

Magnetic Susceptibility of Anisotropically Interacting Spin-pair Systems

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Received September 20, 1993

The Oguchi theory of antiferromagnetism has been modified for antiferromagnetically interacting spin-pair systems with anisotropic exchange interaction. The parallel and perpendicular susceptibilities (χ_{\parallel} and χ_{\perp}) have been expressed as functions of exchange interactions (J_{\parallel} and $\gamma=J_{\perp}/J_{\parallel}$), anisotropic molecular field parameters (κ and κ_{\perp}), g_{\parallel} and g_{\perp} . In contrast to the previous theories, the parallel susceptibilities are not the same as the perpendicular susceptibilities above Neel temperature T_N .

Introduction

Historically, Pierre Weiss introduced the mean field theory that consists in considering only one magnetic atom and replacing its interaction with the remainder of the crystal by an effective field. In 1955, Oguchi developed a theory of ferromagnetism and antiferromagnetism, based on the Heisenberg model of two spin clusters instead of one magnetic atom¹. The Oguchi theory was extended by Ohya-Nishiguchi in 1979, considering inter-pair exchange interactions². Recently, these models have been applied to the susceptibilities of an antiferromagnetic electride, $\text{Cs}^+(15\text{C5})_2\text{e}^{-3}$. Electrides are a new class of ionic compounds, in which anions are trapped electrons. In these models, the interaction between two spins coupled with each other is isotropic, while only z -component has been considered in the Ising model and x - and y - components in the xy model. In this paper, the intermediate case between these two extremes will be presented.

Theory

We take a pair of spins i and j interacting antiferromagnetically with each other, with $J_{\parallel} \neq J_{\perp} = J_{\perp}$. The spin-pair interacts anisotropically with neighbors, with exchange interactions, J'_{\parallel} and J'_{\perp} . The spin Hamiltonian for the magnetic field along the z -axis then becomes

$$\begin{aligned} H &= -2J_{\parallel}[\gamma(S_i^z S_j^z + S_i^y S_j^y) + S_i^x S_j^x] \\ &+ \{\kappa(-\bar{S} + \delta S^z) + h^z/2\} S_i^z + \{\kappa(\bar{S} + \delta S^z) + h^z/2\} S_j^z \\ &= -2J_{\parallel}[\gamma(S_i^z S_j^z + S_i^y S_j^y) + S_i^x S_j^x + a S_i^z + b S_j^z], \end{aligned} \quad (1)$$

where γ is J_{\perp}/J_{\parallel} , $\kappa = (z_{\perp} - 1)J'_{\perp}/J_{\parallel}$, $h^z = g_{\perp} \mu F/J_{\parallel}$, z_{\perp} is the number of the nearest neighbors with the z -component of the exchange interaction. The parameter κ means the strength of the molecular field along z direction. For simplicity, let's take $S = 1/2$. Using the spin states $\alpha, \alpha, 1/2^{1/2}(\alpha, \beta_j + \beta, \alpha)$, β, β , and $1/2^{1/2}(\alpha, \beta_j - \beta, \alpha)$, the eigen values of Eq. (1) are derived as

$$\begin{aligned} E_1 &= -J_{\parallel}(1/2 + a + b) \\ E_2 &= -J_{\parallel}(1/2 + R) \\ E_3 &= -J_{\parallel}(1/2 - a - b) \\ E_4 &= -J_{\parallel}(1/2 + R) \end{aligned} \quad (2)$$

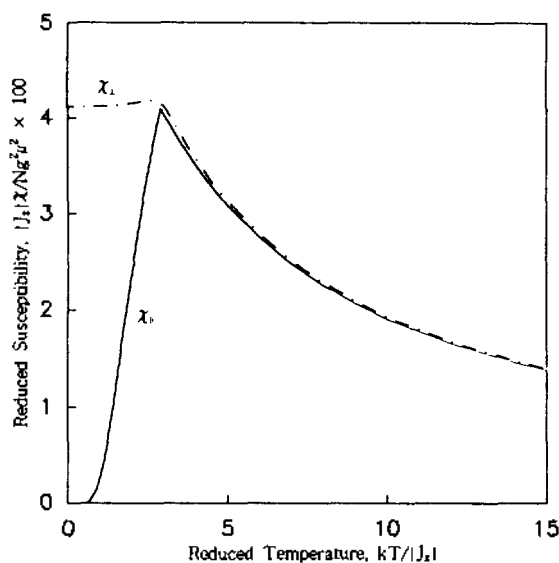


Figure 1. Calculated susceptibility curves. $J_{\parallel}/k = -10$ K, $\gamma = 0.8$, $\kappa = \kappa_{\perp} = 5$ and $g_{\parallel} = g_{\perp} = 2.002322$.

where

$$R = \{\gamma^2 + (b - a)^2\}^{1/2} \quad (3)$$

The magnetization in the external magnetic field along z -axis can be defined self-consistently as

$$\bar{S} + \delta S^z = \text{Tr}\{S^z \exp(-\beta H)\} / \text{Tr}\{\exp(-\beta H)\}, \quad (4)$$

where $\beta = 1/kT$.

The zeroth order term is

$$R\{\exp(\beta J_{\parallel}) + \cosh(\beta J_{\perp} R)\} = -\kappa \sinh(\beta J_{\perp} R). \quad (5)$$

This equation is equivalent to Ohya-Nishiguchi's Eq. (9). At the limit of $R = 1$, the Neel temperature T_N can be calculated from Eq. (5). T_N is the temperature, where the parallel susceptibilities is maximum in Figures 1, 2, and 3.

From the first order term of Eq. (4), the parallel susceptibility is obtained as

$$\chi_{\parallel} = N g_{\parallel}^2 \mu^2 \beta / [2\{1 + \exp(-\beta J_{\parallel}) \cosh(\beta J_{\perp} R) - \beta J_{\perp} \kappa\}]. \quad (6)$$

The spin Hamiltonian for the magnetic field along the x -axis then becomes

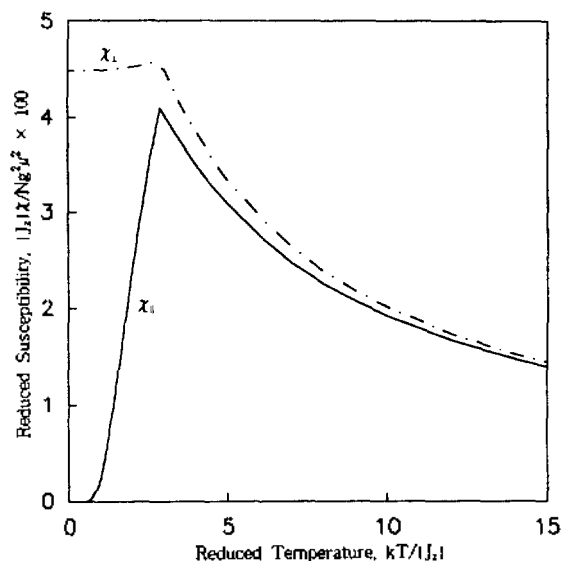


Figure 2. Calculated susceptibility curves. $J_z/k = -10$ K, $\gamma = 0.9999$, $\kappa = 5$, $\kappa_x = 4$ and $g_z = g_x = 2.002322$.

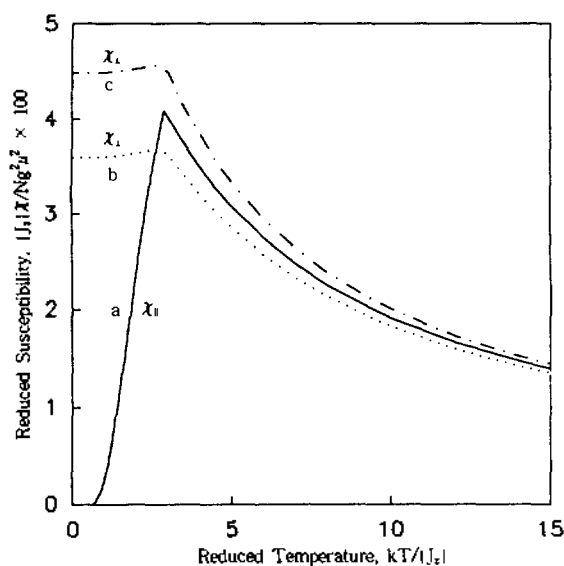


Figure 3. Calculated susceptibility curves. a) $J_z/k \approx -10$ K, $\gamma = 0.8$, $\kappa = 5$, $\kappa_x = 4$ and $g_z = g_x = 2.002322$ (or $\gamma = 1.2$, $\kappa_x = 6$). b) $J_z/k = -10$ K, $\gamma = 1.2$, $\kappa = 5$, $\kappa_x = 6$ and $g_z = g_x = 2.002322$. c) $J_z/k = -10$ K, $\gamma = 0.8$, $\kappa = 5$, $\kappa_x = 4$ and $g_z = g_x = 2.002322$.

$$\begin{aligned}
 H = & -2J_z[\gamma(S_i^x S_j^x + S_i^y S_j^y) + S_i^z S_j^z - \kappa \bar{S}_i^x S_j^x + \kappa_x \bar{S}_i^y S_j^y] \\
 & - 2J_z[\kappa_x \delta S^z + h^z/2](S_i^x + S_j^x) = -2J_z[\gamma(S_i^x S_j^x + S_i^y S_j^y) + S_i^z S_j^z \\
 & + a' S_i^x + b' S_j^x] + \epsilon(S_i^x + S_j^x) = H_0 + H_1, \quad (7)
 \end{aligned}$$

where $a' = -\kappa \bar{S}$, $b' = \kappa_x \bar{S}$, $h^z = g_z \mu H^z / J_z$, $\kappa_x = (z_x - 1) J_x' / J_z$, and $\epsilon = -2J_z(\kappa_x \delta S^z + h^z/2)$. The parameter κ_x stands for the strength of the molecular field along x -direction and z_x is the number of the nearest neighbors with the xy -component in the exchange interaction. The first term H_0 and the second term H_1 of Eq. (7) do not commute. When ϵ is small, the perturbation method can be used. The eigen values of H_0 are obtained as

$$\begin{aligned}
 E_{01} &= -J_z/2 \\
 E_{02} &= -J_z(-1/2 + R) \\
 E_{03} &= -J_z/2 \\
 E_{04} &= -J_z(-1/2 - R)
 \end{aligned} \quad (8)$$

According to Karplus and Schwinger's method, the following self-consistent equation can be solved⁴.

$$2\delta S^z = \text{Tr}\{S_i^z + S_j^z\} \exp(-\beta H) / \text{Tr}\{\exp(-\beta H)\} \quad (9)$$

The perpendicular susceptibility is then given by

$$\chi_{\perp} = N g_z^2 \mu^2 \beta / [2(\text{Tr}\{\exp(-\beta H)\} / D + J_z \kappa_x)], \quad (10)$$

where

$$\begin{aligned}
 D = & [\exp(\beta J_z/2) - \exp\{\beta J_z(-1/2 + R)\}](1 + \gamma/R) / [J_z(1 - R)] \\
 & + [\exp(\beta J_z/2) - \exp\{\beta J_z(-1/2 - R)\}](1 - \gamma/R) / [J_z(1 + R)] \quad (11)
 \end{aligned}$$

$\text{Tr}\{\exp(-\beta H)\}$ is obtained with the eigen values in Eq. (8).

At high temperatures ($T \gg T_N$),

$$\chi_{\parallel} = N g_z^2 \mu^2 / [4(kT - J_z \kappa/2)]. \quad (12)$$

and

$$\chi_{\perp} = N g_z^2 \mu^2 / [4(kT - J_z \kappa_x/2)]. \quad (13)$$

The difference between χ_{\parallel} and χ_{\perp} comes from the molecular field parameters, κ and κ_x , and g anisotropy in the high temperature limit. In the case that $J_z = J_x$ ($\gamma = 1$), Eq. (6), Eq. (10), Eq. (12) and Eq. (13) are equivalent to Ohya-Nishiguchi's equations.

At moderate high temperature ($T \geq T_N$), the perpendicular susceptibility is derived as

$$\begin{aligned}
 \chi_{\perp} = & N g_z^2 \mu^2 / 2 [2J_z \{3 + \exp(-2\beta J_z)\} / 2\beta J_z (1 + \gamma) \\
 & + (1 - \exp(-2\beta J_z))(1 - \gamma) - J_z \kappa_x] \quad (14)
 \end{aligned}$$

As temperature approach to 0 K, the parallel susceptibility decreases to 0, while the perpendicular susceptibility is kept a near constant value

$$\chi_{\perp} = N g_z^2 \mu^2 (\kappa_x - \kappa) / [2J_z \{\kappa(1 + \kappa) + \kappa_x(\kappa - \kappa_x)\}]. \quad (15)$$

Discussion

The calculated χ_{\parallel} and χ_{\perp} values for $J_z/k = -10$ K, $\gamma = 0.8$, $\kappa = \kappa_x = 5$ and $g_z = g_x = 2.002322$ are shown in Figure 1. This shows that there is little difference for anisotropic spin-pair interaction with an isotropic molecular field above T_N . Large difference between χ_{\parallel} and χ_{\perp} above T_N , shown in Figure 2 demonstrate that the difference results from the anisotropic molecular fields, κ and κ_x , where they depend on J_z' , J_x' and the number of the nearest neighbors of the i spin, excluding the j spin. The susceptibilities are obtained with $\gamma = 0.9999$, $\kappa = 5$, and $\kappa_x = 4$ and other parameters are the same as those in Figure 1. It may be concluded that most difference is due to the difference in the molecular fields, κ and κ_x . Although there is no spontaneous magnetic ordering above T_N , still the molecular field plays a significant role in the susceptibilities. This implies that short range order (interaction between a spin-pair and the nearest neighbors) makes the anisotropy. The smaller, κ_x , the bigger the perpendicular susceptibilities, while the parallel components

are the same for $\gamma=1.2$, $\kappa_r=6$ and $\gamma=0.8$, $\kappa_r=4$, shown in Figure 3 b) and c), respectively. The susceptibility curves are qualitatively very similar to the results published by Ohya-Nishiguchi. This is, however, the first result that anisotropic susceptibilities in the paramagnetic region are obtained with the simple mean field theory.

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Analysis of Fourier Transform Jet Emission Spectra of CN ($B^2\Sigma^+ \rightarrow X^2\Sigma^+$)

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Received November 19, 1993

The CN radical was generated in a jet with an inert buffer gas, helium from high voltage dc discharge of the precursor CH_3CN . The Fourier transform emission spectra of the 0-0 band of the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ transition of CN have been obtained with a Bruker IFS-120HR spectrometer. The spectra show an anomalous distribution of rotational intensity which cannot be explained by a simple Boltzmann distribution. The analysis of the transition frequencies provides molecular constants with high accuracy for both the ground and the excited electronic states of the CN radical.

Introduction

Fourier transform (FT) spectroscopy is one of the most convenient methods in obtaining a high resolution spectra of molecules. With development of techniques improving the signal to noise ratio and the resolution of the FT spectra, it has become possible to obtain the rotationally resolved emission spectra of unstable molecules with a FT spectrometer.^{1,2} Recently, FT-UV/VIS spectroscopy has been applied to the study of vibronic transition of unstable molecules which emit relatively strong fluorescence.³

Among many unstable molecules studied in the laboratory, CN radical is one of the most intensively studied diatomic free radicals because of its strong fluorescence and abundance in flames. Astronomically, CN has been observed from several extraterrestrial sources including stellar atmospheres,^{4,5} comets,⁶ and dark interstellar molecular clouds⁷ by a variety kinds of spectroscopic techniques.

The first analysis of the rotational structure of the $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ band was accomplished by Kratzer⁸ in the violet system. Douglas and Routly⁹, and Huber and Herzberg¹⁰ summarized a detailed review of the literature on this molecule. Recently, the microwave and millimeter wave works by Ito *et al.*¹¹ have given very accurate molecular parameters in the ground state. From the analysis of the millimeter wave spectrum, they have determined the spin-rotation interaction constants γ over several vibrational states in the ground electronic state. Very recently, a few papers¹²⁻¹⁴ have reported the molecular parameters from the analysis of the rotationally

resolved electronic spectra with a high resolution FT-UV/VIS spectrometer since the pioneering works of Richard *et al.*³ For this study, they employed a very simple corona-excited supersonic expansion system developed by Engelking¹⁵ which produces continuous, high density of rotationally cooled radicals for spectroscopic studies of unstable molecules. Although they used very similar techniques and experimental setup, the molecular constants obtained did not exactly agree well.

Thus, in this work which is an extension of the previous work,¹⁶⁻¹⁸ the CN radical was generated in a jet with an inert He gas by an electric dc discharge of CH_3CN . The emission spectra of the 0-0 band of the $B \rightarrow X$ transition have been obtained using a FT-UV/VIS spectrometer. The analysis of these spectra provides more accurate molecular parameters for the ground and the excited electronic states.

Experimental Detail

The observation of CN emission spectra has been carried out using the experimental setup similar to those previously described.¹⁷ The precursor CH_3CN was expanded with an inert gas He through a 0.2 mm quartz nozzle into the vacuum chamber which was made of a six-way cross Pyrex glass tube of 5.0 cm in diameter. Since CN radical emits strong fluorescence around $26,000 \text{ cm}^{-1}$, the concentration of CH_3CN in the gas mixture was kept as low as possible by adjusting the opening of the bypass valve connected to the sample chamber during the measurement. The concentration