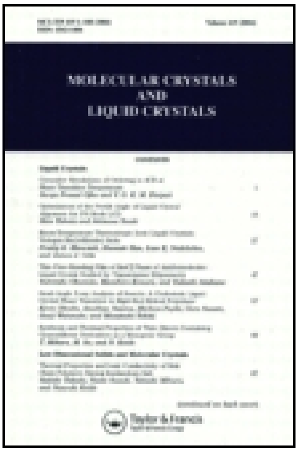

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 04 Oct 2006.

To cite this article: Kazuyoshi Takeda , Toshiyuki Hamano , Tatsuya Kawae , Masako Hitaka , Syuji Kawasaki , Minoru Takahashi & Kazuo Mukai (1996): Organic Radical Solid as Typical One-Dimensional Heisenberg Ferromagnet with Quantum Spin, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 279:1, 107-114

To link to this article: http://dx.doi.org/10.1080/10587259608042182

Mol. Cryst. Liq. Cryst., 1996, Vol. 279, pp. 107–114
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ORGANIC RADICAL SOLID AS TYPICAL ONE-DIMENSIONAL HEISENBERG FERROMAGNET WITH QUANTUM SPIN

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Abstract Quantum statistics for the most isotropic spin (S=1/2) system in one dimension has been studied with a newly synthesized ferromagnetic organic radical crystal of 3-(4-chlorophenyl)-1,5-diphenyl oxoverdazyl. The characteristic field dependence of the magnetic heat capacity of this crystal is quantitatively explained by the theoretical values derived from the Bethe-ansatz technique applied to the quantum transfer matrix, with a unique intrachain exchange constant $J/k_{\rm B}$=5.5 K. By the simultaneous measurement of magnetic susceptibility and heat capacity, the three-dimensional ordering at $T_{\rm c}$=0.21 K, which is triggered by a weak interchain coupling $|zJ'|/k_{\rm B} = 3 \times 10^{-2}$, is confirmed.

INTRODUCTION

Magnetism in low dimensional lattice system has made great progress both theoretically and experimentally. The experiments have been carried out mostly with inorganic and/or metallic compounds in which inevitable anisotropies sometimes have masked the intrinsic feature expected theoretically. Qualitatively different quantum effects are expected between antiferromagnetic and ferromagnetic cases.

The Néel state is not an eigenstate of the Hamiltonian for the antiferromagnets. The interesting problems arising from this inherent property, such as RVB(resonating valence bond) state in the 1d S=1/2 system or VBS(valence bond solid) state in the S=1 system, have been successfully examined with abundant real antiferromagnetic compounds.

The 1d ferromagnetic state, on the contrary, is an exact eigenstate of the Hamiltonian of the 1d ferromagnets. The long-range ordered state is achieved at the lowest temperature $T \rightarrow 0$ K, with the critical index γ=2.0 in magnetic susceptibility $\chi \propto T^{-\gamma}$,or α =1/2 in heat capacity $C_m \propto T^{\alpha}$.[1,2] In addition to these critical properties, the next two points should be remarked. The anisotropies, which are treated as perturbation in 1d Heisenberg antiferromagnets, give significant effects in 1d ferromagnets. Even if a small Ising type anisotropy exists, it bring about dominant contribution of the bound-magnons whose energy level lies below the continuous energy band of spin waves.[3,4] This gives qualitative change in the thermodymamical quantities, especially in the applied fields. The other point is that we can rarely get 1d quantum ferromagnetic substances except a few compounds.

In this study, we focus on the quantitative analysis of the field dependence of magnetic heat capacity of a genuine organic compound,and attempt to check the validity of quantum statistics for the isotropic limit of Heisenberg interaction in one dimension.

EXPERIMENTALS

In this experiment, we use a genuine organic radical crystal 3-(4-chlorophenyl)-1,5-diphenyl-6-oxoverdazyl(p-CDpOV), which is one of the verdazyl radical derivatives whose magnetic properties are investigated by our systematic experiments. The syntheses of these radical crystals are reported elsewhere.[5] Heat capacities were measured above 0.1 K in the external magnetic field of 0-30 kOe, using the usual type of adiabatic calorimeter. The data were taken on about 0.5 g powdered sample. In the temperature range of 0.1-2 K, the heat capacities were measured simultaneously with the ac magnetic susceptibility by the use of a handmade Hartshorn bridge. The ac susceptibility was also measured independently by the Lake Shore ac susceptometer in the region of 1.7-300 K.

RESULTS AND DISCUSSION

The schematic molecular structure of p-CDpOV, which we consider here, is inset in Figure 1. The unpaired electron is expected nearly on each verdazyl radical.[6] Since the momentum for molecular orbitals is generally quenched in organic radicals, only electron spin of $S=1/2$ is relevant to the isotropic intermolecular interactions. Our results of ac magnetic susceptibility measurements, which are shown in Figure 1, can be accounted for the Curie-Weiss law above 13 K with a positive Curie-Weiss temperature $\theta=3.35$ K, $S=1/2$ and the g-factor $g=2.00$ which is nearly equal to $g_e=2.0023$ for a free electron. Below 13 K, the susceptibility deviates from the Curie-Weiss law and shows a characteristics of 1d ferromagnets as in the previous work on another verdazyl derivatives p-CDTV, for which $\theta=3.0$ and the intrachain exchange constant $J/k_B=6.0$ K are obtained.[7,8]

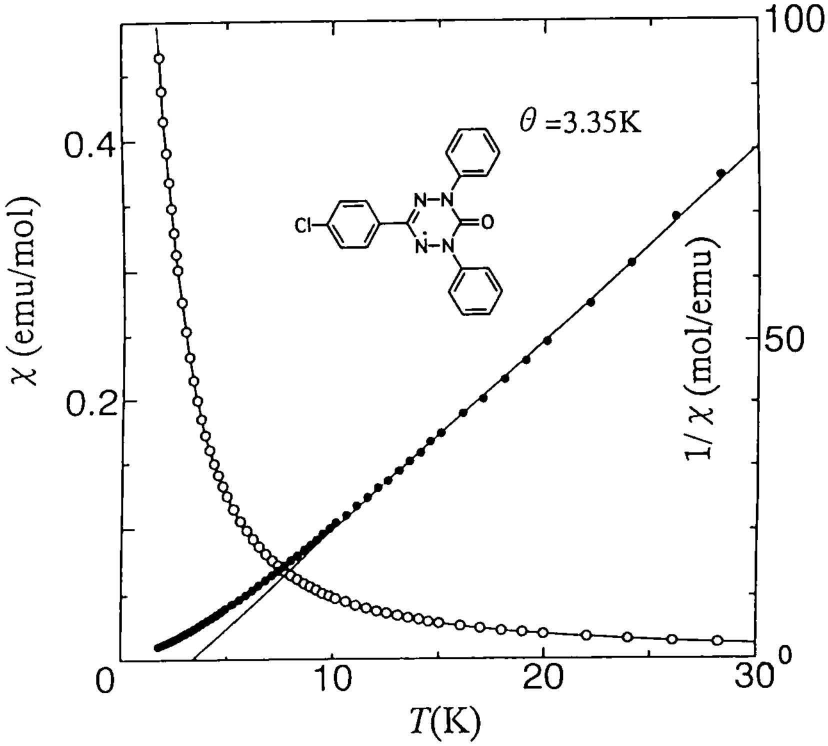

FIGURE 1 Magnetic susceptibility and inverse magnetic susceptibility of p-CDpOV.

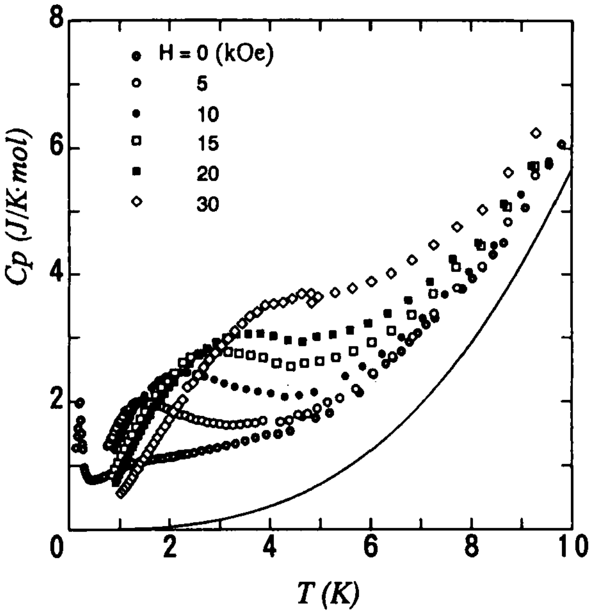

FIGURE 2 The field dependence of the heat capacity of p-CDpOV.

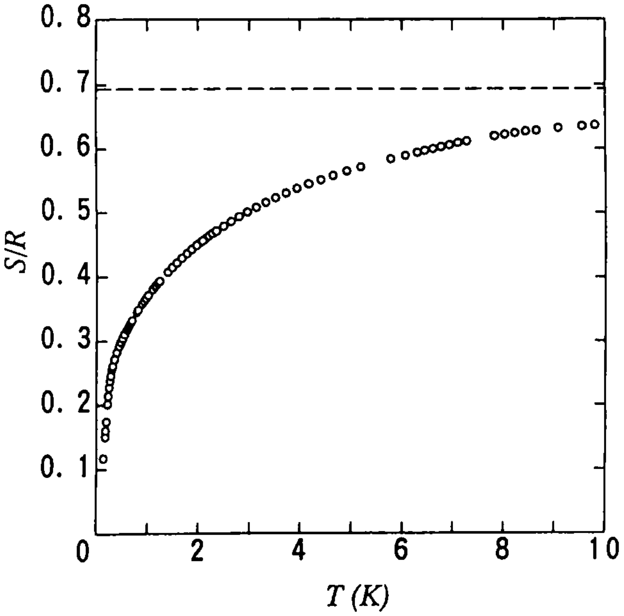

FIGURE 3 The temperature dependence of the magnetic entropy of p-CDpOV in zero field. The solid line indicates $\ln(2S+1)$ for $S=1/2$.

Figure 2 shows the overall results of the total heat capacity of p-CDpOV in external fields. To extract the magnetic heat capacity, we must subtract the lattice contribution $C_{\rm L}$, indicated with the solid line in Figure 2, which is estimated under the following assumptions. (1)The Debye functions to be determined is unique and independent of the fields. (2)The total magnetic entropy is $R\ln(2S+1)$ where $S=1/2$ as confirmed by the susceptibility measurements. (3)Above 10 K, the magnetic heat capacity of $C_{\rm m} = b(H)T^{-2}$ is valid as is usually reasonable in the paramagnetic region. In any case, the ambiguity of $C_{\rm L}$, if any, does not invalidate for the present discussion in the temperature range concerned. The temperature dependence of the magnetic entropy of p-CDpOV is given in Figure 3.

The field dependence of C_m is shown in Figure 4. There are two noteworthy points concerning the results at zero field. One is the indication of the three-dimensional

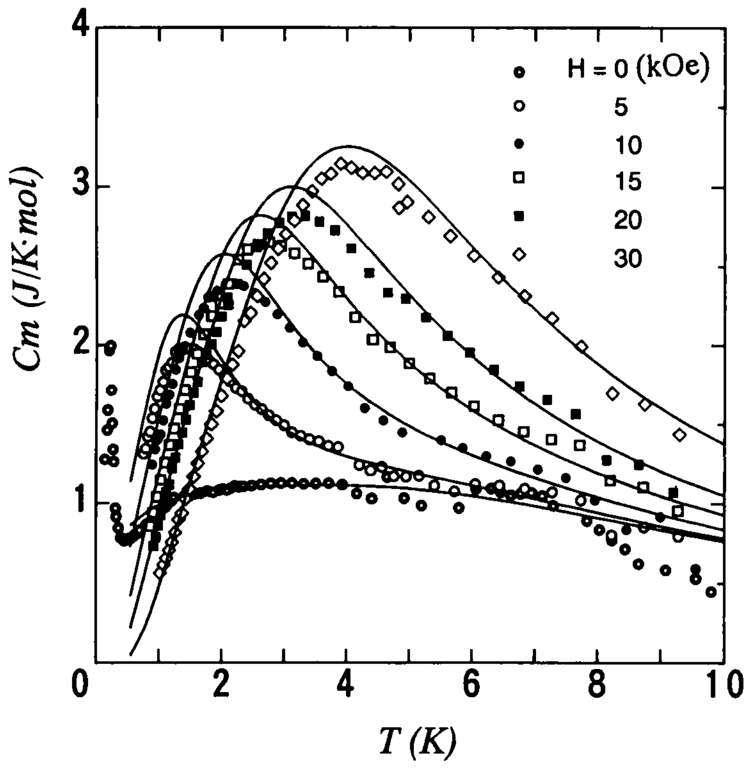

Figure 4 The field dependence of the magnetic heat capacity of p-CDpOV. The solid lines are the theoretical results for the $S=1/2$ ferromagnetic Heisenberg chain with $J/k_{\rm B}=5.5$ K.

ordering accompanied by a sharp peak at T_c=0.21 K, and the other is the appearance of a wide plateau centered around 1-4 K, with its maximum height of about $C_m \simeq 0.134R \simeq 1.11$(J/mol/K), which is a feature of 1d quantum ferromagnets.[1,2,9] (For the 1d Heisenberg antiferromagnet, the corresponding value is $C_m \simeq 0.35R$).[2,9] The peak is easily affected by the small field as will be discussed later, and another round hump appears, increases in height and shifts towards the high temperature region as the field increases. Ordinary ferromagnets do not show such a marked field dependence as in Figure 4. Some reasons for these results may be considered. The first is the excitation of magnetic solitons, and the second is the contribution of bound magnons due to the Ising type anisotropy.[3,4] There has not been the soliton theory for the isotropic quantum chain to describe the present results. The anisotropy of p-CDpOV is too small to excite bound magnons. Therefore we try to give a guantitative explanation of the field dependence of C_m by considering quantum statistics based on the Bethe-ansatz method developed by one of the present authors (M.T.).[10] For the Hamiltonian of the 1d ferromagnetic system

$$\mathcal{H} = -2J\sum_{i=1}^{N} \vec{S}_i \cdot \vec{S}_{i+1} - g\mu_B H \sum_{i=1}^{N} S_i^z \tag{1}$$

the free energy f(T,H) per spin is analytically given for a series of complex numbers $\{p_\ell, \ell = 1,2,3\cdots\}$ by

$$f(T,H) = -T\ln 2 - \frac{T}{2}\sum_{l=1}^{\infty} \ln\left[\frac{(1+p_l^2)(1+\overline{p_l}^2)}{[2\pi T(l-1/2)/J]^4}\right] \tag{2}$$

$$p_l = \frac{2\pi T}{J}\left(l-\frac{1}{2}\right) + \frac{g\mu_B H i}{J} + \frac{p_l}{1+p_l^2} + \frac{T}{Ji}\sum_{j=1}^{\infty} \ln\left[L(p_l,p_j)L(p_l-\overline{p_j})\right], \tag{3}$$

$$L(x,y) = \frac{1-(1-ix)^{-1}+iy}{1-(1+ix)^{-1}-iy}. \tag{4}$$

The heat capacity derived from f(T,H) is shown with solid curves in Figure 4, in which the best fit between the theory and the experiment is obtained for J/k_B=5.5 K. The contribution from the field induced soliton is expected to be minute in the system, although it is a problem left unsolved.

Here we give a qualitative understanding of this drastic field dependence of the 1d ferromagnet in comparison with the weak field dependence of the heat capacity of antiferromagnetic systems. When we consider the simplest chain with two spins, a dimer, the degeneracy (g_0) of the ground state is triplet (g_0=3) and that of the excited state is singlet, and vice versa for the antiferromagnetic case. For a longer chain with more spins, g_0 is always larger for the ferromagnetic case than for the antiferromagnetic case.[9] The degenerate levels are split by the application of the external field. The more multi-split levels appear, the more dominant the contribution of the heat capacity is at lower temperatures ($k_BT < J$).

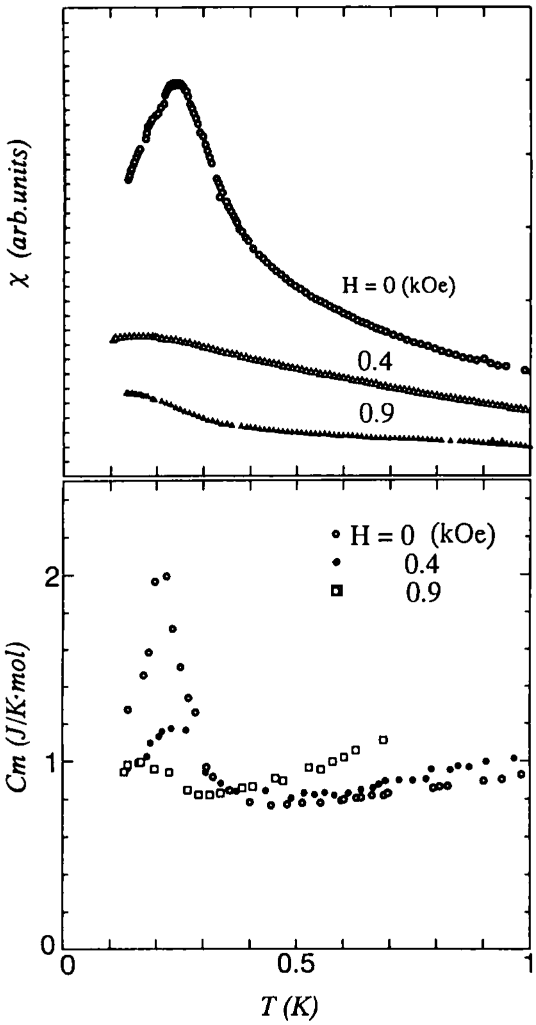

FIGURE 5 Magnetic susceptibility and heat capacity simultaneously observed in external fields.

We consider the interchain interaction J' which triggers the three-dimensional ordering at T_c=0.21 K. Figure 5 shows the results of the simultaneous observations of susceptibility and heat capacity near T_c. Based on the mean field theory, we can estimate the effective interchain coupling J' by a few independent procedures, for example, by $k_B T_c 2S^2(|zJ'|J)^{1/2}$, where z is the number of neighbouring chains. Using the value of T_c=0.21 K and J/k_B=5.5 K, we can estimate $|zJ'|/k_B = 3 \times 10^{-2}$ K, or $|zJ'|/J = 5 \times 10^{-3}$. The interchain exchange field is estimated as $H_c = 2|zJ'| < S > /g_B$=200 Oe. It is expected that the three-dimensional ordering becomes obscure in the field $H > H_c$, as is seen in the results for the powdered sample of p-CDpOV in Figure 4 and 5.

ACKNOWLEDGEMENT

This work was partly supported by the Grant-in-Aid for Scientific Research on Priority Area "Molecular Magnetism" (Area No.228/04242103, 04242104, and 04242101). We are grateful for valuable comments and experimental support by Dr.K.Konishi of Ehime University, and Mr.M.Ito and H.Sakita of Kyushu University.

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