

Evaluating the Curie-Weiss Temperature of a Magnetic System Composed of Nonequivalent Magnetic Ions in Terms of Spin Exchange Constants

Kee Hag Lee,^{†,*} Ji Young Lee,[†] Changhoon Lee,^{‡,a} and Myung-Hwan Whangbo^{‡,*}

[†]Department of Chemistry and Nanoscale Science and Technology Institute, Wonkwang University, Iksan 570-749, Korea
*E-mail: khlee@wonkwang.ac.kr

[‡]Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204
*E-mail: mike_whangbo@ncsu.edu

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Magnetic properties of a system containing magnetic ions are related to its electronic structure,¹⁻⁴ and are commonly probed by measuring the temperature-dependence of its magnetic susceptibility $\chi(T)$ at a given magnetic field, the field-dependence of its magnetization $M(H)$ at a very low temperature, or the magnetic specific heat as a function of temperature. When fitted with a Curie-Weiss law, the paramagnetic region of the $\chi(T)$ vs. T plot leads to the Curie-Weiss temperature θ and the effective magnetic moment μ_{eff} .

For a magnetic system consisting of equivalent magnetic ions, the mean field theory (MFT)²⁻⁴ provides a simple relationship between the θ to spin exchange constants J_s . Surprisingly, however, no such MFT relationship has been available for a magnetic system made up of nonequivalent magnetic ions. Consequently, it is worthwhile to have a MFT relationship between θ and J_s that is valid for a magnetic system composed of nonequivalent magnetic ions.

In this Communication we derive such a MFT relationship and test its validity by evaluating the θ values of the magnetic orthosilicate Fe_2SiO_4 ,⁵⁻⁷ whose magnetic structures were previously investigated in terms of their calculated spin exchange constants.⁷

Under a weak probing magnetic field \mathbf{H} , the magnetic susceptibility, χ , of a magnetic system is given by $\chi = \mathbf{M}/\mathbf{H}$, where \mathbf{M} is the magnetization of the system induced by \mathbf{H} . According to the MFT, the effective magnetic field acting on a given magnetic ion is given by the sum of the applied magnetic field \mathbf{H} and the additional magnetic field arising from its interactions with the surrounding magnetic ions. To derive a relationship between the Curie-Weiss temperature and spin exchange constants for a general magnetic system, we first follow the MFT description of Smart³ by dividing the magnetic lattice into sublattices such that a magnetic ion does not interact with any neighbor within its own sublattice. Given the number of sublattices needed to achieve this condition as n , we label the sublattices by numerical subscripts. Then, the effective magnetic field \mathbf{H}_i acting in the sublattice i is written as

$$\mathbf{H}_i = \mathbf{H} + \sum_{j=1}^n \gamma_{ij} \mathbf{M}_j \quad (i \neq j), \quad (1)$$

where \mathbf{M}_j is the magnetization of the j^{th} sublattice and γ_{ij} is the mean field coefficient for the field exerted on an ion in the i^{th} sublattice by its neighbor on the j^{th} sublattice. Here $\gamma_{ij} = 0$ due to our choice of the sublattices. For $i \neq j$

$$\gamma_{ij} = \frac{nz_{ij}J_{ij}}{Ng^2\beta^2} = \frac{nz_{ij}J_{ij}}{D}, \quad (2)$$

where $D = Ng^2\beta^2$, g is the electron g factor, β is the Bohr magneton, N is Avogadro's number, z_{ij} is the number of j neighbors of the i^{th} atom, and J_{ij} is the exchange constant between the i^{th} atom and its j^{th} neighbor. The vector notations for \mathbf{M}_i and \mathbf{H} can be dropped because the n sublattices are magnetized in the direction of \mathbf{H} in the high temperature region where the material is paramagnetic. Then,

$$M_i = \frac{C}{nT} H_i = \frac{C}{nT} (H + \sum_{j=1}^n \gamma_{ij} M_j) \quad (3)$$

where $i = 1, 2, \dots, n$, and C is the Curie constant, $C = DS(S+1)/3k$. By combining Eqs. (3) with the total magnetization $M = \sum_{i=1}^n M_i$ with $\gamma_{ij} = \gamma_{ji}$ and $\gamma_{ii} = 0$ we have

$$M_1 \left(1 - \frac{C}{nT} \sum_{j=1}^n \gamma_{1j} \right) + M_2 \left(1 - \frac{C}{nT} \sum_{j=1}^n \gamma_{2j} \right) + \dots \\ + M_n \left(1 - \frac{C}{nT} \sum_{j=1}^n \gamma_{nj} \right) = \frac{CH}{T} \quad (4)$$

In systems consisting of chemically identical magnetic ions of spin S , not all these ions may be equivalent due to the difference in their site symmetry. Even for such cases, however, the moments of the nonequivalent magnetic ions are practically identical. For example, the neutron diffraction study of Fe_2SiO_4 at 10 K by Lottermoser *et al.* showed⁵ that the Fe(1) (site symmetry i) and Fe(2) (site symmetry m) sites have the moments 4.41 and 4.40 μ_B , respectively, which consists of two kinds of Fe^{2+} ($S = 2$) ions (Fig. 1).⁸

Therefore, if each spin site is a spin sublattice, it is reasonable to assume that the magnetization in each sublattice is practically equal to the average, M_{av} , of all the moments. Thus, we impose the condition that each spin sublattice

^aPresent address: Department of Chemistry, POSTEC, Pohang, Korea

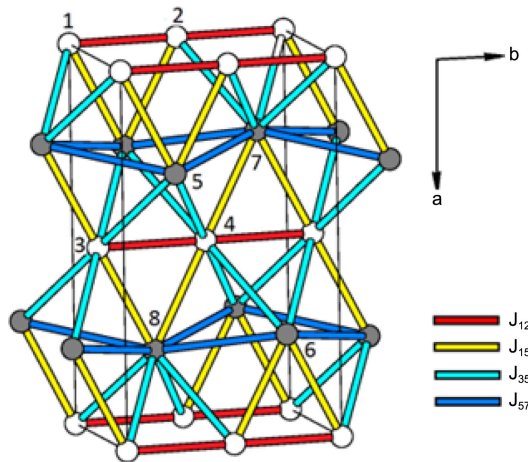


Figure 1. Arrangements of the two kinds of the high-spin Fe^{2+} ($S = 2$) ions in Fe_2SiO_4 : $\text{Fe}(1)$ = unshaded circles, and $\text{Fe}(2)$ = shaded circles. The numbers 1-8 represent the eight Fe atoms that are present in a chemical unit cell. The different spin exchange paths are color-coded (see ref. 7).

contains only one spin site. Then $M_1 = M_2 \dots = M_n = M_{n'}$, and Eq. (4) leads to

$$\frac{M}{H} = \frac{C}{T - \frac{C}{n^2} \sum_{i=1}^n \sum_{j=1}^n \gamma_{ij}} \quad (5)$$

where $M = nM_{n'}$. By comparing Eq. (5) with the Curie-Weiss law, $\chi = M/H = C/(T - \theta)$, the Curie-Weiss temperature θ is written as

$$\theta = \frac{C}{n^2} \sum_{i=1}^n \sum_{j=1}^n \gamma_{ij} \quad (i \neq j) \quad (6)$$

In cases when every magnetic ion has the same number and the same kinds of interactions, the above expression reduces to the usual form found in the literature. Namely,

$$\theta = \frac{C}{n} \sum_{j=1(j \neq i)}^n \gamma_{ij} = \frac{S(S+1)}{3k} \sum_{j=1(j \neq i)}^n z_{ij} J_{ij} \quad (7)$$

In what follows, we use Eq. (6) to calculate the Curie-Weiss temperatures of Fe_2SiO_4 as a representative example consisting of nonequivalent magnetic ions. As depicted in Figure 1, Fe_2SiO_4 has two kinds of high-spin Fe^{2+} ($S = 2$) ions in a unit cell, namely, the ions 1-4 (unshaded circles) and 5-8 (shaded circles).⁷

By treating each ion as a spin sublattice, we have eight sublattices. In general, $\gamma_{ij} = \gamma_{ji}$. Further, it is deduced from the connectivity between these ions (Fig. 1) that $\gamma_{12} = \gamma_{34}$, $\gamma_{57} = \gamma_{68}$,

$$\begin{aligned} \gamma_{15} &= \gamma_{25} = \gamma_{16} = \gamma_{26} = \gamma_{37} = \gamma_{47} = \gamma_{38} = \gamma_{48}, \\ \gamma_{17} &= \gamma_{18} = \gamma_{27} = \gamma_{28} = \gamma_{35} = \gamma_{45} = \gamma_{36} = \gamma_{46}, \text{ and} \\ \gamma_{13} &= \gamma_{14} = \gamma_{23} = \gamma_{24} = \gamma_{56} = \gamma_{58} = \gamma_{67} = \gamma_{78} = 0. \end{aligned}$$

Thus, the θ of Fe_2SiO_4 is given by

Table 1. Calculated spin exchange constants (in meV) and Curie-Weiss temperature (in K) of Fe_2SiO_4 on $U_{\text{eff}} (= 3.6 \text{ eV})$ from the DFT+U calculation

J_{12}	J_{15}	J_{35}	J_{57}	θ_{cal}
-0.79	0.05	-0.67	-1.13	-130

$$\theta = \frac{C}{8^2} (4\gamma_{12} + 16\gamma_{15} + 16\gamma_{35} + 4\gamma_{57}). \quad (8a)$$

It can be deduced from Figure 1 and Eq. (2) that $\gamma_{12} = 2J_{12}(8/D)$, $\gamma_{57} = 4J_{57}(8/D)$, $\gamma_{15} = J_{15}(8/D)$, and $\gamma_{35} = 2J_{35}(8/D)$. Therefore,

$$\theta = \frac{S(S+1)}{3k} (J_{12} + 2J_{15} + 4J_{35} + 2J_{57}) \quad (8b)$$

Table 1 represents the calculated spin exchange constants (in meV) and Curie-Weiss temperature θ_{cal} (in K) of Fe_2SiO_4 on the value of $U_{\text{eff}} (= 3.6 \text{ eV})$ from our calculation using the DFT+U method of Dudarev *et al.*⁹ The experimental Curie-Weiss temperature θ_{exp} was first reported to be -150 K ,¹⁰ and -126 K ¹¹ later. Thus Table 1 shows that the Curie-Weiss temperature is well represented by our equation of 8b for Fe_2SiO_4 .

In summary, for a system containing magnetic ions under nonequivalent local crystal field environments, we derived the relationship between the Curie-Weiss temperature and spin exchange constants. We employed the MFT for spin sublattices in which each spin sublattice has one spin site and there is no interaction between identical spin sublattices and introduced the approximation that each spin site leads to an identical moment.

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