

SPECTROSCOPIC PROPERTIES OF HIGH-SPIN FERROUS ION IN COMPLEXES WITH RHOMBIC DISTORTIONS

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The spectroscopic properties of singlet ground state high-spin Fe^{2+} ion in first-kind rhombic symmetry crystalline environment are considered. Spin Hamiltonian parameters of second order $B_0^{(2)}(D)$, $B_2^{(2)}(E)$ and g_x, g_y, g_z and, for the first time in the available literature, of fourth order $B_0^{(4)}$, $B_2^{(4)}$ and $B_4^{(4)}$, are derived from the microscopic theory. Numerical estimations of these parameters are performed for Fe^{2+} ion in deoxyhemoglobin (deoxymyoglobin) and $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ with various values of the starting parameters $\Delta_1, \Delta_2, \Delta_3, \Delta_4$; λ and ρ close to the experimental data of others. The calculations yield the following ranges for the parameters: $D: 15-5, E: 5-0, B_2^{(4)}: 0.5-0.05, B_4^{(4)}: 0.1-0, B_4^{(3)}: 0.1-0.01\text{cm}^{-1}$. The results of this paper are illustrative for the case of Fe^{2+} in $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, for which the energies Δ_i are not known.

1. Introduction

In six-fold and five-fold coordinated complexes of transition-metal (TM) ions, the distortions of the nearest neighbour ligands can lead to two different kinds of rhombic symmetry [1-3], both formally described by one of the rhombic point groups D_{2h} , D_2 or C_{2v} [4]. We distinguish a first-kind rhombic symmetry — when the symmetry axes (x and y) in the plane perpendicular to the \hat{C}_2 axis (taken as the z axis) coincide with the "ideal" TM ion site — ligand axes, and a second-kind rhombic symmetry — when the symmetry axes x and y bisect the "ideal" TM ion site — ligand axes [1, 2]. For both kinds of rhombic symmetry the crystal field (CF) hamiltonian [5] has the same form in the local coordination frame, whereas the basis of orbital wave functions for a TM ion in the second-kind rhombic symmetry should be that of the first-kind, transformed by a rotation by 45° through the \hat{C}_2 (z) axis [1, 2].

Crystal field calculations for the iron-group ions, involving the states of the whole $3d^n$ configuration, have been strongly advanced in the past several years, though only for

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the cubic and, in part, for the axial symmetries (for a review, see [6]). The rhombic CF for the iron (II) ion has at yet been considered inside some subspaces of low-lying $3d^6$ configuration states (Refs [3, 7–11] and [1, 12, 13] for the first- and second-kind rhombic symmetry, respectively). From Refs [1, 3, 7–13] it follows that in a variety of compounds the ground state of the Fe^{2+} ion is an orbital singlet with a high-spin value $S = 2$ rather well separated from the next energy level. Hence a spin hamiltonian [5] with $S = 2$ can be used for the theoretical description of the spectroscopic and magnetic properties of these ferrous compounds. Thus, the microscopic theory [14] of spin hamiltonian parameters [5, 15] is of interest for several experimental methods, as e. g.: EPR, Mössbauer spectroscopy, specific heat, paramagnetic anisotropy, magnetic susceptibility, direct magnetization measurements [1–3, 7–13, 16].

Hitherto, the action of spin-orbit coupling on the high-spin singlet ground state of ferrous ion has been considered, and the usual D , E and g_x, g_y, g_z [15] have been derived for both kinds of rhombic symmetry [1, 3, 7, 11, 13]. However, a complete spin hamiltonian for $S = 2$ comprises some fourth-order terms as well [11, 14, 15]. Our theoretical predictions for $3d^6(3d^4)$ ions in crystals with axial distortions and the available experimental data (see Refs [17]) have shown the fourth-order parameters to be accessible to determination due to the present refined accuracy of the experimental techniques. Consequently, it is of interest to give a theoretical account of the fourth-order parameters $B_0^{(4)}$, $B_2^{(4)}$ and $B_4^{(4)}$ [14] for rhombic symmetry.

To achieve this aim we consider in this paper, up to fourth-order perturbation theory [14], the action of spin-orbit as well as spin-spin coupling inside the 5D -term states [18] of Fe^{2+} ion in first-kind rhombic symmetry. Applications of the expressions derived for the $B_q^{(k)}$'s are quantitatively discussed for several relevant ferrous compounds. The case of second-kind rhombic symmetry will be studied in a forthcoming paper [19].

On the basis of the $B_q^{(k)}$ parameter values calculated here, the crossing of the lowest-lying energy levels of Fe^{2+} ion in deoxyhemoglobin in a high magnetic field is studied by us in a separate paper [20].

2. Symmetry considerations

The following examples of high-spin singlet ground state ferrous compounds with "first-kind" rhombic distortions can at present be adduced: (i) the deoxy form of hemoglobin (and myoglobin) [7, 8], (ii) the Tutton salt $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ [10, 11], and (iii) vivianite $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ [21–23].

The local symmetry of the iron site in hemoglobin (Fig. 1) "undergoes" the following consecutive changes: deoxygenation of hemoglobin, which is equivalent to a "ligand-type" distortion, lowers the symmetry from D_{4h} to C_{4v} resulting in five-fold coordination, further due to delocalization of the Fe^{2+} ion out of the heme plane (the plane XY in Fig. 1) [8, 9] a "coordinate" distortion [24] arises and the symmetry reduces to rhombic C_{2v} . For Fe^{2+} in the Tutton salt, the sequence $O_h \supset D_{4h} \supset D_{2h}$ seems to be the most appropriate [10, 11]. In vivianite, there are two inequivalent distorted octahedral Fe^{2+} sites of D_{4h} (site I) and C_{2v} (site II) symmetry [21]. Restricting the problem to the nearest neighbour

ligands [9, 11, 21], the appropriate coordination frame for a TM site in these compounds is that shown in Fig. 1.

The splitting of the ground 5D term of Fe^{2+} ion and the orbital wave functions [18] appropriate for the "first-kind" rhombic CF are shown in Fig. 2. There are some states arising from the higher terms 2^S+1L and lying in energy between 5E and 5A_1 states; however, in the 5D approximation, we omit such states in our considerations. This approximation

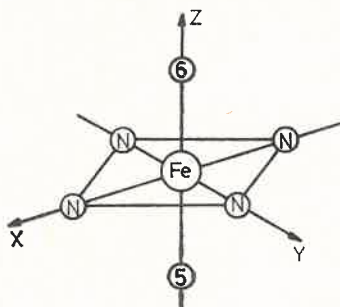


Fig. 1. The iron coordination symmetry in hemoglobin

is fully justified in the present case because these states contribute insignificantly to the spin Hamiltonian parameters [20]. The mixing coefficients $\alpha = \cos \theta$ and $\beta = \sin \theta$ are defined by $\text{tg } 2\theta = 4\Gamma/\sqrt{3}(\epsilon_3 - \epsilon_2)$, where Γ is the second rank rhombic CF parameter [8, 9]

$$V_{rh} = \frac{1}{3} \sqrt{\frac{2}{3}} \Gamma \{ \tilde{O}_{+2}^{(2)}(\hat{L}) + \tilde{O}_{-2}^{(2)}(\hat{L}) \}. \quad (1)$$

The general spin Hamiltonian for any rhombic symmetry is of the form [14]

$$\tilde{\mathcal{H}}_{\text{spin}} = \tilde{\mathcal{H}}_{ZF} + \tilde{\mathcal{H}}_{Ze} \quad (2)$$

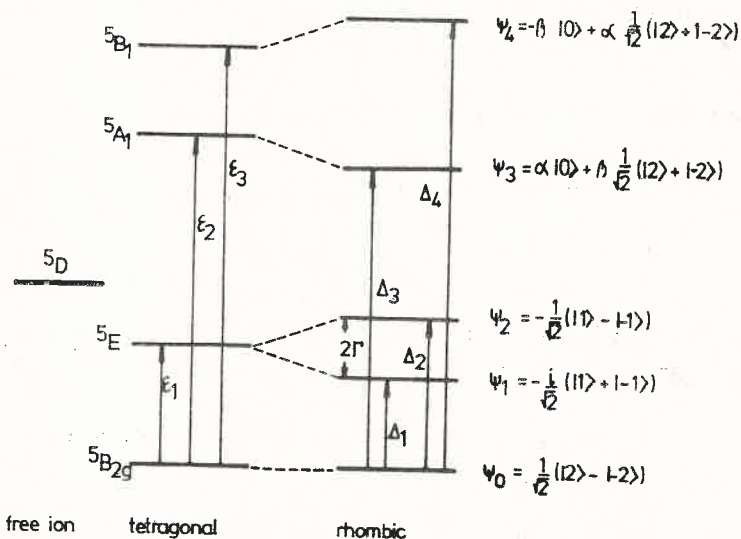


Fig. 2. Splitting of the $(3d^6)^5D$ term in first-kind rhombic crystal field

where the zero field part is

$$\tilde{\mathcal{H}}_{ZF} = B_0^{(2)}\tilde{O}_0^{(2)} + B_2^{(2)}(\tilde{O}_{+2}^{(2)} + \tilde{O}_{-2}^{(2)}) + B_0^{(4)}\tilde{O}_0^{(4)} + B_2^{(4)}(\tilde{O}_{+2}^{(4)} + \tilde{O}_{-2}^{(4)}) + B_4^{(4)}(\tilde{O}_{+4}^{(4)} + \tilde{O}_{-4}^{(4)}), \quad (3)$$

and the Zeeman electronic part

$$\tilde{\mathcal{H}}_{Ze} = \mu_B(g_x H_x \hat{S}_x + g_y H_y \hat{S}_y + g_z H_z \hat{S}_z). \quad (4)$$

For the *first-kind* rhombic symmetry, the tensor operators [14] $\tilde{O}_q^{(k)}$ (\hat{L}) in Eq. (1) and $\tilde{O}_q^{(k)}$ (\hat{S}) in Eq. (3) are expressed in the local coordination frame $\{XYZ\}$ (Fig. 1).

3. Spin Hamiltonian parameters

To derive explicit expressions for the spin Hamiltonian parameters from the general formulas [14], the matrices of the orbital operators \hat{L} and $\tilde{O}^{(2)}(\hat{L})$ within the states $\{\psi_i\}$ defined in Fig. 2 have to be calculated. Once these matrices are known, we can construct the relevant matrices as well for the other admissible cases of energy level structure for a $3d^4$ and $3d^6$ configuration having one of the other states ψ_i as ground state [17]. Hence it seems worth while to give these matrices explicitly in this paper (Appendix I).

By the general method [14, 17], we obtain the following microscopic expressions for the parameters $B_q^{(k)}$ and g_i (Eqs (3), (4)) for *first-kind* rhombic symmetry

a. second-order parameters:

$$B_0^{(2)} = -\frac{1}{3}\lambda^2 \left[\frac{1}{A_1} + \frac{1}{A_2} - 8 \left(\frac{\beta^2}{A_3} + \frac{\alpha^2}{A_4} \right) \right] + 2\varrho, \quad B_2^{(2)} = -\frac{1}{\sqrt{6}}\lambda^2 \left(\frac{1}{A_1} - \frac{1}{A_2} \right), \quad (5)$$

$$g_x = 2 \left(1 - \frac{\lambda}{A_2} \right), \quad g_y = 2 \left(1 - \frac{\lambda}{A_1} \right), \quad g_z = 2 \left[1 - 4\lambda \left(\frac{\beta^2}{A_3} + \frac{\alpha^2}{A_4} \right) \right], \quad (6)$$

b. fourth-order parameters, which we write explicitly as a sum of three contributions [14]:

$$B_q^{(4)} = B_q^{(4)}(\lambda^4) + B_q^{(4)}(\lambda^2\varrho) + B_q^{(4)}(\varrho^2), \quad (7)$$

where λ is the spin-orbit and ϱ is spin-spin coupling constant

$$\begin{aligned} B_0^{(4)}(\lambda^4) = & \frac{2}{35}\lambda^4 \left\{ \frac{3}{2} \left(\frac{1}{A_1^3} + \frac{1}{A_2^3} \right) + \frac{5}{2} \frac{1}{A_1 A_2} \left(\frac{1}{A_1} + \frac{1}{A_2} \right) \right. \\ & + 64 \left(\frac{\beta^4}{A_3^3} + \frac{\alpha^4}{A_4^3} \right) + 64 \frac{\alpha^2 \beta^2}{A_3 A_4} \left(\frac{1}{A_3} + \frac{1}{A_4} \right) \\ & - \frac{1}{2A_1^2} \left(\frac{u_+^2 + 16\beta^2}{A_3} + \frac{v_-^2 + 16\alpha^2}{A_4} \right) - \frac{1}{2A_2^2} \left(\frac{u_-^2 + 16\beta^2}{A_3} + \frac{v_+^2 + 16\alpha^2}{A_4} \right) \\ & + \frac{8\beta^2}{A_3^2} \left(\frac{u_+^2 - 1}{A_1} + \frac{u_-^2 - 1}{A_2} \right) + \frac{8\alpha^2}{A_4^2} \left(\frac{v_-^2 - 1}{A_1} + \frac{v_+^2 - 1}{A_2} \right) \\ & \left. - \frac{1}{A_1 A_2} \left(\frac{3\alpha^2 - 17\beta^2}{A_3} + \frac{3\beta^2 - 17\alpha^2}{A_4} \right) + \frac{16\alpha\beta}{A_3 A_4} \left(\frac{u_+ v_-}{A_1} - \frac{u_- v_+}{A_2} \right) \right\}, \quad (8a) \end{aligned}$$

$$B_2^{(4)}(\lambda^4) = \frac{4}{7\sqrt{10}} \lambda^4 \left\{ \frac{1}{2} \left(\frac{1}{A_1^2} - \frac{1}{A_2^2} \right) \left(\frac{1}{A_1} + \frac{1}{A_2} - \frac{4\beta^2}{A_3} - \frac{4\alpha^2}{A_4} \right) \right. \\ \left. - \frac{2\beta^2}{A_3^2} \left(\frac{u_+^2+1}{A_1} - \frac{u_-^2+1}{A_2} \right) - \frac{2\alpha^2}{A_4^2} \left(\frac{v_-^2+1}{A_1} - \frac{v_+^2+1}{A_2} \right) \right. \\ \left. - 4\alpha\beta \left[\frac{\sqrt{3}}{A_1 A_2} \left(\frac{1}{A_3} - \frac{1}{A_4} \right) + \frac{1}{A_3 A_4} \left(\frac{u_+ v_-}{A_1} + \frac{u_- v_+}{A_2} \right) \right] \right\}, \quad (8b)$$

$$B_4^{(4)}(\lambda^4) = \frac{1}{\sqrt{70}} \lambda^4 \left\{ \frac{1}{A_1^3} + \frac{1}{A_2^3} - \frac{1}{A_1 A_2} \left(\frac{1}{A_1} + \frac{1}{A_2} \right) \right. \\ \left. + \frac{1}{A_1^2} \left(\frac{u_+^2}{A_3} + \frac{v_-^2}{A_4} \right) + \frac{1}{A_2^2} \left(\frac{u_-^2}{A_3} + \frac{v_+^2}{A_4} \right) + \frac{1}{A_1 A_2} \left(\frac{3\alpha^2 - \beta^2}{A_3} + \frac{3\beta^2 - \alpha^2}{A_4} \right) \right\}, \quad (8c)$$

$$B_0^{(4)}(\lambda^2 \varrho) = \frac{1}{3^{\frac{2}{5}}} \lambda^2 \varrho \left\{ -\frac{5}{4} \left(\frac{1}{A_1^2} + \frac{1}{A_2^2} \right) + \frac{7}{2} \frac{1}{A_1 A_2} \right. \\ \left. + 16\alpha^2 \beta^2 \left(\frac{1}{A_3^2} + \frac{1}{A_4^2} - \frac{1}{A_3 A_4} \right) \right. \\ \left. + \frac{1}{\sqrt{3}} \left[\frac{8\beta v_+ - \alpha u_+}{A_1 A_3} + \frac{8\alpha u_- + \beta v_-}{A_1 A_4} - \frac{8\beta v_- + \alpha u_-}{A_2 A_3} + \frac{8\alpha u_+ + \beta v_+}{A_2 A_4} \right] \right\}, \quad (9a)$$

$$B_2^{(4)}(\lambda^2 \varrho) = \frac{2}{7} \sqrt{\frac{3}{10}} \lambda^2 \varrho \left\{ \sqrt{3} \left(\frac{1}{A_1^2} - \frac{1}{A_2^2} \right) \right. \\ \left. - 16\alpha\beta \left(\frac{1}{A_1} + \frac{1}{A_2} + \frac{\beta^2}{A_3} + \frac{\alpha^2}{A_4} \right) \left(\frac{1}{A_3} - \frac{1}{A_4} \right) \right\}, \quad (9b)$$

$$B_4^{(4)}(\lambda^2 \varrho) = \frac{4}{\sqrt{70}} \lambda^2 \varrho \left\{ \frac{3}{4} \left(\frac{1}{A_1^2} + \frac{1}{A_2^2} \right) + \frac{3}{2} \frac{1}{A_1 A_2} \right. \\ \left. + \frac{\alpha\sqrt{3}}{A_3} \left(\frac{u_+}{A_1} + \frac{u_-}{A_2} \right) - \frac{\beta\sqrt{3}}{A_4} \left(\frac{v_-}{A_1} - \frac{v_+}{A_2} \right) \right\}, \quad (9c)$$

$$B_0^{(4)}(\varrho^2) = \frac{1}{3^{\frac{2}{5}}} \varrho^2 \left[3 \left(\frac{1}{A_1} + \frac{1}{A_2} \right) - \left(\frac{\alpha^2}{A_3} + \frac{\beta^2}{A_4} \right) \right], \quad (10a)$$

$$B_2^{(4)}(\varrho^2) = -\frac{18}{7\sqrt{10}} \varrho^2 \left(\frac{1}{A_1} - \frac{1}{A_2} \right), \quad (10b)$$

$$B_4^{(4)}(\varrho^2) = \frac{12}{\sqrt{70}} \varrho^2 \left(\frac{\alpha^2}{A_3} + \frac{\beta^2}{A_4} \right), \quad (10c)$$

the coefficients u_{\pm} and v_{\pm} are defined by Eq. (A5) in Appendix I.

The expressions (5) and (6) are equivalent to the expressions derived by previous authors [7, 11, 36], except that they include moreover the effects of the higher 5E_g states,

and spin-spin coupling. Comparison of the expressions (5) and (6) with those of Refs [7, 3, 11] suggests that B_2^2 , g_x and g_y of Ref. [11] are slightly incorrect; the sign of B_2^2 in Ref. [11] should be changed to the opposite, and g_x and g_y should be read as in Eq. (6) above.

The expressions (8)–(10) are derived for the first time in the literature. If the rhombic crystal field component reduces to zero, e.g. $\alpha = 1$, $\beta = 0$ and $\Delta_1 \equiv \Delta_2$, the parameters $B_2^{(2)}$ and $B_2^{(4)}$ vanish and the above expressions for the other $B_q^{(k)}$ tend to coincide with those derived for the tetragonal case [17].

4. Application

From Mössbauer spectroscopy studies [8, 9], the following energy values appear to be the most appropriate for Fe^{2+} ion in deoxyhemoglobin (deoxymyoglobin): ε_1 ranging from 300 to 900, ε_2 from 6,000 to 8,000, ε_3 from 16,000 to 17,000, Δ_1 from 300 to 600, Δ_2 from 500 to 900 and Γ from 0 to 300 cm^{-1} . Hence the mixing coefficient α equals 1 almost exactly for these ranges of Γ and $(\varepsilon_3 - \varepsilon_2)$ values. To take into account the covalent reduction [25] of the free-ion spin-orbit coupling constant λ_0 [17], the calculations are performed for $\lambda = -100, -90, -80, -60 \text{ cm}^{-1}$ [8, 9]. Table I gives the spin Hamiltonian parameters thus calculated for some sets of the starting parameter values, as indicated (all values, besides the dimensionless g_i , in Tables I and II, are given in cm^{-1}). The other values involved in the calculations are taken to be as: $\alpha = 1.0$; $\rho = 0.18$ [17], $\Delta_3 = 8,000$ and $\Delta_4 = 17,000 \text{ cm}^{-1}$.

The only existing experimental data of Nakano et al. [7] yield $D = 5 \text{ cm}^{-1}$, $E \ll D$ from magnetic susceptibility and $D = 5.3$, $E = 0.9 \text{ cm}^{-1}$ from paramagnetic anisotropy. Hence, to obtain agreement with those data [7], we had to allow for a wider range of Δ_1 , Δ_2 values than that predicted from Mössbauer spectroscopy [8, 9]. The theoretical values of the fourth-order parameters $B_0^{(4)}$, $B_2^{(4)}$, $B_4^{(4)}$ (Table I) suggest that the determination of the $B_q^{(4)}$'s from electron paramagnetic resonance should be feasible, though liquid nitrogen temperature and high magnetic field would be necessary. Experimental methods for the determination of the spin Hamiltonian parameters have been discussed by us in detail elsewhere [20].

From Mössbauer spectroscopy [10], specific heat, and susceptibility data [11] on the Fe^{2+} ion in $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, it follows that the energy Δ_1 lies between 200 and 400, Δ_2 between 500 and 700, and $\lambda = -90 \text{ cm}^{-1}$. However, no data are known on Δ_3 and Δ_4 , so we assume tentatively (i) $\Delta_3 = 5,000$, $\Delta_4 = 8,000$ and (ii) $\Delta_3 = 7,000$, $\Delta_4 = 13,000 \text{ cm}^{-1}$, which are reasonable values for other Fe^{2+} compounds [17]. Hence, a tentative value of the coefficient is about 1 to 0.99. To consider the dependence of the $B_q^{(k)}$'s on $\alpha(\beta)$, we performed the same calculations as in Table II for $\alpha = 0.99$ and 0.97. However, it appears that the $B_0^{(2)}$, $B_0^{(4)}$, $B_4^{(4)}$ are very slightly and $B_2^{(4)}$ but slightly modified in comparison with the values calculated with $\alpha = 1.0$ in Table II.

Gill and Ivey [11] have considered the fourth-order spin Hamiltonian parameters restricting themselves to the parameter $B_4^0 \equiv \frac{1}{8} B_0^{(4)}$ in our notation. The value $B_0^{(4)} = -0.296 \text{ cm}^{-1}$ deduced from experiment by them is in good agreement with our theoretical

TABLE I

A. Fe^{2+} in deoxyhemoglobin: $\lambda = -90$

Δ_2	600	800		900	
Δ_1	400	400	600	500	800
$B_0^{(2)}$	-9.6	-8.5	-6.2	-6.8	-4.7
$B_2^{(2)}$	-2.8	-4.1	-1.4	-2.9	-0.5
D	14.4	12.7	9.4	10.2	7.1
E	3.4	5.1	1.7	3.6	0.6
g_x	2.300	2.226	2.226	2.200	2.200
g_y	2.450	2.450	2.300	2.360	2.226
g_z	2.042	2.042	2.042	2.042	2.042
$B_0^{(4)}$	0.279	0.208	0.093	0.117	0.048
$B_2^{(4)}$	0.080	0.097	0.019	0.047	0.004
$B_4^{(4)}$	0.102	0.112	0.039	0.063	0.022

B. Fe^{2+} in deoxyhemoglobin: $\lambda = -80$

Δ_2	500	600	800		900
Δ_1	300	400	400	600	800
$B_0^{(2)}$	-10.0	-7.5	-6.6	-4.9	-3.7
$B_2^{(2)}$	-3.5	-2.2	-3.3	-1.1	-0.4
D	15.0	11.3	10.0	7.3	5.5
E	4.3	2.7	4.0	1.3	0.4
g_x	2.320	2.266	2.200	2.200	2.178
g_y	2.534	2.400	2.400	2.266	2.200
g_z	2.038	2.038	2.038	2.038	2.038
$B_0^{(4)}$	0.373	0.174	0.130	0.058	0.030
$B_2^{(4)}$	0.133	0.050	0.060	0.012	0.003
$B_4^{(4)}$	0.138	0.066	0.071	0.026	0.014

C. Fe^{2+} in deoxyhemoglobin: $\lambda = -60$

Δ_2	550	600		700	800
Δ_1	300	400	500	450	500
$B_0^{(2)}$	-5.3	-4.1	-3.5	-3.5	-3.0
$B_2^{(2)}$	-2.2	-1.2	-0.5	-1.2	-1.1
D	7.9	6.1	5.2	5.2	4.5
E	2.7	1.5	0.6	1.4	1.4
g_x	2.218	2.200	2.200	2.172	2.150
g_y	2.400	2.300	2.240	2.266	2.240
g_z	2.028	2.028	2.028	2.028	2.028
$B_0^{(4)}$	0.108	0.056	0.037	0.038	0.027
$B_2^{(4)}$	0.044	0.016	0.005	0.011	0.008
$B_4^{(4)}$	0.049	0.023	0.013	0.017	0.014

Fe²⁺ in Fe(NH₄)₂(SO₄)₂ · 6H₂O: λ = -90¹

Δ_2	600		700		
	300	400	300	400	500
$B_0^{(2)}$	-10.4	-8.2	-9.8	-7.6	-6.2
$B_2^{(2)}$	-5.5	-2.8	-6.3	-3.5	-1.9
D	15.7	12.3	14.7	11.3	9.3
E	6.8	3.4	7.7	4.3	2.3
g_x	2.300	2.300	2.258	2.258	2.258
g_y	2.600	2.450	2.600	2.450	2.360
$B_0^{(4)}$	0.485	0.271	0.421	0.229	0.148
$B_2^{(4)}$	0.220	0.074	0.226	0.084	0.033
$B_4^{(4)}$	0.281	0.134	0.290	0.136	0.081
$B_0^{(2)}$	-11.5	-9.2	-10.8	-8.6	-7.2
D	17.2	13.8	16.3	12.9	10.9
$B_0^{(4)}$	0.496	0.277	0.433	0.235	0.152
$B_2^{(4)}$	0.230	0.079	0.238	0.089	0.036
$B_4^{(4)}$	0.246	0.110	0.258	0.114	0.065

¹ The upper part of Table II refers to $\Delta_3 = 5,000$ and $\Delta_4 = 8,000$ (then $g_z = 2.090$), and the lower part to $\Delta_3 = 7,000$ and $\Delta_4 = 13,000$ (then $g_z = 2.055$). $B_2^{(2)}(E)$, g_x and g_y do not depend on Δ_3 , Δ_4 .

predictions except for the sign. As mentioned in Section 3, the sign of $B_2^2 \equiv E$ in Ref. [11] is incorrect and this may have led to the erroneous sign of B_4^0 as well. Hence, the analysis of Gill and Ivey [11] should be reconsidered, and moreover it follows from Table II that in detailed analysis the parameters $B_2^{(4)}$ and $B_4^{(4)}$ should be taken into account as well. It would be highly stimulating to compare our theoretical $B_q^{(k)}$ values with other experimental data, but no such data are at present available.

The electronic structure of Fe²⁺ in Fe₃(PO₄)₂ · 8H₂O (vivianite) is less studied and the energies Δ_i (Fig 2) are not known [21-23]. Hence, no detailed calculations of the spin Hamiltonian parameters can be performed for Fe²⁺ in this compound. However, the values calculated in Tables I and II can serve for tentative predictions of the sign and order of magnitude of the $B_q^{(k)}$'s in this case as well.

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APPENDIX I

Tables of matrix elements

$$L_{\alpha\beta}^{(k)} \equiv \langle \psi_\alpha | \tilde{O}^{(k)}(\hat{L}) | \psi_\beta \rangle, \quad (\text{A1})$$

of orbital operator [14] for

$k = 1$ (Table AI), e.g.:

$$\tilde{O}^{(1)}(\hat{L}) \equiv \hat{L} = \sum_q \hat{L}_q^{(1)} e_q^{[11]}, \quad (\text{A2})$$

$k = 2$ (Table AII), e.g.:

$$\tilde{O}^{(2)}(\hat{L}) = \sum_q \tilde{O}_q^{(2)} e_q^{[21]} \quad (\text{A3})$$

within the states $\{\psi_i\}$ of $3d^6$ configuration (cf. Fig. 2) in the first-kind rhombic symmetry. The following abbreviations are used below

$$a = e_0^{[k]}; \quad e_{\pm q} = e_{+q}^{[k]} \pm e_{-q}^{[k]}; \quad r = \frac{3}{2\sqrt{2}} \quad (\text{A4})$$

$$u_{\pm} = (\alpha \sqrt{3} \pm \beta); \quad v_{\pm} = (\alpha \pm \sqrt{3} \beta) \quad (\text{A5})$$

TABLE AI

States	ψ_0	ψ_1	ψ_2	ψ_3	ψ_4
ψ_0	0	$-\frac{1}{\sqrt{2}} e_{+1}$	$\frac{i}{\sqrt{2}} e_{-1}$	$2i\beta a$	$2i\alpha a$
ψ_1	$-\frac{1}{\sqrt{2}} e_{+1}$	0	a	$\frac{u_+}{\sqrt{2}} e_{-1}$	$\frac{v_-}{\sqrt{2}} e_{-1}$
ψ_2	$\frac{i}{\sqrt{2}} e_{-1}$	$-a$	0	$\frac{i}{\sqrt{2}} u_- e_{+1}$	$-\frac{i}{\sqrt{2}} v_+ e_{+1}$
ψ_3	$2i\beta a$	$-\frac{u_+}{\sqrt{2}} e_{-1}$	$-\frac{i}{\sqrt{2}} u_- e_{+1}$	0	0
ψ_4	$2i\alpha a$	$-\frac{v_-}{\sqrt{2}} e_{-1}$	$-\frac{i}{\sqrt{2}} v_+ e_{+1}$	0	0

TABLE AII

States	ψ_0	ψ_1	ψ_2	ψ_3	ψ_4
ψ_0	$-3a$	$-ir\sqrt{3}e_{-1}$	$-r\sqrt{3}e_{+1}$	$-2r\alpha e_{-2}$	$2r\beta e_{-2}$
ψ_1	$ir\sqrt{3}e_{-1}$	$\frac{3}{2}a - r\sqrt{3}e_{+2}$	$-ir\sqrt{3}e_{-2}$	$irv_- e_{+1}$	$-iru_+ e_{+1}$
ψ_2	$r\sqrt{3}e_{+1}$	$-ir\sqrt{3}e_{-2}$	$\frac{3}{2}a + r\sqrt{3}e_{+2}$	$-rv_+ e_{-1}$	$-ru_- e_{-1}$
ψ_3	$2r\alpha e_{-2}$	$irv_- e_{+1}$	$-rv_+ e_{-1}$	$3(\alpha^2 - \beta^2)a - 3\sqrt{2}\alpha\beta e_{+2}$	$-2r(\alpha^2 - \beta^2)e_{+2} - 6\alpha\beta a$
ψ_4	$-2r\beta e_{-2}$	$-iru_+ e_{+1}$	$-ru_- e_{-1}$	$-2r(\alpha^2 - \beta^2)e_{+2} - 6\alpha\beta a$	$-3(\alpha^2 - \beta^2)a + 3\sqrt{2}\alpha\beta e_{+2}$

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