Development of MagSaki Software for Magnetic Analysis of Dinuclear High-spin Cobalt(II) Complexes in an Axially Distorted Octahedral Field

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MagSaki software was developed for the magnetic analysis of dinuclear high-spin cobalt(II) complexes. This software performs magnetic analysis to determine magnetic parameters using several types of theoretical calculations, such as the following: (1) a mononuclear complex in an isotropic octahedral field, (2) a mononuclear complex in an axially distorted octahedral field, (3) a dinuclear complex in an isotropic octahedral field, (4) a dinuclear complex in an axially distorted octahedral field and (5) a mono- and dinuclear complex in an isotropic tetrahedral field. The calculation for the axially distorted dinuclear case is based specifically on a new theoretical method that we reported, and the MagSaki software is the first of its kind that evaluates the exchange couping in an axially distorted octahedral field.

Keywords: Magnetism, High-spin cobalt(II), Axial symmetry, Exchange Coupling, MagSaki

1 Introduction

Magnetism of transition metal complexes is important to coordination chemistry since magnetic behavior is strongly influenced by coordination geometry and the electronic configuration of metal ions. In general, it is not difficult to analyze the magnetic behavior for most of the first-transition elements because the orbital angular momentum is negligible and only spin angular momentum should be considered. However, in the case of high-spin cobalt(II) complexes, orbital angular momentum cannot be neglected, and spin-orbit coupling should be taken into account [1]. Thus, the magnetic equations for the cobalt(II) complexes are highly complex, while the equations for other first-transition elements are rather simple.

In 1963, Lines introduced a method for the calculation of the magnetic analysis of a high-spin cobalt(II) complex in an axially distorted octahedral field [2], considering the axial-field splitting Δ and the spin-orbit coupling λ. In the 1960s, Figgis also introduced a method considering the axial field [3–6], showing that the axial-field treatment is useful for analyzing the cryomagnetic data of mononuclear cobalt(II) complexes. This successful study corresponded to a mononuclear case, but,

in 1971, Lines reported a theory for the analysis of the magnetic exchange coupling between two high-spin cobalt(II) ions of pure O_h symmetry using a temperature-dependent Hamiltonian [7]. This remarkable theory enabled the analysis of the magnetic data of some dinuclear cobalt(II) complexes [8], but it was limited to only highly symmetrical cases.

Very recently, a new set of magnetic equations was introduced for dinuclear cobalt(II) complexes in an axially distorted octahedral field, and the cryomagnetic data of two dicobalt(II) complexes were successfully analyzed [9]. In this method, the axial splitting parameter Δ is adopted according to Figgis and Lines, avoiding over-parameterization to describe the axial distortion. The axial-splitting parameter Δ is defined as the splitting of the orbital degeneracy of the ground term by the asymmetric ligand component in the absence of any spin-orbit coupling and is taken to be positive when the orbital singlet is lowest. This permits the data to be analyzed with the use of only four variables, the axial-splitting parameter Δ, the spin-orbit coupling λ, the orbital reduction factor κ, and the exchange coupling parameter *J*. The axial zero-field splitting parameter *D* and the anisotropic *g*-factors, g_z and g_x, can be calculated using the four variables. To the best of my knowledge, this is the first standard analytic method for the magnetism of dinuclear high-spin cobalt(II) complexes in the lower symmetry, except for the specific low-temperature study [10]. In addition, the MagSaki software is the first of its kind designed to evaluate exchange coupling in an axially distorted octahedral field.

2 Theory

Magnetic susceptibility χ_A is calculated by the van Vleck formula (Equations 1 and 2).

$$\chi_A = \frac{\chi_z + 2\chi_x}{3} \tag{1}$$

$$\chi_{z(x)} = N \frac{\sum_n \left(\frac{\left(E_{z(x),n}^{(1)}\right)^2}{kT} - 2E_{z(x),n}^{(2)} \right) \exp\left[\frac{-E_n^{(0)}}{kT}\right]}{\sum_n \exp\left[\frac{-E_n^{(0)}}{kT}\right]} \tag{2}$$

where $E_n^{(0)}$ is the energy of level *n* in zero field. $E_n^{(1)}$ and $E_n^{(2)}$ are called first- and second-order Zeemann coefficients, respectively. To apply this formula it is necessary to calculate the Zeemann coefficients $E_n^{(0)}$, $E_n^{(1)}$ and $E_n^{(2)}$, which can be obtained by solving the secular determinant. The coefficients obtained for the axially distorted octahedral fields have been reported in our previous paper [9]. The effective magnetic moment μ_{eff} is calculated by Equation 3.

$$\mu_{\text{eff}} = \sqrt{\frac{3kT\chi_A}{N\beta^2}} \tag{3}$$

where the symbols have their usual meanings.

3 Main Functions

MagSaki calculates the magnetic susceptibility and effective magnetic moment for the following cases; (1) mononuclear cobalt(II) complex in an isotropic octahedral field, (2) mononuclear cobalt(II)

complex in an axially distorted octahedral field, (3) dinuclear cobalt(II) complex in an isotropic octa-hedral field, (4) dinuclear cobalt(II) complex in an axially distorted octahedral field, and (5) mono- and dinuclear cobalt(II) complex in an isotropic tetrahedral field. MagSaki draws a graph of the resulting data vs. temperature and also obtains the best-fitting magnetic parameters using some optimization programs. The observed magnetic data and parameters can be stored as a file.

4 General Operations

4.1 Running MagSaki

Double clicking on the MagSaki icon from the Macintosh finder can start the program. MagSaki then displays a main window (Figure 1). Double clicking on a file owned or created by the application may also start MagSaki. Only one file may be opened if more than one file is selected.
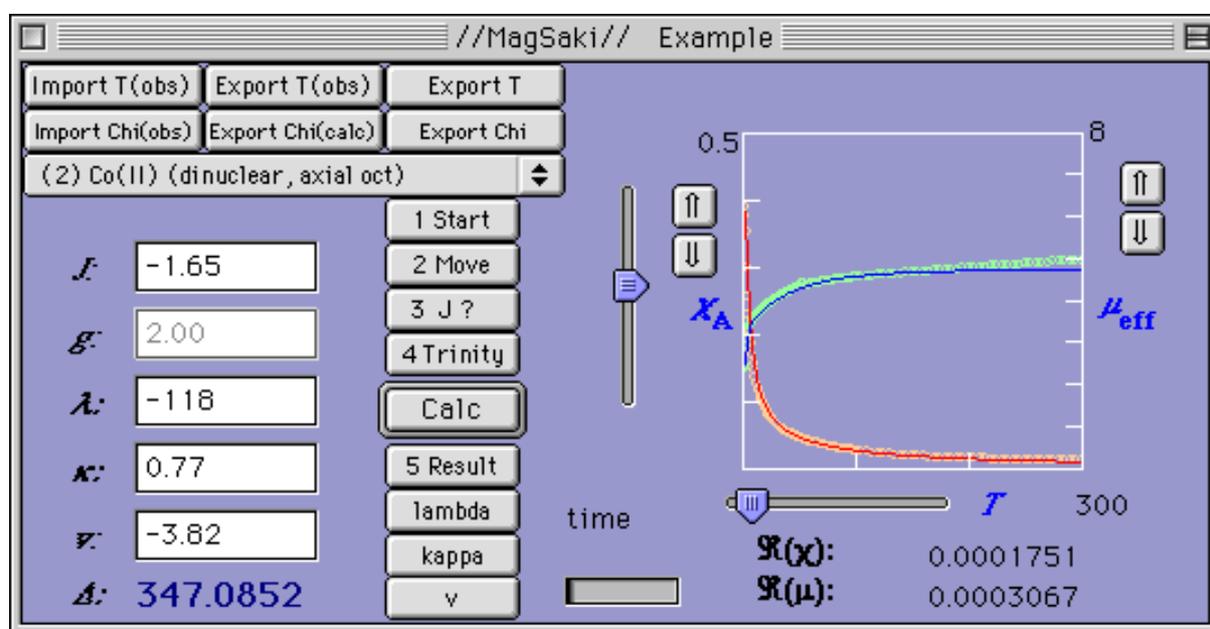
Figure 1. Main window of MagSaki.

4.2 The MagSaki's Window

MagSaki displays the main window including the control buttons, parameter-input fields, and cryo-magnetic graph canvas. When the window is closed, MagSaki quits.

4.3 Import/Export Buttons and Pop-Up Menu

At the top of the main window, there are some buttons and a pop-up menu. The buttons are used to import or export data such as temperature, magnetic susceptibility, and effective magnetic moment. The pop-up menu is used to select the calculation modes.

4.4 Parameter Input Fields

To the left of the main window are several input fields. Magnetic parameters typed in the fields are used in the calculation. Resulting parameters obtained by using the optimization program also appear in the fields.

4.5 Buttons for Magnetic Calculations

Next to the parameter input fields are some buttons that are used to execute each calculation program. The 'Calc' button starts the magnetic calculation using the input parameters and draws two theoretical curves, magnetic susceptibility and effective magnetic moment, in a graphics area. Other buttons are used to start each optimization program to analyze the observed cryomagnetic data.

4.6 Cryomagnetic Graph

The right part of the main window is the cryomagnetic graphic area. Around the cryomagnetic graph are some small buttons and sliders that are used to expand or reduce the scale of the horizontal and vertical axes. The observed magnetic susceptibility [χ_A(obs)] and effective magnetic moment [μ_{eff}(obs)] data are plotted using orange and green circles, respectively. Theoretical curves for χ_A(obs) and μ_{eff}(obs) are shown in red and in blue, respectively. R values defined as $R(\chi_A) = \Sigma[\chi_A$(obs) - χ_A(calc)$]^2/\Sigma\chi_A$(obs)^2 and $R(\mu_{eff}) = \Sigma[\mu_{eff}$(obs) - μ_{eff}(calc)$]^2/\Sigma\mu_{eff}$(obs)^2 are shown under the graph.

5 Magnetic Parameters

The magnetic parameters used in the calclations are listed below.

Table 1. Magnetic parameters used in MagSaki version 1.0, 2001.

Symbol	Meaning
D	Axial zero-field splitting parameter
g	g-factor
J	Exchange coupling parameter
T	Temperature
TIP	Temperature-independent paramagnetism
v	$v = \Delta/(\kappa\,\lambda)$*
Δ	Axial splitting parameter
κ	Orbital reduction factor containing the admixture
λ	Spin-orbit coupling parameter
μ_{eff}	Effective magnetic moment per atom
χ_A	Atomic magnetic susceptibility

* Sometimes v is defined as $v = \Delta/|\lambda|$; however, for this study, it is defined as $v = \Delta/(\kappa\,\lambda)$.

6   Magnetic Analysis

6.1   Isotropic octahedral case

First, a calculation mode "(1) Co(II) (mononuclear, axial oct)" should be selected from the pop-up menu to optimize two parameters, λ and κ, fixing v to 0. However, this treatment is not recommended since v cannot usually be fixed to 0. Optimization of λ and κ can be made automatically by clicking each minimization button. The default minimization function is $\Sigma[\chi_A(\text{obs})/\chi_A(\text{calc}) - 1]^2$.

6.2   Axially distorted octahedral case

A calculation mode "(1) Co(II) (mononuclear, axial oct)" should be selected from the pop-up menu to optimize three parameters λ, κ, and v. Simultaneous optimization can be achieved by first clicking the "1 Start" button to launch the program. The program finds the best parameter set of λ, κ, and v among the default 245 parameter sets of the three parameters. The "Move" program can roughly optimize the obtained parameter set by clicking the "2 Move" button. Final optimization can be made with the "Trinity" program by clicking the "3 Trinity" button. The default minimization function is $\Sigma[\chi_A(\text{obs})/\chi_A(\text{calc}) - 1]^2$.

6.3   Dinuclear complex in a pure octahedral field

A calculation mode "(3) Co(II) (dinuclear, isotropic oct)" should be selected from the pop-up menu to optimize λ, κ, and J. The parameters λ and κ should be determined first using only high-temperature data that are not affected by J, and then J can be obtained using whole-temperature data. This calculation is based on the so-called "Lines theory" [7].

6.4   Dinuclear complex in an axially distorted octahedral field

A calculation mode "(2) Co(II) (dinuclear, axial oct)" should be selected from the pop-up menu to optimize λ, κ, v, and J. The parameters λ, κ, and v should be determined first by using only high-temperature data that are not affected by J. Optimization of the three parameters can be accomplished similarly to the method described in 5.2 for an axially distorted octahedral case. J can be obtained using whole-temperature data. This calculation can be made using the theory we reported [9].

6.5   Isotropic tetrahedral case

In the case of tetrahedral geometry, the Heisenberg model can be used [11]. A calculation mode "(4) Co(II) (dinuclear, 3/2 - 3/2)" should be selected from the pop-up menu to determine J and g. Temperature-independent paramagnetism (TIP) can be taken into account. When the ground state is ^4A or ^4E, this mode can be used even if the coordination geometry is not tetrahedral.

7   Requirements

The program was developed using Realbasic [12] on a Power Macintosh 7300/180 (Inertia, OS: J1-7.5.5). The Program will run on any Macintosh PPC with System 7 or higher. A windows version

is now under development, however, at this time, the full functions are possible only on a Macintosh PPC.

8 Distribution

Information about distribution of the current MagSaki program is available on the Sakiyama Laboratory Home Page (http://www-sci.yamagata-u.ac.jp/~saki/).

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