Spin Hamiltonian of Fe^{2+} and Co^{2+} spin in the trigonal crystal field

Masatsugu Suzuki* and Itsuko S. Suzuki
Department of Physics, State University of New York at Binghamton, Binghamton, New York 13902-6016
(Dated: January 8, 2005)

The magnetic properties of $M\mathrm{Cl}_2$[1–4] and $M_c\mathrm{Ta}_2\mathrm{S}_2\mathrm{C}$[5] with M = Fe and Co is mainly determined by magnetic behaviors of magnetic M ions in a crystal field such that the anion octahedra surrounding the M ions are trigonally elongated along the c-axis. The crystal field splitting of the d levels is usually stronger than the spin-orbit coupling, but weaker than the exchange interaction between M atoms. Here we present a simple review on the spin Hamiltonian of Fe^{2+} and Co^{2+} under the trigonal crystal field. The program of the Mathematica 5.0 is also attached to the Appendix. This note is used as supplement for Ref. 4.

PACS numbers:

I. SPIN HAMILTONIAN OF Fe^{2+} IN THE TRIGONAL CRYSTAL FIELD

The free-ion 3d^6 ^{5}D state of the Fe^{2+} is split by the cubic crystal field into the orbital doublet (E) and orbital triplet (T_2), the latter being the lowest one.[1,2] We consider the splitting of the orbital triplet by the perturbing Hamiltonian given by

$$H_0 = -\lambda' \mathbf{l}\cdot\mathbf{S} - \delta(l_z^2 - 2/3), \tag{1}$$

where $\lambda' = k\lambda$ ($k \approx 1$ but less than unity) and S is the spin angular momentum of the magnitude 2. A fictitious angular momentum l of the magnitude 1 represents the triplet state (l is antiparallel to the real orbital angular momentum L $(= -k\mathbf{l})$. Since $l_z + S_z$ is a constant of the motion, its eigenvalue m can be used to classify the various states, where $m = l'_z + S'_z$, $l_z|l'_z\rangle = l'_z|l'_z\rangle$ (l'_z = 1, 0, -1), and $S_z|S'_z\rangle = S'_z|S'_z\rangle$ (S'_z =2, 1, 0, -1, -2). Figure 1(a) shows the splitting of the ground orbital triplet by the spin-orbit coupling λ' (< 0) and the trigonal field δ (> 0), where each energy level E normalized by $|\lambda'|$ is plotted as a function of x $(= \delta/\lambda')$. The energy levels are denoted by E_3 ($m = \pm3$), $E_2^{(\pm)}$ ($m = \pm2$), $E_1^{(i)}$ (i = 1, 2, 3) ($m = \pm1$), $E_0^{(0)}$ and $E_0^{(\pm)}$ ($m = 0$). The ground level is either $E_0^{(+)}$ or $E_1^{(1)}$, depending on the sign of x. All the energy states except for $E_1^{(1)}$ and $E_0^{(+)}$ might be neglected, since these lowest levels lie 100 cm^{-1} below the others. Thus we may use a fictitious spin $s = 1$ for the lowest three states denoted by the eigenkets $|\psi_0\rangle$ for the singlet and $|\psi_{\pm1}\rangle$ for the doublet:

$$\begin{aligned} |\psi_{\pm1}\rangle &= c_1|\pm1,0\rangle + c_2|0,\pm1\rangle + c_3|\mp1,\pm2\rangle \quad (E = E_1^{(1)}), \\ |\psi_0\rangle &= a_1|1,-1\rangle + a_2|0,0\rangle + a_3|-1,1\rangle \quad (E = E_0^{(+)}). \end{aligned}$$

The parameters c_1, c_2, c_3, a_1, a_2, and a_3 are defined by

$$\begin{aligned} c_1 &= \alpha(-\sqrt{3}/(1+\xi_1)), c_2 = \alpha, c_3 = \alpha\sqrt{2}/(1-\xi_1), \\ a_1 &= a_3 = -\sqrt{3}/(6+\xi_0^2)^{1/2}, a_2 = \xi_0/(6+\xi_0^2)^{1/2}, \end{aligned}$$

where $\alpha = [3/(1+\xi_1)^2 + 1 + 2/(1-\xi_1)^2]^{-1}$, and the parameters ξ_0 and ξ_1 are related to the energy $E_1^{(1)}$ and $E_0^{(+)}$ through

$$E_1^{(1)}/\lambda' = -x/3 + 1 + \xi_1, E_0^{(+)}/\lambda' = -x/3 + 1 + \xi_0.$$

The g-factors can be evaluates as $g_c = g_c^{(0)} + \Delta g$ and $g_a = g_a^{(0)} + \Delta g$, where Δg is due to the effect of spin-orbit coupling in admixing the upper orbital levels into the ground three orbitals, and $g_c^{(0)}$ and $g_a^{(0)}$ are given by

$$\begin{aligned} g_c^{(0)} &= \langle\psi_\pm|V_z|\psi_{\pm1}\rangle = -kc_1^2 + 2c_2^2 + (k+4)c_3^2, \\ g_a^{(0)} &= \sqrt{2}\langle\psi_0|V_x|\psi_{\pm1}\rangle \\ &= -k(c_1a_2 + c_2a_3) + 2\sqrt{3}(c_1a_1 + c_2a_2) + 2\sqrt{2}c_3a_3, \end{aligned} \tag{2}$$

where $V_z = -kl_Z + 2S_z$ and $V_x = -kl_x + 2S_x$. For a given k, the two $g_c^{(0)}$ and $g_a^{(0)}$ values are functions of the single parameter x and so they bear a functional relationship to each other. In Fig. 1(b) we show the $g_c^{(0)}$ and $g_a^{(0)}$ as a function of x with k as a parameter: $g_c^{(0)} > g_a^{(0)}$ for $x < 0$ and $g_c^{(0)} < g_a^{(0)}$ for $x > 0$. Note that $x = -1.27$ for FeCl_2. If we take the z axis parallel to the c axis, and x, y axes perpendicular to it, we have $S_x = qs_x$, $S_y = qs_y$, and $S_z = ps_z$, where

$$\begin{aligned} p &= \langle\psi_{\pm1}|\pm S_z|\psi_{\pm1}\rangle = c_2^2 + 2c_3^2, \\ q &= \langle\psi_0|S_x \mp iS_y|\psi_{\pm1}\rangle\sqrt{2} \\ &= \sqrt{3}(c_1a_1 + c_2a_2) + \sqrt{2}c_3a_3. \end{aligned} \tag{3}$$

In Fig. 1(c) we show the parameters p and q as a function of x: $p < q$ for $x > 0$ and $p > q$ for $x < 0$. The resultant spin Hamiltonian for Fe^{2+} is given by

$$H = -D\sum_i (s_{iz}^2 - 2/3) - 2J\sum_{\langle i,j\rangle} \mathbf{s}_i\cdot\mathbf{s}_j - 2J_A\sum_{\langle i,j\rangle} s_{iz}s_{jz}, \tag{4}$$

where $J = q^2K$ and K is the isotropic exchange energy with the form of $-2K\mathbf{S}_i\cdot\mathbf{S}_j$ between the real spins $\mathbf{S}_i$ and $\mathbf{S}_j$, $D \approx \delta/10$ (> 0) is the single ion anisotropy, and J_A $(= J(p^2 - q^2)/q^2)$ (see Fig. 1(d)) is the anisotropic exchange interaction. The second term is the isotropic exchange interaction, and third term is the anisotropic exchange interaction. The spin anisotropy parameter D_{eff}

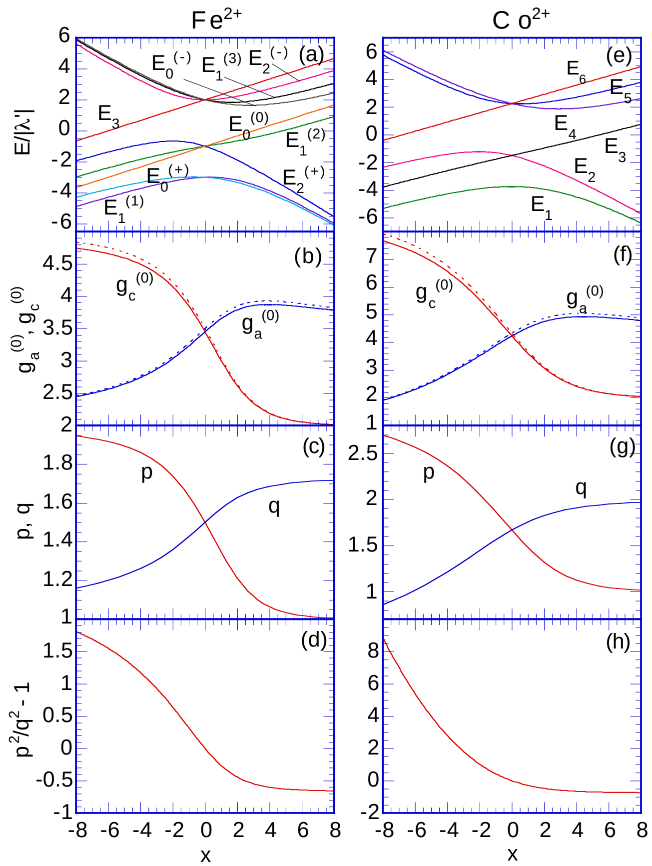

FIG. 1: Derivation from Fe^{2+} spin Hamiltonian: (a) the energy levels, (b) g-factors $g_c^{(0)}$ and $g_a^{(0)}$ with k (= 0.9 and 1), (c) spin anisotropy parameters p, q and (d) $p^2/q^2 - 1$, as a function of x $(= \delta/\lambda')$. $x = -1.27$ for $Fe_{0.33}Ta_2S_2C$. Derivation from Co^{2+} spin Hamiltonian: (e) the energy levels, (f) g-factors $g_c^{(0)}$ and $g_a^{(0)}$ with k (= 0.9 and 1), (g) spin anisotropy parameters p, q and (h) $p^2/q^2 - 1$, as a function of x $(= \delta/\lambda')$. $x = 1.68$ for $Co_{0.33}Ta_2S_2C$ (from Ref. 5).

is defined as D_{eff} $(= D(s - 1/2) + 2zsJ_A)$ is negative. The XY symmetry appears when $D_{eff} < 0$.

II. SPIN HAMILTONIAN OF Co^{2+} IN THE TRIGONAL CRYSTAL FIELD

In a cubic crystal field the free-ion $3d^7$ ^4F state is split into two orbital triplets and one orbital singlet with a triplet the lowest.[1,3,4] We consider the splitting of the ground state orbital triplet $^4T_1$ into six Kramers doublets. The perturbing Hamiltonian consists of the spin-orbit coupling and trigonal distortion of the crystal field,

$$H_0 = -(3/2)k\lambda \mathbf{l}\cdot\mathbf{S} - \delta(l_z^2 - 2/3), \tag{5}$$

where $\lambda' = k\lambda$, λ is the spin-orbit coupling constant and may be different from its free-ion value of -180 cm^{-1}, and k is the orbital reduction factor due to admixture of ^4P into $^4T_1$ and is less than but of order unity, δ is the trigonal field strength, and S is the spin angular momentum of the magnitude 3/2. A fictitious angular momentum l of the magnitude 1 represents the triplet state (l is antiparallel to the real orbital angular momentum $\mathbf{L} = -3k\mathbf{l}/2$). Since $l_z + S_z$ is a constant of the motion, its eigenvalue m can be used to classify the various states, where $m = l'_z + S'_z$, $l_z|l'_z\rangle = l'_z|l'_z\rangle$ (l'_z = 1, 0, -1), and $S_z|S'_z\rangle = S'_z|S'_z\rangle$ (S'_z = 3/2, 1/2, -1/2, -3/2). In Fig. 1(e) we show the energy level E of the six Kramers doublets normalized by $|\lambda'|$, as a function of x $(= \delta/\lambda')$: one E_s $(m = \pm 5/2)$, $E_q^{(\pm)}$ $(m = \pm 3/2)$, and $E_c^{(0)}$, $E_c^{(1)}$, and $E_c^{(2)}$ $(m = \pm 1/2)$. For all values of x, $E_c^{(0)}$ is the lowest energy. The wave functions $|\psi_{\pm 1}\rangle$, $|\psi_{\pm 3}\rangle$, and $|\psi_{\pm 4}\rangle$ for $m = \pm 1/2$ are given by

$$\begin{aligned}
|\psi_{\pm 1}\rangle &= c_1|\mp 1, \pm 3/2\rangle + c_2|0, \pm 1/2\rangle \\
&\quad + c_3|\pm 1, \mp 1/2\rangle \ \ (E_{\pm 1} = E_c^{(0)}), \\
|\psi_{\pm 3}\rangle &= c_4|\mp 1, \pm 3/2\rangle + c_5|0, \pm 1/2\rangle \\
&\quad + c_6|\pm 1, \mp 1/2\rangle \ \ (E_{\pm 3} = E_c^{(1)}), \\
|\psi_{\pm 4}\rangle &= c_7|\mp 1, \pm 3/2\rangle + c_8|0, \pm 1/2\rangle \\
&\quad + c_9|\pm 1, \mp 1/2\rangle \ \ (E_{\pm 4} = E_c^{(2)}),
\end{aligned}$$

where the parameters c_i (i = 1 - 9) are defined by

$$\begin{aligned}
c_1 &= \beta_0\sqrt{6}/\zeta_0, c_2 = -\beta_0, c_3 = \beta_0\sqrt{8}/(\zeta_0 + 2)), \\
c_4 &= \beta_1\sqrt{6}/\zeta_1, c_5 = -\beta_1, c_6 = \beta_1\sqrt{8}/(\zeta_1 + 2)), \\
c_7 &= \beta_2\sqrt{6}/\zeta_2, c_8 = -\beta_2, c_9 = \beta_2\sqrt{8}/(\zeta_2 + 2)),
\end{aligned}$$

with $\beta_j = [6/\zeta_j^2 + 1 + 8/(\zeta_j + 2)^2]^{1/2}$ (j = 0, 1, 2) The parameter ζ_j (j = 0, 1, 2) is related to $E_c^{(j)}/\lambda'$ as

$$E_c^{(j)}/\lambda' = -x/3 + 3(\zeta_j + 3)/4,$$

and

$$x = \delta/\lambda' = 3(\zeta_j + 3)/4 - 9/(2\zeta_j) - 6/(\zeta_j + 2).$$

The wave functions $|\psi_{\pm 2}\rangle$ and $|\psi_{\pm 5}\rangle$ for $m = \pm 3/2$ are given by

$$\begin{aligned}
|\psi_{\pm 2}\rangle &= d_1|0, \pm 3/2\rangle + d_2|\pm 1, \pm 1/2\rangle \ \ (E_{\pm 2} = E_q^{(+)}), \\
|\psi_{\pm 5}\rangle &= d_3|0, \pm 3/2\rangle + d_4|\pm 1, \pm 1/2\rangle \ \ (E_{\pm 5} = E_q^{(-)}),
\end{aligned}$$

where the parameter d_i (i = 1- 4) is defined by

$$\begin{aligned}
d_1 &= \gamma^{(+)}9/(2\sqrt{6}), d_2 = \gamma^{(+)}(2x/3 + E_q^{(+)}/\lambda'), \\
d_3 &= \gamma^{(-)}9/(2\sqrt{6}), d_4 = \gamma^{(-)}(2x/3 + E_q^{(-)}/\lambda'),
\end{aligned}$$

with $\gamma^{(\pm)} = [(9/(2\sqrt{6}))^2 + (2x/3 + E_q^{(\pm)}/\lambda')^2]^{1/2}$. Since there are only two states in this lowest Kramers doublet, the true spin S $(= 3/2)$ can be replaced by a fictitious spin s within the ground state. The g-factors can be evaluates as $g_c = g_c^{(0)} + \Delta g$ and $g_a = g_a^{(0)} + \Delta g$, where Δg is due to the effect of spin-orbit coupling in admixing the upper orbital levels into the ground orbital triplet. The values of $g_c^{(0)}$ and $g_a^{(0)}$, are given by

$$\begin{aligned} g_c^{(0)} &= 2\langle\psi_{\pm1}|V_z|\psi_{\pm1}\rangle = (3k+6)c_1^2 + c_2^2 - (3k+2)c_3^2, \\ g_a^{(0)} &= 2\langle\psi_{\pm1}|V_x|\psi_{\mp1}\rangle = 4\sqrt{3}c_1c_3 + 4c_2^2 - (3\sqrt{2}k)c_2c_3, \end{aligned} \tag{6}$$

with $V_z = -(3k/2)l_Z + 2S_z$ and $V_x = -(3k/2)l_x + 2S_x$. In Fig. 1(f) we show the values of $g_a^{(0)}$ vs $g_c^{(0)}$ with k as a parameter (k = 0.9, 0.95, and 1.0): $g_c^{(0)} \rangle g_a^{(0)}$ for $x < 0$ and $g_c^{(0)} < g_a^{(0)}$ for $x > 0$.

If we take the z axis parallel to the c axis, and x, y axes perpendicular to it, we have $S_x = qs_x$, $S_y = qs_y$, and $S_z = ps_z$;

$$\begin{aligned} p &= 2\langle\psi_{\pm1}|\pm S_z|\psi_{\pm}\rangle = 3c_1^2 + c_2^2 - c_3^2, \\ q &= \langle\psi_{\pm1}|S_x \pm iS_y|\psi_{\mp1}\rangle = 2c_2^2 + 2\sqrt{3}c_1c_3. \end{aligned} \tag{7}$$

In Fig. 1(g) we show the parameters p and q as a function of x: $p < q$ for x >0 and $p > q$ for $x < 0$. The spin Hamiltonian of Co^{2+} may be written as

$$H = -2J\sum_{\langle i,j\rangle} \mathbf{s}_i\cdot\mathbf{s}_j - 2J_A\sum_{\langle i,j\rangle} s_{iz}s_{jz}, \tag{8}$$

where $J_i = q^2K$ and K is the isotropic exchange energy with the form of $-2K\mathbf{S}_i\cdot\mathbf{S}_j$ between the real spins $\mathbf{S}_i$ and $\mathbf{S}_j$, and $J_A = (p^2 - q^2)/q^2J$ is the anisotropic exchange interaction. The first term of the spin Hamiltonian is an Heisenberg-type exchange interaction and the second term is anisotropic exchange interaction. Since $s = 1/2$, there is no single ion anisotropy. The ratio J_A/J (= $(p^2-q^2)/q^2$) (see Fig. 1(h)) provides a measure for the spin symmetry of the system.

III. VAN VLECK SUSCEPTIBILITY OF Co^{2+}

Acording to Lines,[3] the Van Vleck susceptibility for Co^{2+} is expressed as

$$\chi_V^c = \frac{2N_A\mu_B^2}{2s+1}\frac{|\langle\psi_{+1}|V_z|\psi_{+3}\rangle|^2}{E_{+3}-E_{+1}} + \frac{|\langle\psi_{+1}|V_z|\psi_{+4}\rangle|^2}{E_{+4}-E_{+1}}, \tag{9}$$

$$\begin{aligned} \chi_V^a &= \frac{2N_A\mu_B^2}{2s+1}\frac{|\langle\psi_{+1}|V_x|\psi_{+2}\rangle|^2}{E_{+2}-E_{+1}} + \frac{|\langle\psi_{+1}|V_x|\psi_{-3}\rangle|^2}{E_{-3}-E_{+1}} \\ &+ \frac{|\langle\psi_{+1}|V_x|\psi_{-4}\rangle|^2}{E_{-4}-E_{+1}} + \frac{|\langle\psi_{+1}|V_x|\psi_{5}\rangle|^2}{E_{+5}-E_{+1}}, \end{aligned} \tag{10}$$

with $s = 1/2$, where the matrix elements are given by

$$\begin{aligned} \langle\psi_{+1}|V_z|\psi_{+3}\rangle &= (3k/2+3)c_1c_4 + c_2c_5 - (3k/2+1)c_3c_6, \\ \langle\psi_{+1}|V_z|\psi_{+4}\rangle &= (3k/2+3)c_1c_7 + c_2c_8 - (3k/2+1)c_3c_9, \\ \langle\psi_{-1}|V_x|\psi_{-2}\rangle &= -(3\sqrt{2}k/4)(d_1c_1 + d_2c_2) \\ &+\sqrt{3}c_2d_1 + 2c_3d_2, \end{aligned}$$

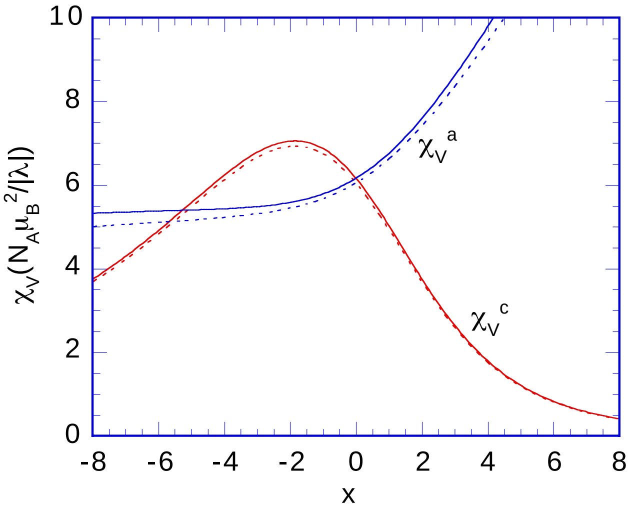

FIG. 2: Plot of Van Vleck susceptibility χ_V^c and χ_V^a as a function of x, where k (= 0.9 and 1.0) is changed.

$$\begin{aligned} \langle\psi_{-1}|V_x|\psi_{+3}\rangle &= \sqrt{3}c_3c_4 + 2c_2c_5 + \sqrt{3}c_1c_6 \\ &-(3\sqrt{2}k/4)(c_3c_5 + c_2c_6), \\ \langle\psi_{-1}|V_x|\psi_{+4}\rangle &= \sqrt{3}c_3c_7 + 2c_2c_8 + \sqrt{3}c_1c_9 \\ &-(3\sqrt{2}k/4)(c_3c_8 + c_2c_9), \\ \langle\psi_{-1}|V_x|\psi_{-5}\rangle &= 2c_3d_4 + \sqrt{3}c_2d_3 \\ &-(3\sqrt{2}k/4)(c_1d_3 + c_2d_4), \end{aligned}$$

and

$$|\langle\psi_{-i}|V_x|\psi_{-j}\rangle| = |\langle\psi_j|V_x|\psi_i\rangle| = |\langle\psi_i|V_x|\psi_j\rangle|.$$

In Fig. 2 we show the plot of $\chi_V^c/N_A\mu_B^2/|\lambda|$ and $\chi_V^a/N_A\mu_B^2/|\lambda|$ as a function of x with k as a parameter (k = 0.9, 0.95, 1.0). For $x = 1.68$ and $k = 0.9$ for Co^{2+} spin for $CoCl_2$, the Van Vleck susceptibility can be calculated as $\chi_V^c = 4.19\ N_A\mu_B^2/(|\lambda|)$ and $\chi_V^a = 7.29\ N_A\mu_B^2/(|\lambda|)$: $\chi_V^c = 6.1\times10^{-3}$ (emu/Co mole) and $\chi_V^a = 10.6\times10^{-3}$ (emu/Co mole) when $\lambda = -180$ cm^{-1} = -259 K.

APPENDIX: MATHEMATICA 5.0 PROGRAMS

Program-1
Spin Hamiltonian for Fe^{2+} spins in the trigonal field
Program-2
Spin Hamiltonian for Co^{2+} spins in the trigonal field

* suzuki@binghamton.edu

[1] J. Kanamori, Prog. Theor. Phys. **20**, 890 (1958).

[2] K. Inomata and T. Oguchi, J. Phys. Soc. Jpn. **23**, 765 (1967).
[3] M.E. Lines, Phys. Rev. **131**, 546 (1963).
[4] T. Oguchi, J. Phys. Soc. Jpn. **20**, 2236 (1965).
[5] M. Suzuki, I.S. Suzuki, to be appeared in Phys. Rev. B. (2005): arXiv.org, cond-mat/0402501.