Experimental Study of Quantum Statistics for the $S = \frac{1}{2}$ Quasi-One-Dimensional Organic Ferromagnet

K. Takeda and K. Konishi*
Department of Applied Science, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan

K. Nedachi and K. Mukai
Department of Chemistry, Faculty of Science, Ehime University, Matsuyama 790, Japan
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Using a genuine organic ferromagnetic radical crystal ($C_{10}H_{10}N_4SCl$) which was synthesized recently, we experimentally examined the results of quantum statistics for a one-dimensional Heisenberg ferromagnet with spin $S = \frac{1}{2}$. The characteristic thermodynamical properties expected of the most isotropic Heisenberg system, such as magnetic susceptibilities with the critical index of $\gamma = 2.0$ and field dependence of magnetic heat capacity, are herein revealed.

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The one-dimensional (1D) magnet with localized spins is one of the simplest systems for solving many-body problems from which exact or correct physical quantities have been derived. For 1D Heisenberg antiferromagnets with spin $S = \frac{1}{2}$, the exact ground-state energy, the energy-dispersion relation, and various thermodynamical quantities have been obtained [1], while in addition, such a heuristic picture of the resonating valence bond (RVB) [2] state has also been studied [3]. For $S = 1$ 1D Heisenberg antiferromagnets, intensive studies have been carried out concerning the Haldane conjecture [4]; ground-state properties, hidden-order parameters, energy gaps, or thermodynamical properties [5]. The physical properties expected of these $S = \frac{1}{2}$ and $S = 1$ systems have been experimentally checked with abundant real antiferromagnetic compounds. The inevitable small anisotropies (in exchange integrals or crystalline fields) present in these substances may generally by treated as perturbations, without losing any of the intrinsic physical properties which originate in dominant quantum effects in these antiferromagnetic systems.

For 1D ferromagnetic systems, however, the situation differs somewhat from the case of antiferromagnets, in the following two points. First, if the anisotropies are of the Ising type and even if they are small, they cannot be treated as perturbations, because they bring about significant effects of the bound magnons whose energy levels lie below the continuous energy band of spin waves [6]. This gives rise to a qualitative change in the thermodynamical quantities, especially in an applied field. Second, we can rarely obtain 1D quantum ferromagnetic substances, except for such compounds as $(C_6H_{11}NH_3)CuCl_3$ (CHAC) [7], $K_2Cu_{0.59}Zn_{0.41}F_4$ [8], and γ-phase p-NPNN (nitrophenyl nitrony nitroxide) [9]. The effects of the bound magnons were studied by susceptibility measurements of CHAC, while the static thermodynamical quantities for isotropic Heisenberg systems were investigated on these compounds only in zero external field.

In this Letter, we present one more prototype thermodynamical behavior which can be expected of the 1D isotropic Heisenberg ferromagnet with $S = \frac{1}{2}$ in an applied field, using a genuine organic radical crystal [3-(4-chlorophenyl)-1,5-dimethyl-6-thioxoverdazyl; p-CDTV]. The theoretically predicted critical index of the magnetic susceptibility $\gamma = 2.0$ is herein examined, while the characteristic field dependence of the magnetic heat capacity is herein revealed to be intrinsic to the 1D isotropic Heisenberg system independent of the bound magnons.

An illustration of the molecular structure of p-CDTV is inset in Fig. 1. The radical crystal of p-CDTV was recently synthesized during a project to find new functional materials and was found to be ferromagnetic [10]. We found it orders ferromagnetically at $T_c = 0.67$ K by weak interchain interactions [11]. In this report, however, we focus our interests on thermal and magnetic behavior at higher temperatures than T_c. The crystal structure has not yet been determined.

In order to get the critical exponent of the magnetic susceptibility (χ), we have to check its relaxation effects. For that purpose, we employed the ac method with the fields $h(\nu) = 0.1$, 0.5, 2, 4, and 10 Oe (peak to peak) and the frequencies $\nu = 5$, 25, 125, 500, and 1000 Hz. No relaxation effects were detected under the present experimental conditions down to 1.7 K. The diamagnetization contribution to χ was corrected (-1.33×10^{-4} emu/mol). Above 20 K, χ obeys the Curie-Weiss law with the positive Weiss temperature of 3.0 ± 0.2 K, indicating that the effective interactions are ferromagnetic. Below about 20 K, however, χ deviates from the Curie-Weiss law as demonstrated in Fig. 1. This leads us to analyze the

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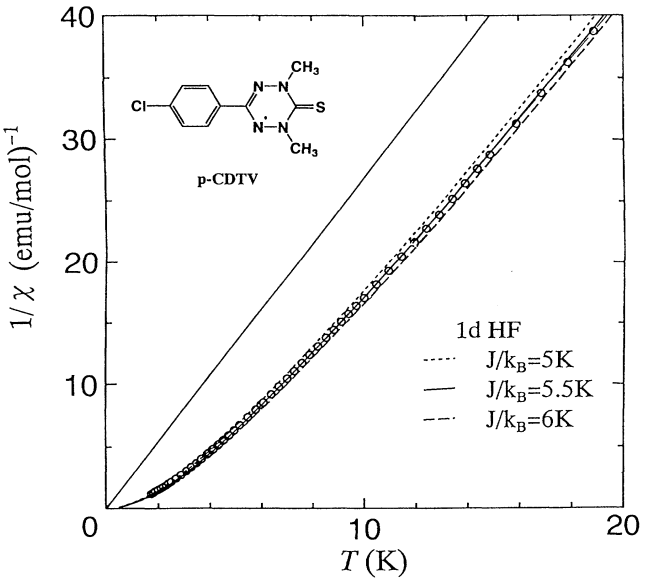

FIG. 1. Inverse magnetic susceptibility of p-CDTV at low temperatures. Above 5 K, the observed values (open circles) obey the theoretical results for the 1D isotropic Heisenberg ferromagnet (HF) with $J/k_B = 5.5 \pm 0.5$ K [13]. The straight line corresponds to χ of the paramagnet with $g = 2.00$ and $S = \frac{1}{2}$.

low-temperature behavior of χ based on the quasi-1D ferromagnetic Heisenberg model, where the Hamiltonian is given by

$$\mathcal{H} = -2J\sum_{i}^{N}[S_i^z S_{i+1}^z - \tfrac{1}{4} + \eta(S_i^x S_{i+1}^x + S_i^y S_{i+1}^y)] - g\mu_B H\sum_i S_i^z - 2J'\sum_{\langle ij\rangle} \boldsymbol{S}_i \cdot \boldsymbol{S}_j , \quad (1)$$

where J and J' are the intra- and inter-chain exchange constants, respectively, η is the anisotropy parameter, and N is the number of spins. The applied field is denoted by H. As in the case of almost all radical crystals, the g factor can be expected to be $g = 2.00 \pm 0.02$ [9,12], nearly equal to the g factor of electrons (2.0023), due to the quenching of the angular momentum of molecular orbitals. This is the main reason for the isotropy to be found in the spin system in radical crystals rather than in compounds with metallic ions (such as Cu^{2+}). Here we consider the isotropic system with $\eta = 1$ and $J' = 0$ as the first approximation. By the exact diagonalization method up to $N = 11$ spins, χ_{1D} is obtained for $S = \frac{1}{2}$ as

$$\chi_{1D} = \frac{Ng^2\mu_B^2}{4k_BT}\left[1 + \left(\frac{J}{k_BT}\right)^a\right], \quad (2)$$

with $a = 1$ for $k_BT/J > 1$ [13]. For lower temperatures, however, a depends on T ($a \to 4/5$ for $T \to 0$), and the critical index γ in $\chi_{1D} \propto T^{-\gamma}$ is predicted to be $\gamma = 1.8$–2.0. It should be noted that our data are well reproduced by Eq. (2) with $J/k_B = 5.5 \pm 0.5$ K and $g = 2.00$, as in Fig. 1. At lower temperatures below 5 K, we need to consider the effects from the interchain interaction which triggers three-dimensional ordering at $T_c = 0.67$ K, thus producing an effect on the value of the susceptibility. By the mean field theory, χ for the quasi-1D system is expressed as

$$\chi = \chi_{1D}/(1 - 2zJ'\chi_{1D}/Ng^2\mu_B^2), \quad (3)$$

where z is the number of neighboring chains. The three-dimensional transition temperature T_c is approximated as the temperature at which the denominator of Eq. (3) becomes zero. For estimating J' at low temperatures, we need a more accurate notation of χ_{1D} than that provided by Eq. (2) for $k_BT/J < 1$. The thermodynamical quantities for the 1D isotropic Heisenberg ferromagnet with $S = \frac{1}{2}$ were studied on the basis of both the modified spin-wave theory and the Bethe-ansatz integral-equation method by Takahashi and Yamada (TY) [14,15], where the susceptibility is expressed as

$$\chi_{1D}^{TY} = \frac{Ng^2\mu_B^2}{8J}\left[0.1667\left(\frac{2J}{k_BT}\right)^2 + 0.581\left(\frac{2J}{k_BT}\right)^{1.5} + 0.68\left(\frac{2J}{k_BT}\right)^1 + 0\left(\frac{2J}{k_BT}\right)^{0.5}\right]. \quad (4)$$

This gives a critical index of $\gamma = 2.0$ for $T \to 0$. Using χ_{1D}^{TY} for χ_{1D} in the denominator of Eq. (3), we obtain an estimate of interchain interaction $zJ'/k_B = 0.21 \pm 0.02$ K (or $zJ'/J = 3.8 \times 10^{-2}$).

Now that we have obtained the value of zJ', we can evaluate the experimental χ_{1D} corrected for the

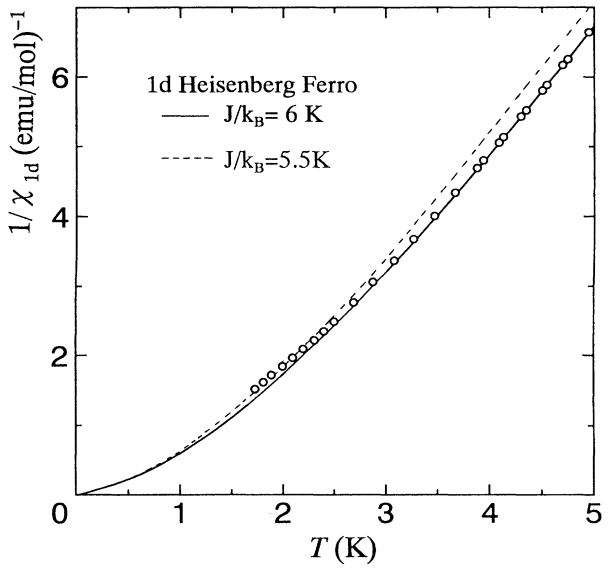

FIG. 2. Inverse susceptibility of p-CDTV corrected for the isolated 1D system (open circles). Theoretical results for the 1D isotropic Heisenberg ferromagnet [14,15] are drawn for $J/k_B = 5.5$ and 6.0 K.

isolated chains again from Eq. (3) by using the value of zJ' and the observed value of χ, as shown in Fig. 2. By this correction, χ_{1D} becomes smaller than χ, as T becomes lower; although the correction is less than 1% at 5 K ($k_BT/J \approx 1$), it amounts to more than 20% at 1.7 K ($k_BT/J \approx 0.3$). From Fig. 2, we note that the experimental value of χ_{1D} is nicely reproduced by the TY theory with $\gamma = 2.0$ and $J/k_B = 6.0 \pm 0.3$ above 1.7 K, which is the low-temperature limit of our present experiment. The exact index for the classical Heisenberg spin system also gives $\gamma = 2.0$ [16].

When Ising-type anisotropy ($\eta < 1$) exists in a 1D Heisenberg ferromagnet, χ_{1D} unexpectedly changes from Eqs. (2) and (4) because of the contribution of the bound magnons [6]. The above results for p-CDTV suggest the exclusion of the anisotropy in this spin system. In order to check the anisotropy effects in p-CDTV in more detail, experiments in the applied field are desirable. Although our ac method does not operate under an applied field, it was possible to examine the anisotropy effects by the following heat capacity measurements in an applied field.

The low-temperature heat capacity of p-CDTV crystals (0.3136 g) was measured in the applied fields $H = 0$, 0.25, 0.50, 1, 2, 5, 10, 15, 20, and 30 kOe. The magnetic heat capacity (C_m) was obtained by subtracting the lattice contribution, which was evaluated by referring to the heat capacity of the bromine radical crystal with a similar molecular structure [10,11]. (C_m is larger than the lattice contribution below 5 K in zero field, and much larger than that in the applied fields below 10 K.) The field dependence of C_m is shown in Fig. 3. The

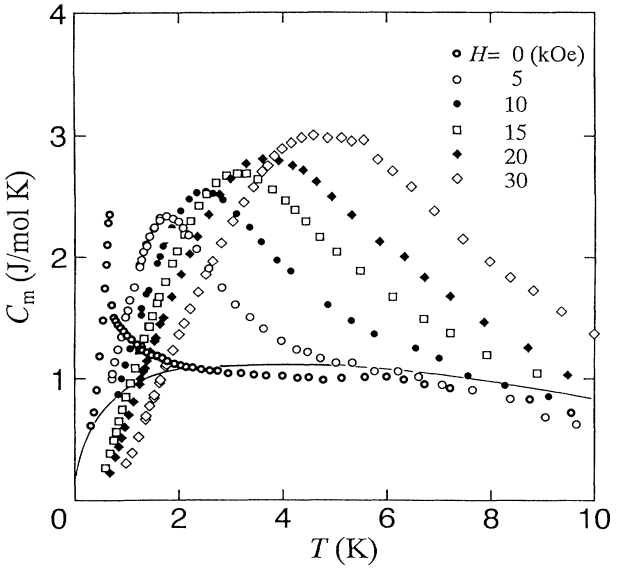

FIG. 3. Field dependence of magnetic heat capacity of p-CDTV. The solid line represents the theoretical results for the isotropic Heisenberg ferromagnet with $J/k_B = 6.0$ K.

overall behavior of the heat capacity is qualitatively similar to the field dependence of the 1D ferromagnetic Ising system $(CH_3)_3NHCoCl_3 \cdot 2H_2O$ [17]. In zero field, C_m of p-CDTV shows a sharp peak at $T_c = 0.67$ K associated with the three-dimensional ordering and maintains comparable values around $C_{max} = 0.134R$ (R is the gas constant) above 2 K, which is a characteristic feature of 1D isotropic Heisenberg ferromagnets [13]. There is a small discrepancy between the observed values of C_m and the theoretical ones for $J/k_B = 6.0$ K and $J' = 0$ K. This may be due to the entropy compensation between the short-range ordering above 2 K and the three-dimensional ordering at lower temperatures. About 80% of the magnetic entropy for $S = \frac{1}{2}$ is consumed below 10 K, while the remaining 20% can be expected to be consumed at higher temperatures.

In the case of $H = 5$ kOe, which is much larger than the interchain exchange field $H_c = 2zJ'\langle S\rangle/g\mu_B \approx 1.5$ kOe, the sharp peak completely disappears and another broad hump of C_m appears at around 1.8 K instead, which then grows and shifts up to higher temperatures in higher fields as demonstrated in Fig. 3. (Even in $H = 0.25$ kOe, the peak at T_c collapses only to leave a trace of a cusplike anomaly at 0.6 K, with the broad hump making an appearance at around 0.8 K.) This kind of field dependence of C_m has not previously been reported for a real Heisenberg ferromagnet with $S = \frac{1}{2}$. Before comparing these results with the theory for the 1D isotropic Heisenberg ferromagnet, we need to examine whether or not a small Ising-type anisotropy exists in p-CDTV. If it does exist, it may exert a great influence on $C_{m'}$, as it does in the case for χ of CHAC [7]. We calculated the field dependence of C_m following the theoretical work by Johnson and Bonner, setting $J/k_B = 6.0$ K ($J' = 0$). (For $H \gg H_c = 1.5$ kOe, we may effectively neglect the effects from J'.) An example of the calculations for $\eta = 0.98$, $H = 5$, and 30 kOe is shown in Fig. 4. We can see the dominant contribution of the bound magnons to C_m. Nevertheless, it is clear that we cannot explain our experimental results (Fig. 3) by adjusting the values of η (<1), H, and J in this theory.

For the 1D isotropic Heisenberg limit ($\eta = 1$), the field dependence of C_m has been numerically evaluated by Bonner for some discrete fields $g\mu_BH/J = 0.5$, 1.0, 1.5, and 2.0 [18]. In Fig. 5, we compare C_m of p-CDTV for $H = 20$ kOe, which is nearly equal to $g\mu_BH/J = 0.5$, with the theoretical results for the corresponding field. This agreement is appreciable between them, beyond any possible experimental ambiguities. The theoretical evaluation of C_m for an arbitrary value of H may be possible, in principle, starting from the free energy expressed by Takahashi *et al.* on the basis of the Bethe-ansatz integral method [9]. The results of such an evaluation will be presented elsewhere. In the case of $\eta \geq 1$, we cannot expect bound magnons within the system. The thermodynamical behavior may be qualitatively the same as that observed here,

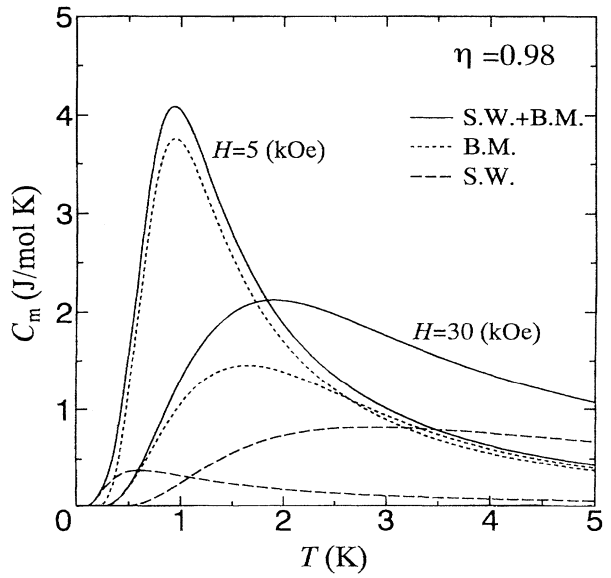

FIG. 4. Theoretical results for the field dependence of magnetic heat capacity of the 1D anisotropic Heisenberg ferromagnet for $\eta = 0.98$ and $J/k_B = 6.0$K. S.W. indicates the spin-wave and B.M. the bound-magnon contribution.

as long as η does not significantly exceed 1: When η becomes so large that the Hamiltonian is effectively of an *XY* type, the spin-wave dispersion itself begins to differ from the Heisenberg type [19].

The present study has demonstrated prototype thermodynamical behavior expected of the most isotropic Heisenberg ferromagnet in one dimension, including the magnetic susceptibility with the critical index $\gamma = 2.0$ and the field dependence of the magnetic heat capacity.

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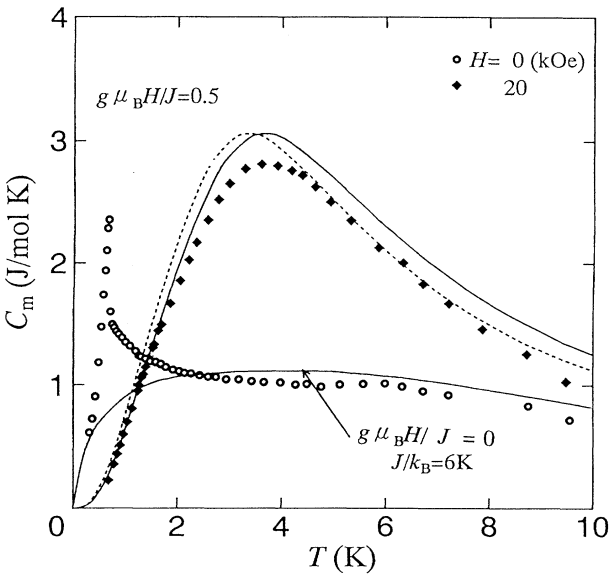

FIG. 5. Magnetic heat capacities of *p*-CDTV in the applied fields $H = 0$ and 20 kOe. The theoretical results for the 1D isotropic Heisenberg ferromagnet are given for $g\mu_B H/J = 0$ ($H = 0$, $J/k_B = 6.0$ K) and for $g\mu_B H/J = 0.5$ ($\cdots$; $H = 20.5$ kOe, $J/k_B = 5.5$ K; $H = 22.3$ kOe, $J/k_B = 6.0$ K).

*Present address: Department of Physics, Faculty of Science, Ehime University, Matsuyama 790, Japan.

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