnetic interactions and the non-cubic trigonal CF yields $D \neq 0$ and $\Delta g \neq 0$.

Since the CFPs B_{kq} in the Wybourne notation have a more explicit physical meaning and are more widely used in the recent literature, their values are also provided in tables 1–5 to facilitate direct comparison with the available literature data. Tables 2 and 3 and figure 1(c) show that D becomes nearly zero when v and v' yield vanishing $B'_{20} = v - 2\sqrt{2}v'$. Hence, the second-rank non-cubic CFP B'_{20} contributes significantly to D, whereas the remaining contributions come from the fourth-rank non-cubic CFP B_{40}. We also find that $D_{SO(PTM)} > 0$ for $B'_{20} > 0$ and $D_{SO(PTM)} < 0$ for $B'_{20} < 0$ (see tables 1–3), whereas $D_{SO(CDM)} > 0$ for $B'_{20} > 0$ and $D_{SO(CDM)} < 0$ for $B'_{20} < 0$ are obtained only when assuming $B'_{40} = 0$. The differences between $D_{SO(CDM)}$ and $D_{SO(PTM)}$ may be attributed to the neglect in the PTM of the contributions to D from B'_{40}. Additionally, assuming $B'_{40} = 0$ we find that $D(B'_{20} = 0)_{CDM} = 0$, $D(B'_{20})_{CDM} \approx -D(-B'_{20})_{CDM}$, and $\Delta g(B'_{20} = 0)_{CDM} = 0$, $\Delta g(B'_{20})_{CDM} \approx -\Delta g(-B'_{20})_{CDM}$.

2.3. Applications to several crystals

The $Ni^{2+}(3d^8)$ ions in such crystals as Al_2O_3, $LiNbO_3$, and α-$LiIO_3$ exhibiting typical trigonal symmetry sites provide good examples for use in the examination of the MSH theory. The following parameter values have been reported [11] (in cm^{-1}): $B = 816$, $C = 3224$, $Dq = 792$, $\xi_d = 540$, $v = -950$, $v' = 600$ for Ni^{2+}:$LiNbO_3$; $B = 850$, $C = 3600$, $Dq = 775$, $\xi_d = 595$, $v = -550$, $v' = 200$ for Ni^{2+}:α-$LiIO_3$; and $B = 800$, $C = 3400$, $Dq = 1000$, $\xi_d = 565$, $v = 600$, $v' = 500$ for Ni^{2+}:Al_2O_3. Using these parameter values as well as those for the SS or SOO parameters M^0, M^2, and the Trees corrections α listed in table 5, we obtain the MSH parameters D, $\Delta g_{\parallel}$, and $\Delta g_{\perp}$ in agreement with the experimental ones [11] for Ni^{2+}:$LiNbO_3$ and Ni^{2+}:α-$LiIO_3$ (see table 5). However, for Ni^{2+}:Al_2O_3 we obtain

Table 5. Input values of the free-ion parameters B, C, ξ_d (with fixed $M^0 = 2.3674$, $M^2 = 1.2918$ [29], $\alpha = 43.48$ in cm^{-1} [28]) and the CF parameters [11] together with the calculated values of the SH parameters for $Ni^{2+}(3d^8)$ ions in several crystals with C_3 site symmetry. All values are in (cm^{-1}) except for k and Δg.

Crystal system		Ni^{2+}:Al_2O_3	Ni^{2+}:α-$LiIO_3$	Ni^{2+}:$LiNbO_3$
Free-ion parameters	B	800	850	816
	C	3400	3600	3224
	ξ_d	565	595	540
Crystal field parameters	Dq	1000	775	792
	v	390	−550	−950
	v'	550	200	600
	B_{20}	−1166	−1116	−2647
	B_{40}	−11 924	−11 018	−10 658
	B_{43}	−17 601	−12 898	−13 433
	k	0.87	0.92	0.83
ZFS parameters	D_{SO}[a]	−1.57	−2.85	−5.24
	D_{SO}[b]	−1.1427	−2.7685	−4.7884
	D_{SS}[b]	−0.1685	−0.0846	−0.2257
	D_{SOO}[b]	−0.0010	−0.0016	−0.0035
	$D_{SO-SS-SOO}$[b]	−0.0626	−0.1407	−0.2785
	D_{Total}[c]	−1.3748	−2.9954	−5.2961
	$D_{exp.}$ [11]	−1.38	−3.21	−5.31
$\Delta g_\parallel = g_e - g_\parallel$ ($g_e = 2.0023$)	$\Delta g_{\parallel SO}$[a]	−0.1948	−0.2787	−0.2367
	$\Delta g_{\parallel SO}$[b]	−0.1920	−0.2751	−0.2350
	$\Delta g_{\parallel SS}$[b]	0.0000	0.0000	0.0000
	$\Delta g_{\parallel SOO}$[b]	−0.0047	−0.0056	−0.0061
	$\Delta g_{\parallel SO-SS-SOO}$[b]	0.0003	−0.0002	0.0006
	$\Delta g_{\parallel Total}$[c]	−0.1964	−0.2809	−0.2405
	$\Delta g_{\parallel exp.}$ [11]	−0.1934	−0.2777	−0.2377
$\Delta g_\perp = g_e - g_\perp$	$\Delta g_{\perp SO}$[a]	−0.1819	−0.2577	−0.1987
	$\Delta g_{\perp SO}$[b]	−0.1806	−0.2539	−0.1966
	$\Delta g_{\perp SS}$[b]	0.0000	0.0000	0.0000
	$\Delta g_{\perp SOO}$[b]	−0.0044	−0.0052	−0.0051
	$\Delta g_{\perp SO-SS-SOO}$[b]	0.0003	−0.0002	0.0005
	$\Delta g_{\perp Total}$[c]	−0.1847	−0.2593	−0.2012
	$\Delta g_{\perp exp.}$ [11]	−0.1836	−0.2547	−0.1977

[a] The PTM results [11].
[b] Present CDM results.
[c] Present CDM results, which simultaneously consider the SO, SS, and SOO interactions.

$D = -0.9072\ cm^{-1}$, i.e. considerably less than $D_{exp} = -1.38\ cm^{-1}$ [11]. This may well be due to the inaccuracy in the (fixed) input CF parameters. Considering the non-cubic CFPs v and v' as adjustable parameters, the CDM calculations yield the best match of the theoretical and experimental D, $\Delta g_\parallel$, and $\Delta g_\perp$ for $v = 390\ cm^{-1}$ and $v' = 550\ cm^{-1}$ (see table 5).

It should be pointed out that for the Ni^{2+} centres in these crystals the site symmetry C_{3v} is, in fact, an approximation of the actual C_3 one. Only for the distortion angle $\varphi = 0$ of the rotation of the upper and lower oxygen triangles in the octahedron away from the σ_v plane (see figure 1 in [22]) does the C_3 symmetry reduce to C_{3v}. The CFA/MSH package enables one to study also the additional contributions to the SH parameters arising from the low (C_3) symmetry effects (LSE) due to the non-zero 'imaginary' CFP Im $B_{43}(C_3)$ induced by $\varphi \neq 0$. In view of the limited data on the CFPs available in the literature, we provide only tentative estimates

of Im $B_{43}(C_3)$ based on the superposition model (SPM) and then consider its importance for MSH parameters.

Within the superposition model (SPM) [31, 32], Im B_{43} can be determined from the relation [23]

$$\text{Im } B_{43} = 6\sqrt{35}\bar{A}_4 Q^{t_4} \sin^3\beta \cos\beta \sin 6\varphi \tag{13}$$

where parameters Q^{t_4}, $\bar{A}_4$, and β have been defined in [23]. Adopting the available values of φ: 0.68° and 2.15° [30], equation (13) yields Im B_{43}: 314 and 1389 cm^{-1} for Ni^{2+}:$LiNbO_3$ and Ni^{2+}:Al_2O_3, respectively. Using these parameters we obtain $D = -1.3609$ and -5.2931 cm^{-1} for Ni^{2+}:Al_2O_3 and Ni^{2+}:$LiNbO_3$, respectively. It turns out that the contributions to the SH parameters from the non-zero Im B_{43} are quite small and do not exceed 1% for the two crystals. The value of φ for Ni^{2+}:α-$LiIO_3$ is not available, but can be expected to be small. Hence, the low symmetry (C_3) effects induced by the angle φ appear to be negligible.

In order to illustrate the relative importance of various mechanisms, it is convenient to define the parameters D_{X+Y} describing the simultaneous action of any two magnetic interactions X and Y (X, Y = SO, SS, SOO). For example, for Ni^{2+}:$LiNbO_3$ the CDM yields (in cm^{-1}): $D_{SO-SS-SOO} = -0.279$, $D_{SS} = -0.226$, $D_{SOO} = -0.0035$, $D_{SO} = -4.788$, and $D_{Total} = -5.296$. Thus D_{SO+SS} (=−4.996) ≠ D_{SO}+D_{SS} (=−5.004), D_{SO+SOO} (=−5.089) ≠ D_{SO}+D_{SOO} (=−4.792), and D_{SOO+SS} (=−0.229) ≠ D_{SOO}+D_{SS} (=−0.229), i.e. the following relationship holds:

$$D_{SO-SS-SOO} \approx D_{SO-SS} + D_{SO-SOO} + D_{SS-SOO} \tag{14}$$

where $D_{SO-SOO} = D_{SO+SOO} - (D_{SO} + D_{SOO})$, $D_{SO-SS} = D_{SO+SS} - (D_{SO} + D_{SS})$, and $D_{SS-SOO} = D_{SS+SOO} - (D_{SS} + D_{SOO})$. Similar results are obtained for Ni^{2+}:α-$LiIO_3$ and Ni^{2+}:Al_2O_3 crystals. On the other hand, we also find that $|D_{SS}| > |D_{SOO}|$ as shown in table 5, whereas $|D_{SO-SOO}| > |D_{SO-SS}| > |D_{SOO-SS}|$. This indicates that the contribution to D from the combined effect due to the SO and SOO interactions is larger than that from the combined effect due to the SO and SS interactions. Thus, although $|D_{SOO}|$ alone is quite small, the combined effect $|D_{SO-SOO}|$ due to the SO and SOO interactions is appreciable. Hence, in detailed calculations the SOO interaction should be taken into account.

3. Summary

The microscopic origin of the SH (spin Hamiltonian) parameters D, $g_\parallel$, and $g_\perp$ for $Ni^{2+}(3d^8)$ ions in trigonal crystal fields has been investigated using the CFA/MSH computer package. The contributions to the SH parameters arising from the SS (spin–spin) and SOO (spin–other-orbit) interactions, which have been omitted in previous works, have been taken into account in addition to the major ones due to the SO (spin–orbit) interaction. The SH parameters arise not only from the three individual microscopic mechanisms (SO, SS, SOO) but are also due to the combined SO–SS–SOO mechanism. Although the SO mechanism is the most important one, the contributions to the SH parameters from the other three mechanisms are appreciable and should not be omitted, especially for the ZFS parameter D. These conclusions are expected to hold for other systems, such as $3d^2$ ions at axial symmetry sites. Since the SH parameters for the transition metal ions in crystals are very sensitive to the changes in the crystal structure, more accurate EPR determination of the structural disorder and lattice distortions [4, 5, 7, 9] can be only reliable if the contributions to the SH parameters arising from the SS and SOO interactions are taken into account.

Using the CDM (complete diagonalization method), we have also investigated the accuracy of the PT (perturbation theory) expressions [11]. The present results corroborate the finding [14] that the approximate PT formulae [11] for the g-factors: $g_\parallel$ and $g_\perp$ work well

in most of the CF parameter ranges, whereas that for the ZFS parameter D fails in several cases. Hence the PTM [11] cannot provide the accurate predictions required to study the structural disorder and lattice distortions, and can only be used for *approximate* estimations of the SH parameters. To obtain better information concerning the structural disorder and lattice distortions, one must adopt the CDM. Our recent study [5] also shows that the PTM for $3d^3$ ions is not suitable for studies of the structural disorder in crystals. The reason is that only the contributions from the SO interaction within a few lowest lying exited states are taken into account in the PTM [11], which is not enough for accounting accurately for the ZFS parameter D. Practical applications of the MSH theory to Ni^{2+} ions at trigonal symmetry sites in $LiNbO_3$, α-$LiIO_3$, and Al_2O_3 are provided. The theoretical SH parameters are in good agreement with the experimental data. We have also considered tentatively the low symmetry (C_3) effects induced by the non-zero angle φ. It appears that the effect on D is quite small and may be omitted for these crystals.

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