Interplay of exchange and crystal-field effects in the magnetic susceptibility of $Cs_2CrCl_5 \cdot 4H_2O$

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The magnetic susceptibility of $Cs_2CrCl_5 \cdot 4H_2O$ ($S=\frac{3}{2}$) in one direction (Z) is interpreted with an Ising model where both the crystal-field and the exchange interactions are considered on equal footing. Since the one-dimensional Ising model in the presence of a crystal field can be solved exactly for any spin, the susceptibility parallel to the Z direction is calculated for $S=\frac{3}{2}$ and an excellent agreement with the experimental results is obtained with a suitable choice of exchange ($J=-0.038k$) and crystal-field ($D=-0.16k$) parameters.

I. INTRODUCTION

Recently, Carlin and Burriel[1] measured the single-crystal susceptibility of $Cs_2CrCl_5 \cdot 4H_2O$ over the temperature interval 40 mK–4.2 K. They gave a theoretical interpretation of these results in terms of a spin-$\frac{3}{2}$ linear-chain Heisenberg antiferromagnet with the crystal-field and the exchange interactions taken to be of comparable magnitude. In their calculations, they assumed the crystal-field and the exchange interactions to be small compared with thermal energies. As a result, the theoretical calculations of Carlin and Burriel[1] fit the experimental results at high temperatures and down to the temperatures at which the susceptibility maxima occur, but fail to reproduce the experimental results at low temperature ($0-0.28$ K).

In this Comment an attempt is made to interpret the experimental data using a one-dimensional Ising model in the presence of a crystal field. Since the Ising model in one dimension and in the presence of a crystal field can be solved exactly for any spin,[2] the exact susceptibility for $S=\frac{3}{2}$ is calculated in this model and compared with the susceptibility in the Z direction. This model involves only two parameters–the crystal field (D) and the exchange interaction (J)—and excellent agreement with the experimental results is obtained over the whole temperature range ($0-4.2$ K) with a suitable choice of D and J. These values are very close to the values obtained by Carlin and Burriel.[1] The susceptibilities along the b and y axes[1] cannot be compared, as the transverse Ising model for arbitrary spin has not yet been solved. This model has been solved[3,4] for spin $\frac{1}{2}$ only and the calculation shows that susceptibility maxima appear in the transverse directions as well. There is no reason for change in this susceptibility behavior for higher spins. Therefore, we can expect susceptibility maxima along the b axis also, without assuming any long-range order.

The crystal structure of the compound under investigation is discussed in detail by Carlin and Burriel.[1] The magnetic ion in $Cs_2CrCl_5 \cdot 4H_2O$ is Cr^{3+} which is a d^3 ion and has an $^4A_2$ ground state in the octahedral crystal field. It is a spin-$\frac{3}{2}$ system and the ground state suffers a splitting ($S_z=\pm\frac{3}{2}$ and $S_z=\pm\frac{1}{2}$) due to the D_{4h} symmetry of the crystal field as determined by crystal-structure analysis.[1]

II. THEORY

The Hamiltonian for the one-dimensional Ising problem for an N-spin ring in the presence of an axial crystal field is given by[2]

$$H=\sum_{n=1}^{N}[D(S_n^z)^2-2JS_n^zS_{n+1}^z] \ . \tag{1}$$

Since $S_{n+1}^z \equiv S_1^z$, regrouping the terms in the form

$$H=\sum_{n=1}^{N}\{\tfrac{1}{2}D[(S_n^z)^2+(S_{n+1}^z)^2]-2JS_n^zS_{n+1}^z\} \ , \tag{2}$$

one notes that the partition function Z can be expressed in S^z representation as

$$Z=\mathrm{Tr}\prod_{n=1}^{N}T_n=\mathrm{Tr}T^N \ , \tag{3}$$

where all the transfer matrices T_n have an identical Hermitian form

$$T_n=T=e^{-\beta H} \ , \tag{4}$$

where $\beta=1/kT$ and the matrix elements are given by

$$\langle S|T|S'\rangle=\exp\{2\beta Jss'-\frac{\beta D}{2}[(s)^2+(s')^2]\} \ , \tag{5}$$

where s,s' are the projections of spin $\vec{s}$.

Starting from the Hamiltonian [Eq. (2)], the transfer matrix T for $S=\frac{3}{2}$ is obtained as follows.

s \ s'	$\frac{3}{2}$	$\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{3}{2}$
$\frac{3}{2}$	$e^{9K-9\alpha}$	$e^{3K-5\alpha}$	$e^{-3K-5\alpha}$	$e^{-9K-9\alpha}$
$\frac{1}{2}$	$e^{3K-5\alpha}$	$e^{K-\alpha}$	$e^{-K-\alpha}$	$e^{-3K-5\alpha}$
$-\frac{1}{2}$	$e^{-3K-5\alpha}$	$e^{-K-\alpha}$	$e^{K-\alpha}$	$e^{3K-5\alpha}$
$-\frac{3}{2}$	$e^{-9K-9\alpha}$	$e^{-3K-5\alpha}$	$e^{3K-5\alpha}$	$e^{9K-9\alpha}$

where $K=J/2kT$ and $\alpha=D/4kT$. Diagonalizing this transfer matrix, eigenvalues and eigenvectors are obtained as follows.

Eigenvalues:

$$\begin{aligned}
\lambda_1 &= e^{-9\alpha}\cosh(9K) + e^{-\alpha}\cosh K + \{[e^{-9\alpha}\cosh(9K) - e^{-\alpha}\cosh K]^2 + 4e^{-10\alpha}\cosh^2(3K)\}^{1/2} ,\\
\lambda_2 &= e^{-9\alpha}\cosh(9K) + e^{-\alpha}\cosh K - \{[e^{-9\alpha}\cosh(9K) - e^{-\alpha}\cosh K]^2 + 4e^{-10\alpha}\cosh^2(3K)\}^{1/2} ,\\
\lambda_3 &= e^{-9\alpha}\sinh(9K) + e^{-\alpha}\sinh K + \{[e^{-9\alpha}\sinh(9K) - e^{-\alpha}\sinh K]^2 + 4e^{-10\alpha}\sinh^2(3k)\}^{1/2} ,\\
\lambda_4 &= e^{-9\alpha}\sinh(9K) + e^{-\alpha}\sinh K - \{[e^{-9\alpha}\sinh(9K) - e^{-\alpha}\sinh K]^2 + 4e^{-10\alpha}\sinh^2(3K)\}^{1/2} .
\end{aligned} \tag{6}$$

It is evident that λ_1 is the largest eigenvalue.

Eigenvectors:

$$\begin{aligned}
|\psi_1\rangle &= \frac{1}{[2(1+\kappa_1^2)]^{1/2}}\begin{pmatrix}1\\ \kappa_1\\ \kappa_1\\ 1\end{pmatrix}, \quad \text{where } \kappa_1 = [\lambda_1 - 2e^{-9\alpha}\cosh(9K)]/[2e^{-5\alpha}\cosh(3K)] ,\\
|\psi_2\rangle &= \frac{1}{[2(1+\kappa_2^2)]^{1/2}}\begin{pmatrix}1\\ \kappa_2\\ \kappa_2\\ 1\end{pmatrix}, \quad \text{where } \kappa_2 = [\lambda_2 - 2e^{-9\alpha}\cosh(9K)]/[2e^{-5\alpha}\cosh(3K)] ,\\
|\psi_3\rangle &= \frac{1}{[2(1+\kappa_3^2)]^{1/2}}\begin{pmatrix}1\\ \kappa_3\\ -\kappa_3\\ -1\end{pmatrix}, \quad \text{where } \kappa_3 = [\lambda_3 - 2e^{-9\alpha}\sinh(9K)]/[2e^{-5\alpha}\sinh(3K)] ,\\
|\psi_2\rangle &= \frac{1}{[2(1+\kappa_4^2)]^{1/2}}\begin{pmatrix}1\\ \kappa_4\\ -\kappa_4\\ -1\end{pmatrix}, \quad \text{where } \kappa_4 = [\kappa_4 - 2e^{-9\alpha}\sinh(9K)]/[2e^{-5\alpha}\sinh(3K)] .
\end{aligned} \tag{7}$$

Using correlation functions,[5] the susceptibility is obtained[2] as

$$\chi = \frac{N\mu_B^2}{kT(1+\kappa_1^2)}\left[\frac{(\kappa_1\kappa_3+3)^2}{1+\kappa_3^2}\left(\frac{\lambda_1+\lambda_3}{\lambda_1-\lambda_3}\right) + \frac{(\kappa_1\kappa_4+3)^2}{1+\kappa_4^2}\left(\frac{\lambda_1+\lambda_4}{\lambda_1-\lambda_4}\right)\right] , \tag{8}$$

where g is assumed to be 2.0. The λ's and κ's are obtained from Eqs. (6) and (7).

III. RESULTS AND DISCUSSION

The successful analysis of the susceptibility data of $Cs_2CrCl_5 \cdot 4H_2O$ parallel to the Z direction has been carried out in terms of an Ising linear-chain antiferromagnet which has been solved exactly.[2] This model includes the crystal-field effect which is comparable to the exchange interaction, and no approximation is involved regarding their strengths as compared with the thermal energies. Therefore, the present calculations reproduce the experimental results at high as well as low temperatures, while Carlin and Burriel[1] were able to reproduce the experimental data at high temperatures ($T > 0.28$ K) only. Using the present model the exact susceptibilities have been calculated with different D and J parameters and the results are shown in Figs. 1 and 2, respectively. As is evident from Figs. 1 and 2, the susceptibilities are less sensitive to D and more sensitive to J. Therefore, D was fixed at the value obtained by Carlin and Burriel[1] and J was varied to reproduce the experimental results. The best-fit results are shown in Fig. 3 and the best-fit parameters were found to be $D = -0.16k$ and $J = -0.038k$. In this figure, the theoretical results are shown by a full line curve and the experimental results are shown by dots. Here, no long-range order is considered

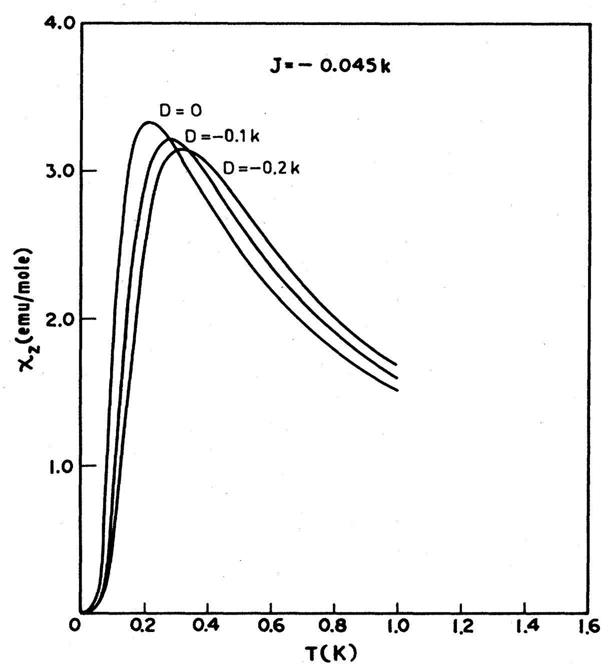

FIG. 1. Variation of susceptibility with temperature for different values of the crystal-field parameter (D).

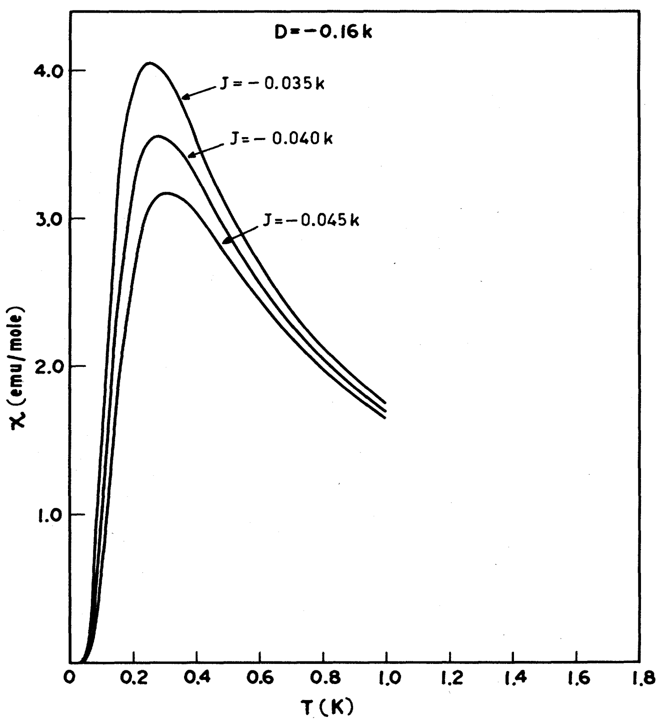

FIG. 2. Variation of susceptibility with temperature for different values of the exchange parameter (J).

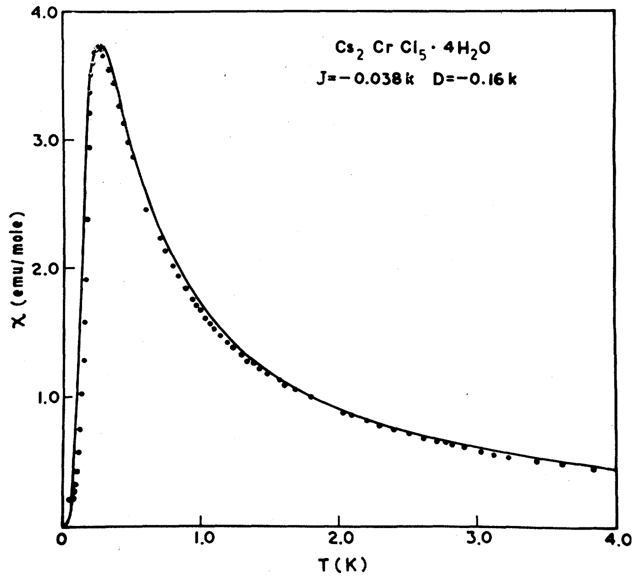

FIG. 3. Magnetic susceptibility in the z direction.

and, therefore, it contradicts the statement of Carlin and Burriel.[1] They have stated an ordering temperature (0.185 ± 0.005) K from the maximum slope of the susceptibility curve, which is not very clear. There is no evidence for the existence of antiferromagnetic ordering at this temperature either from specific-heat or neutron-scattering experiments. As the present calculation (Fig. 3) shows, the susceptibility can have maximum slope even in the absence of long-range order and, therefore, the existence of long-range order is not at all necessary to explain the experimental results. Of course, any approximate theory (e.g., mean field or correlated effective field) should demand the existence of long-range order[6] (even in one dimension) in order to produce the susceptibility maxima in the z direction as well as in other directions. Since the transverse Ising model for $S=\frac{3}{2}$ has not yet been solved exactly, the susceptibilities along the b and y axes[1] cannot be reproduced with the present model.

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