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The NMR Chemical Shift for $4d^n$ Systems(III). Calculation of the NMR Shift for a $4d^1$ System in a Strong Crystal Field Enviroment of Tetragonal Symmetry

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The NMR shift arising from the electron angular momentum and electron spin dipolar-nuclear spin angular momentum interactions has been investigated for a $4d^1$ system in a strong crystal field environment of tetragonal symmetry. A general formula for NMR shift is used to compute the NMR shifts along the (100), (010), (001), (110) and (111) axes. We find that from the computed results, the NMR shift along the (100) and (010) axes is consistent with each other in a strong crystal field environment of tetragonal symmetry, but the NMR shift along the (001) axis is about triply greater in magnitude than those along the (100) and (010) axes and is opposite in sign to those along (100) and (010) axes. In this work, we express the expansion coefficients $a_l^{(\omega)}$ and $b_l^{(\omega)}$ of A_i and B_i in terms of $g_m^{(\omega)}$ and $h_m^{(\omega)}$ and two matrices c_{lm} and d_{lm} of radial dependence. The NMR shift is also separated into the contributions of multipolar terms. We find that $1/R^3$ term contributes dominantly to the NMR shift along the (100), (010), (001) and (110) axes while along the (111) axis $1/R^5$ term dominantly contributes. However, the contribtions of the other terms may not be negligible.

Introduction

Since early 1960, a great deal of interest has been concentrated on interpretation of NMR shift due to the interaction of a paramagnetic system with NMR nucleus and the shift has been classified as arising both contact and pseudo contact mechanisms.[1] The pseudo contact NMR shift, ΔB, was first given by McConnel and Robertson in the form

$$\frac{\Delta B}{B} = -\frac{2}{3}\frac{S(S+1)}{3kT}\frac{(3\cos^2\theta-1)}{R^3}F(g) \qquad (1)$$

which was extended by Kurland and McGravey[2] in terms of magnetic susceptibility components, χ_{ii}

$$\frac{\Delta B}{B} = -\frac{1}{3R^3}\left\{\left(\chi_{zz}-\frac{1}{2}(\chi_{xx}+\chi_{yy})\right\}(3\cos^2\theta-1)\right. \\ \left. +\frac{3}{2}(\chi_{xx}-\chi_{yy})\sin^2\theta\cos^2\phi\right\} \qquad (2)$$

In equation (1) and (2), R is the distance between the paramagnetic center and NMR nucleus and θ is the angle between the principal axis of the complex and the vector between the paramagnetic center and the NMR nucleus. Here, $F(g)$ is a fuction of the principal g-value.

Stiles[4] has examined theoretically the contribution of molecular magnetic multipoles higher than dipole to the pseudo contact shift and has expressed the NMR shifts as[5]

$$\frac{\Delta B}{B} = \sum_{L=2}^{K}\sum_{M=0}^{L}\frac{(A_{LM}\cos M\phi - B_{LM}\sin M\phi)P_L^M(\cos\theta)}{R^{L+1}} \qquad (3)$$

where $K=2(l-1)$ for a specific l-electron, $P_L^M(\cos\theta)$ the associated Legendre polynomials and the coefficient A_{LM} and B_{LM} measure the anisotropy in the multipolar magnetic susceptibilities of the molecule. Recently Golding and stubbs[6] have pointed out an error in Stiles's calculation using equa-

tion (3). They have calculated the pseudo contact shift for a nucleus at various distances R along the z axis from a $3d^1$ transition metal ion in a crystal field of octahedral symmetry, with a tetragonal crystal field component along the z axis and with a trigonal crystal field component along the (111) axis. We have recently evaluated the hyperfine integrals which are required to investigate the NMR shift for $4d^1$ system[7] by the nonmultipole expansion method[8] and the NMR shift arising from the electron orbital angular momentum and the electron spin dipolar–nuclear spin angular momentum interactions has been calculated for $4d^1$ system in a strong crystal field environment of octahedral symmetry.[9]

The purpose of this work is to derive a general expression for the NMR shift arising from the electron orbital angular momentum and the electron spin dipolar–nuclear spin angular momentum interactions for a $4d^1$ system with a tetragonal distortion along the z axis using the nonmultipole expansion method and to calculate the NMR shift for this system. We also compare the NMR results with those for a $4d^1$ system in a strong crystal field of octahedral symmetry.

Theory

The hamiltonian representing the various interactions we shall consider in this paper may be written as[10, 11, 13]

$$\mathcal{H}=-\frac{\hbar^2}{2m_e}V^2-\frac{Ze^2}{4\pi\varepsilon_0 r}+V(r)+\delta(l_z^2-2)+\xi l\cdot S+\mu_B(l+2S)B+\mathcal{H}_{hf} \tag{4}$$

where $V(C)+\delta(l_z^2-2)$ is the complete tetragonal crystal field potential, δ is the distortion parameter and

$$\mathcal{H}_{hf}=\frac{\mu_0}{4\pi}g_N\mu_B\mu_N\left\{\frac{2l_N\cdot I}{r_N^3}+g_S\left[\frac{3(r_N\cdot S)r_N\cdot I}{r_N^5}-\frac{S\cdot I}{r_N^3}\right]\right\} \tag{5}$$

here r and r_N are the electron radius vectors about the electron bearing atom and the nucleus with nuclear spin angular momentum, I, respectively. The quantity B is the applied magnetic field and the other symbols have their usual meaning.

A $4d^1$ system in a strong crystal field of octahedral symmetry results in a $^2T_2$ ground state. The spin–orbit interactions and the tetragonal distortion interactions split the threefold degenerate $^2T_2$ level into three doubly spin degenerate levels. The eigenvalues and the corresponding eigenfunctions are given by[11]

$$e_1=\frac{\zeta}{4}+\frac{\delta}{2}-\frac{A}{2}$$
$$\phi_1^-=a|-1^-\rangle+b|\zeta_1^-\rangle$$
$$\phi_1^+=a|1^+\rangle-b|\zeta_1^-\rangle \tag{6}$$

$$e_2=\frac{\zeta}{4}+\frac{\delta}{2}+\frac{A}{2}$$
$$\phi_2^-=b|-1^-\rangle-a|\zeta_1^-\rangle$$
$$\phi_2^+=b|1^+\rangle+a|\zeta_1^-\rangle \tag{7}$$

$$e_3=-\frac{\zeta}{2}-\delta$$
$$\phi_3^-=-|1^-\rangle$$
$$\phi_3^+=|-1^+\rangle \tag{8}$$

Where

$$-|1\rangle=\frac{1}{\sqrt{2}}(4d_{xz}+i4d_{yz})$$
$$|-1\rangle=\frac{1}{\sqrt{2}}(4d_{xz}-i4d_{yz})$$
$$\zeta_1=i4d_{xy}=\frac{1}{\sqrt{2}}[|2\rangle-|-2\rangle] \tag{9}$$
$$A^2=\left\{\frac{9}{4}\zeta^2-3\delta\zeta+9\delta^2\right\}$$
$$a^2=\frac{1}{2}-\frac{1}{2}(\zeta/2-3\delta)A^{-1}$$
$$b^2=\frac{1}{2}+\frac{1}{2}(\zeta/2-3\zeta)A^{-1}$$

and

$$ab=(\zeta/\sqrt{2})A^{-1} \tag{10}$$

The electronic wave functions which we shall use in this paper may be expressed, in real notation, as

$$|4d_{xz}\rangle=\left(\frac{\beta^9}{21\pi}\right)^{1/2}xzr\exp(-\beta r)$$
$$|4d_{yz}\rangle=\left(\frac{\beta^9}{21\pi}\right)^{1/2}yzr\exp(-\beta r)$$
$$|4d_{xy}\rangle=\left(\frac{\beta^9}{21\pi}\right)^{1/2}xyr\exp(-\beta r) \tag{11}$$

where β is the optimized orbital exponent.[12]

The magnetic field interaction, $\mu_B(l+2S)\cdot B$, is then added and treated as a perturbation to yield new eigenfunctions $|\phi^n\rangle$ and the corresponding eigenvalues, E_n. The principal values of the NMR shielding tensor σ are determined by considering the magnetic field B as parallel to the x, y and z axis and then averaged by using a Boltzmann distribution.

The NMR shift is given by

$$\frac{\Delta B}{B}=\frac{2}{3}\frac{\mu_B^2}{kT}\frac{\mu_0}{4\pi}\frac{\sum_{i=1}^{3}(A_i+B_ikT)\exp(-E_i/kT)}{\sum_{i=1}^{3}\exp(-E_i/kT)} \tag{12}$$

A_i and B_i may be expressed in terms of spherical harmonics,

$$A_i=a_1^{(i)}\sqrt{2\pi/91}\,[Y_{6-4}(\theta,\phi)+Y_{64}(\theta,\phi)]+a_1^{(i)}\sqrt{\pi/13}\,Y_{60}(\theta,\phi)+a_3^{(i)}\sqrt{2\pi/35}\,[Y_{4-4}(\theta,\phi)+Y_{44}(\theta,\phi)]+a_4^{(i)}\sqrt{\pi}\,Y_{40}(\theta,\phi)+a_5^{(i)}\sqrt{\pi/5}\,Y_{20}(\theta,\phi)+a_6^{(i)}\sqrt{\pi}\,Y_{00}(\theta,\phi) \tag{13}$$

$$B_i=b_1^{(i)}\sqrt{2\pi/91}\,[Y_{6-4}(\theta,\phi)+Y_{64}(\theta,\phi)]+b_2^{(i)}\sqrt{\pi/13}\,Y_{60}(\theta,\phi)+b_3^{(i)}\sqrt{2\pi/35}\,[Y_{4-4}(\theta,\phi)+Y_{44}(\theta,\phi)]+b_4^{(i)}\sqrt{\pi}\,Y_{40}(\theta,\phi)+b_5^{(i)}\sqrt{\pi/5}\,Y_{20}(\theta,\phi)+b_6^{(i)}\sqrt{\pi}\,Y_{00}(\theta,\phi) \tag{14}$$

for $i=1, 2, 3$.

The coefficients $a_l^{(i)}$ and $b_l^{(i)}$ for $l=1-6$ are functions of the internuclear distance R, the spin orbit coupling constant ζ and the distortion parameter δ. If we may define matrices $g_m^{(i)}$ and $h_m^{(i)}$ as shown in Table 1 and 2 respectively, the coefficients $a_l^{(i)}$ and $b_l^{(i)}$ may then be expressed in terms of these matrices $g_m^{(i)}$ and $h_m^{(i)}$ and two matrices $c_{lm}(t)$ and $d_{lm}(t)$ of radial dependence as follows;

$$a_l^{(i)}=\sum_{m=1}^{4}c_{lm}(t)\,g_m^{(i)} \tag{15}$$

TABLE 1: The Matrix Elements $g_m^{(i)}$

m	i = 1	2	3
1	a^4	b^4	0
2	$\sqrt{2}a^3b$	$-\sqrt{2}ab^3$	0
3	a^2b^2	a^2b^2	0
4	$-2ab^3$	$2a^3b$	0

TABLE 2: The Matrix Elements $h_m^{(i)}$

m	i = 1	2	3
1	$\frac{a^4+b^4}{e_1-e_2}$	$\frac{b^4+a^4}{e_2-e_1}$	0
2	$\frac{a^2b^2}{e_1-e_2}$	$\frac{b^2a^2}{e_2-e_1}$	0
3	$\frac{(\sqrt{2}ab^3-\sqrt{2}a^3b)}{e_1-e_2}$	$\frac{(\sqrt{2}ab^3-\sqrt{2}a^3b)}{e_2-e_1}$	0
4	$\frac{a^2}{e_1-e_3}$	$\frac{b^2}{e_2-e_3}$	$\frac{a^2}{e_3-e_1}+\frac{b^2}{e_3-e_2}$
5	$\frac{\sqrt{2}ab}{e_1-e_3}$	$-\frac{\sqrt{2}ab}{e_2-e_3}$	$\frac{\sqrt{2}ab}{e_3-e_1}-\frac{\sqrt{2}ab}{e_3-e_2}$
6	$\frac{b^2}{e_1-e_3}$	$\frac{a^2}{e_2-e_3}$	$\frac{a^2}{e_3-e_2}+\frac{b^2}{e_3-e_1}$

TABLE 3: The Matrix Elements $C_{lm}(t)$

$C_{lm}(t)$	$C_{lm}(t)$ for $R\to\infty$
$C_{11}=0$	0
$C_{12}=(16/231)S_1$	$297000/R_7\beta_4$
$C_{13}=-(20/231)S_1$	$-371250/R_7\beta_4$
$C_{14}=-(2/231)S_1$	$-37125/R_7\beta_4$
$C_{21}=(32/1617)S_1$	$594000/7R^7\beta^4$
$C_{22}=-(16/1617)S_1$	$-297000/7R^7\beta^4$
$C_{23}=(8/1617)S_1$	$1485000/7R^7\beta^4$
$C_{24}=(4/1617)S_1$	$74250/7R^7\beta^4$
$C_{31}=0$	0
$C_{32}=(4/231)F_3+(4/231)F_8$	$2250/R^5\beta^2$
$C_{33}=-(4/231)F_3+(4/693)F_8+(4/63)f_1$	$-2700/R^5\beta^2$
$C_{34}=(8/693)F_8+(2/63)f_1$	$-225/R^5\beta^2$
$C_{41}=(16/24255)F_4+(32/2205)f_1$	$-2520/R^5\beta^2$
$C_{42}=(8/1155)F_{10}-(46/24255)F_7-(38/24255)F_7$ $+(4/1155)F_6$	$3600/7R^5\beta^2$
$C_{43}=-(8/1155)F_{10}+(38/24255)F_7-(128/24255)F_9$ $-(4/1155)F_6-(8/24255)F_4+(46/24255)F_1$ $+(8/2205)f_1$	$-6480/7R^5\beta^2$
$C_{44}=-(64/2455)F_9+(4/735)f_1$	$-2070/7R^5\beta^2$
$C_{51}=-(8/441)T_4-(8/441)t_1$	$-48/R^3$
$C_{52}=(2/441)T_1-(2/441)T_5$	0
$C_{55}=(6/441)T_1+(2/441)T_5+(4/441)T_4+(4/147)t_1$	$72/R^3$
$C_{54}=(4/441)T_1+(4/441)t_1$	$24/R^3$
$C_{61}=-(8/2205)N_1-(8/315)n_1$	0
$C_{62}=-(8/735)N_1$	0
$C_{63}=(4/735)N_1-(4/105)n_1$	0
$C_{64}=-(8/2205)N_1-(8/315)n_1$	0

$$b_l^{(i)}=\sum_{m=1}^{6} d_{lm}(t)\,h_m^{(i)} \qquad (16)$$

where $t=2\beta r$.

The matrix elements $c_{lm}(t)$ and $d_{lm}(t)$, together with their asymptotic expansions for $R\to\infty$ are listed in Table 3 and 4, respectively.

TABLE 4: The Matrix Elements $d_{lm}(t)$

$d_{lm}(t)$	$d_{lm}(t)$ for $R\to\infty$
$d_{11}=(4/231)S_1$	$74250/R^7\beta^4$
$d_{12}=-(32/231)S_1$	$-594000/R^7\beta^4$
$d_{13}=-(14/231)S_1$	$-259875/R^7\beta^4$
$d_{14}=0$	0
$d_{15}=(4/231)S_1$	$74250/R^7\beta^4$
$d_{16}=-(4/231)S_1$	$-74250/R^7\beta^4$
$d_{21}=-(8/1617)S_1$	$-148500/7R^7\beta^4$
$d_{22}=-(64/1617)S_1$	$-1188000/7R^7\beta^4$
$d_{23}=(4/539)S_1$	$24750/7R^7\beta^4$
$d_{24}=(32/1617)S_1$	$594000/7R^7\beta^4$
$d_{25}=-(8/539)S_1$	$-49500/7R^7\beta^4$
$d_{26}=(8/1617)S_1$	$148500/7R^7\beta^4$
$d_{31}=(2/231)F_8-(2/63)f_1$	$225/R^5\beta^2$
$d_{32}=-(8/231)F_3+(20/693)F_8+(4/63)f_1$	$-4950/R^5\beta^2$
$d_{33}=-(4/231)F_3-(20/693)F_8-(2/63)f_1$	$-2025/R^5\beta^2$
$d_{34}=0$	0
$d_{35}=(2/231)F_8+(2/63)f_1$	$-225/R^5\beta^2$
$d_{36}=-(2/231)F_8-(2/63)f_1$	$225/R^5\beta^2$
$d_{41}=(4/1155)F_{10}-(4/735)f_1$	$2070/7R^5\beta^2$
$d_{42}=-(8/1155)F_{10}+(76/24255)F_7-(256/24255)F_9$ $-(16/8085)F_4-(8/1155)F_6+(92/24255)F_1$ $-(8/245)f_1$	$-1530/7R^5\beta^2$
$d_{43}=-(8/1155)F_{10}+(46/24255)F_1+(38/24255)F_7$ $+(64/24255)F_9-(4/1155)F_6-(4/735)f_1$	$-90/7R^5\beta^2$
$d_{44}=(92/24255)F_1-(76/24255)F_7$	$-1800/7R^5\beta^2$
$d_{45}=(4/1155)F_{10}-(46/24255)F_1+(38/24255)F_7$ $+(4/735)f_1$	$2430/7R^5\beta^2$
$d_{46}=-(4/1155)F_{10}-(4/735)f_1$	$-1530/7R^5\beta^2$
$d_{51}=(4/735)T_3-(4/441)t_1$	$-4/R^3$
$d_{52}=(4/147)T_1+(8/147)T_4+(4/441)T_5$ $+(8/735)T_3+(32/441)t_1$	$72/R^3$
$d_{53}=-(2/147)T_1+(2/441)T_5-(4/441)t_1$	$-24/R^3$
$d_{54}=-(4/441)T_1-(4/441)T_5$	$-40/R^3$
$d_{55}=(2/441)T_1+(2/441)T_5+(4/735)T_3+(4/441)t_1$	$8/R^3$
$d_{56}=-(4/735)T_3-(4/441)t_1$	$-4/R_3$
$d_{61}=-(4/735)N_1+(8/315)n_1$	0
$d_{62}=(16/2205)N_1+(8/315)n_1$	0
$d_{63}=(32/2205)N_1+(8/315)n_1$	0
$d_{64}=-(8/2205)N_1$	0
$d_{65}=-(8/2205)N_1-(8/315)n_1$	0
$d_{66}=(4/735)N_1+(8/315)n_1$	0

Results and Discussion

It should be indicated here that for calculation of $c_{lm}(t)$ and $d_{lm}(t)$, we adopt the hyperfine integrals for 4d orbitals listed elsewhere[7]. They are given in terms of a series which are linear combinations of the radial integrals. In those hyperfine integrals, radial series corresponding to $1/R^3$, $1/R^5$ and $1/R^7$ terms are represented as T_i, F_i and S_i, respectively. In a strong crystal field environment of tetragonal symmetry, the symmetry of a $4d^1$ system is reflected in the appearance in the result for $\Delta B/B$ of only those combinations of spherical harmonics $Y_{lm}(\Theta,\Phi)$ that transforms as the identity representation a_{1g} of the point group D_{4h}.[13] Therefore, eq. (12) contains $a_2^{(i)}\sqrt{\pi/5}\;Y_{20}(\Theta,\Phi)(1/R^3)$ term, which is different from the octahedral case.

The NMR shifts are tabulated in Table 5*a* for a $4d^1$ system

in a strong crystal field environment of tetragonal symmetry and in Table 5b for a $4d^1$ system in a strong crystal field environment of octahedral symmetry for a comparison. Here, we choose β as $2.8481/a_0$, the spin–orbit coupling constant as $1030\,cm^{-1}$ and the distortion parameter as $1000\ cm^{-1}$. These parameter values are similar to those for Mo^{5+} ion. The temperature is taken as $T=300$ K. As shown in Table 5a, $\Delta B/B$ for specific R-values along the (100) and (010) axes are consistent with each other for a $4d^1$ system in a strong crystal field of tetragonal symmetry. However, as R increases the NMR shift for a $4d^1$ system in a strong crystal field environment of tetragonal symmetry not only changes, markrdly in magnitude but also in sign, which is different from a $4d^1$ system in a strong crystal field environment of octahedral symmetry, as shown in Table 5b. This result represents an anisotropic NMR shielding for a $4d^1$ system in a strong crystal field environment of tetragonal symmetry. Along the (100), (010) and (110) axes, $\Delta B/B$ values are negative for all values of R except for $R\geqslant 0.1$ nm while along the (001) axis, $\Delta B/B$ is positive. The NMR shift along the (111) axis is, however, negative for all values of R.

As shown in Table 5*b*, $\Delta B/B$ for a $4d^1$ system in a strong crystal field environment of octahedral symmetry along the (100), (010), (001) and (111) axes is negative for all values of R while along the (110) axis, the NMR shift is positive and the decreasing rate of $\Delta B/B$ is greater than that for a $4d^1$ system in a strong crystal field environment of tetragonal symmetry, as R increases. We also find that along the (001) axis, $\Delta B/B$ for a $4d^1$ system in a strong crystal field environment of tetragonal symmetry is almost triply greater in magnitude than those along the (100) and (010) axes.

The NMR results for a $4d^1$ system both in strong tetragonal and octahedral crystal fields using eq. (12) and the corresponding multipolar terms, $1/R^3$, $1/R^5$ and $1/R^7$, given in eq. (13) and (14) are listed in Table 6 and 7. A comparison of the multipolar terms with the exact solution given by eq. (12) shows that the multipolar results are in agreement with the exact results when $R\leqslant 0.25$ nm. It is also found that along the (100), (001) and (110) axes, $1/R^3$ term is the dominant contribution to the NMR shift while along the (111) axis, $1/R^5$ term dominantly contributes to the NMR shift. Along the ali axes, the contributions of the other terms may not, however, neglected, as shown in Table 6. For a $4d^1$ system in strong crystal field environment of octahedral symmetry, $1/R^5$ term is the dominant contribution to the NMR shift, as shown in Table 7. It is necessary to mention that along the (100), (010) and (110) axes, the decreasing rate of $1/R^3$, $1/R^5$ and $1/R^7$ terms in a strong crystal field of tetragonal symmetry is almost the same as that along the (001) and (111) axes while their sign is opposite, as R inceases. We find that along the (001) axis, $1/R^3$, $1/R^5$ and $1/R^7$ terms

TABLE 5: $\Delta B/B$(ppm) for Specific R Values for a $4d^1$ Systems

(a) In a Strong Crystal Field of Tetragonal Symmetry ($\delta=1000\ cm^{-1}$, $\zeta=1030\ cm^{-1}$ and $T=300$ K)

R(nm)	$\Delta B/B$ (ppm)				
	(100) axis	(010) axis	(001) axis	(110) axis	(111) axis
0.05	1025.504	1025.504	−1474.254	1033.948	−307.945
0.10	86.991	86.991	92.482	82.487	−279.005
0.15	−63.398	−63.398	206.742	−67.409	−58.260
0.20	−43.187	−43.197	111.394	−44.804	−12.223
0.25	−25.259	−25.259	59.690	−25.899	−3.471
0.30	−15.430	−15.430	34.761	−15.712	−1.269
0.35	−9.986	−9.986	21.838	−10.124	−0.552
0.40	−6.797	−6.797	14.570	−6.870	−0.272
0.45	−4.822	−4.822	10.193	−4.863	−0.147
0.50	−3.539	−3.539	7.405	−3.563	−0.085

(b) In a Strong Crystal Field of Octahedral Symmetry[9] ($\delta=0\ cm^{-1}$, $\zeta=1030\ cm^{-1}$, $T=300$ K)

R(nm)	$\Delta B/B$(ppm)				
	(100) axis	(010) axis	(001) axis	(110) axis	(111) axis
0.05	−92044.372	−92044.372	−92044.372	147206.318	−162486.232
0.10	−879.293	−879.293	−879.293	1216.944	−1401.049
0.15	−60.923	−60.923	−60.923	91.390	−100.156
0.20	−8.432	−8.432	−8.432	13.395	−14.525
0.25	−1.787	−1.787	−1.787	2.847	−3.076
0.30	−0.504	−0.504	−0.504	0.796	−0.856
0.35	−0.173	−0.173	−0.173	0.271	−0.290
0.40	−0.069	−0.069	−0.069	0.107	−0.113
0.45	−0.031	−0.031	−0.031	0.047	−0.049
0.50	−0.015	−0.015	−0.015	0.020	−0.023

TABLE 6: A Comparision of the Exact Values of $\Delta B/B$(ppm) Calculated Using Eq.(12) with the Multipolar Terms in a Strong Crystal Field of Tetragonal Symmetry

(a) Along the (100) (or (010)) Axis (δ=1000 cm^{-1}, ζ=1030 cm^{-1} and T=300K)

R(nm)	$\Delta B/B$(ppm)				
	$1/R^3$	$1/R^5$	$1/R^7$	Sum of all multipolar terms	From eq. (12)
0.05	798.584	181.828	88.943	1069.355	1025.504
0.10	−137.765	130.185	131.567	023.987	86.991
0.15	−122.817	30.860	30.703	−61.255	−63.398
0.20	−56.444	7.846	5.459	−43.139	−43.197
0.25	−29.025	2.582	1.186	−25.258	−25.259
0.30	−16.799	1.038	0.332	−15.430	−15.430
0.35	−10.589	0.480	0.113	−9.986	−9.986
0.40	−7.087	0.246	0.044	−6.797	−6.797
0.45	−4.978	0.137	0.019	−4.822	−4.822
0.50	−3.629	0.081	0.009	−3.539	−3.539

(b) Along the (001) Axis

R(nm)	$\Delta B/B$(ppm)				
	$1/R^3$	$1/R^5$	$1/R^7$	Sum of all multipolar terms	From eq.(12)
0.05	−1597.169	475.793	−309.026	−1430.402	−1474.254
0.10	275.531	311.067	−457.120	129.478	92.482
0.15	245.635	69.924	−106.673	208.886	206.742
0.20	112.887	17.530	−18.966	111.451	111.394
0.25	58.051	5.760	−4.120	59.691	59.690
0.30	33.599	2.315	−1.153	34.761	34.761
0.35	21.158	1.071	−0.392	21.838	21.838
0.40	14.175	0.549	−0.154	14.570	14.570
0.45	9.955	0.305	−0.067	10.193	10.193
0.50	7.257	0.180	−0.043	7.405	7.405

(c) Along the (110) Axis

R(nm)	$\Delta B/B$(ppm)				
	$1/R^3$	$1/R^5$	$1/R^7$	Sum of all multipolar terms	From eq. (12)
0.05	798.594	175.017	104.198	1077.800	1033.948
0.10	−137.765	103.115	154.133	199.483	82.487
0.15	−122.817	21.583	35.968	−65.265	−67.109
0.20	−56.444	5.302	6.395	−44.747	−44.804
0.25	−29.025	1.738	1.389	−25.898	−25.899
0.30	−16.799	0.699	0.389	−15.712	−15.712
0.35	−10.579	0.323	0.132	−10.124	−10.124
0.40	−7.087	0.166	0.052	−6.780	−6.870
0.45	−4.978	0.092	0.023	−4.863	−4.863
0.50	−3.629	0.054	0.011	−3.563	−3.563

(d) Along the (111) Axis

R(nm)	$\Delta B/B$(ppm)				
	$1/R^3$	$1/R^5$	$1/R^7$	Sum of all multipolar terms	From eq. (12)
0.05	0.173	−186.516	−77.750	−264.093	−307.945
0.10	−0.030	−126.969	−115.011	−242.010	−279.005
0.15	−0.027	−29.250	−26.839	−56.116	−58.260
0.20	−0.012	−7.382	−4.772	−12.166	−12.223
0.25	−0.006	−2.427	−1.037	−3.470	−3.471
0.30	−0.003	−0.986	−0.290	−1.269	−1.269
0.35	−0.002	−0.451	−0.099	−0.552	−0.552
0.40	−0.002	−0.232	−0.039	−0.272	−0.272
0.45	−0.001	−0.128	−0.017	−0.147	−0.147
0.50	−0.001	−0.076	−0.008	−0.085	−0.085

TABLE 7: A comparision of the Exact Values of $\Delta B/B$(ppm) Claculated using eq. (11) of Reference (9) with the Multipolar Terms in a Strong Crystal field of Octahedral Symmetry[9]

(a) Along the (100) (010) or (001) Axes (δ=0 cm^{-1}, ζ=1030 cm^{-1} and T=300 K)

R(nm)	$\Delta B/B$(ppm)			
	$1/R^5$	$1/R^7$	Sum of all multipolar terms	Exact
0.05	−219.546	−91038.574	−91258.120	−92044.372
0.10	−48.772	−775.432	−824.114	−879.293
0.15	−2.895	−56.646	−59.541	−60.923
0.20	−0.184	−8.228	−8.411	−8.432
0.25	−0.041	−1.746	−1.787	−1.787
0.30	−0.016	−0.488	−0.504	−0.504
0.35	−0.007	−0.166	−0.173	−0.173
0.40	−0.004	−0.065	−0.069	−0.069
0.45	−0.002	−0.029	−0.031	−0.031
0.50	−0.001	−0.014	−0.015	−0.015

(b) Along the (110) Axis[9]

R(nm)	$\Delta B/B$(ppm)			
	$1/R^5$	$1/R^7$	Sum of all multipolar terms	Exact
0.05	54.887	147937.683	147992.570	147206.318
0.10	12.193	1259.930	1272.123	1216.944
0.15	0.724	29.049	92.773	91.390
0.20	0.046	13.370	13.416	13.395
0.25	0.010	2.837	2.847	2.847
0.30	0.004	0.792	0.796	0.796
0.35	0.002	0.269	0.271	0.271
0.40	0.001	0.106	0.107	0.107
0.45	0.001	0.046	0.047	0.047
0.50	0.000	0.022	0.022	0.022

(c) Along the (111) Axis[9]

R(nm)	$\Delta B/B$(ppm)			
	$1/R^5$	$1/R^7$	Sum of all multipolar terms	Exact
0.05	146.364	−161846.344	−161699.980	−162486.232
0.10	32.515	−1378.385	−1345.870	−1401.049
0.15	1.930	−100.703	−98.773	−100.156
0.20	0.122	−14.627	−14.505	−14.525
0.25	0.027	−3.103	−3.076	−3.076
0.30	0.011	−0.867	−0.856	−0.856
0.35	0.005	−0.295	−0.290	−0.290
0.40	0.003	−0.116	−0.113	−0.113
0.45	0.001	−0.051	−0.049	−0.049
0.50	0.001	−0.024	−0.023	−0.023

are bigger in magnitude than those along the (100), (010) and (110) axes while along the (111) axis, those terms are significantly smaller in magnitude than those along the other axes and have a negative sign, as shown in Table 6.

This work may be applied to investigate the NMR shift, electronic and geometric structure for $4d^n$ systems and to calculate the hyperfine interaction tensor components for these systems.

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