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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

A Typical S=1/2 One-Dimensional Heisenberg Antiferromagnet: [3,3′-Diethyl-2,2′-Oxacarbocyanine]-$TCNQF_4$

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Version of record first published: 24 Sep 2006

To cite this article: Seishi Takagi, Masaharu Tanaka, Hiroyuki Deguchi, Masaki Mito & Kazuyoshi Takeda (1999): A Typical S=1/2 One-Dimensional Heisenberg Antiferromagnet: [3,3′-Diethyl-2,2′-Oxacarbocyanine]-$TCNQF_4$, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 334:1, 247-255

To link to this article: http://dx.doi.org/10.1080/10587259908023323

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Mol. Cryst. and Liq. Cryst., 1999, Vol. 334, pp. 247-255
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A Typical S=1/2 One-Dimensional Heisenberg Antiferromagnet: [3,3'-Diethyl-2,2'-Oxacarbocyanine]-$TCNQF_4$

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The measurements of the magnetic susceptibility, electron-spin-resonance (ESR) and heat capacity on the title substance have revealed that the substance is a typical S=1/2 Heisenberg antiferromagnetic chain. The intrachain exchange interaction energy is estimated to be J/k=-55K. No three-dimensional long range ordering due to interchain interaction has been observed down to 1.1K. Furthermore, the critical behavior of the magnetic susceptibility at low temperatures, which has been predicted theoretically by Eggert *et al.* (Phys. Rev. Lett. **73** (1994) 332), is successfully examined. The ESR linewidth of a single crystal, which strongly depends on the direction of the external magnetic filed, is well explained on the basis of the spin-diffusion theory for one-dimensional magnets.

Keywords: organic ion-radical salt; $TCNQF_4$; antiferromagnetic chain; magnetic susceptibility; ESR; heat capacity

INTRODUCTION

One-dimensional(1-D) Heisenberg antiferromagnets have been studied theoretically and experimentally for many years. The temperature dependence of the magnetic susceptibility for S=1/2 antiferromagnetic(AFM) short chains has been numerically calculated for the first time by Bonner and Fisher[1]. The Hamiltonian for the chains is expressed by

$$H = -2J\sum_{i=1}^{N} \boldsymbol{S}_i \cdot \boldsymbol{S}_{i+1} \quad , \qquad \boldsymbol{S}_{N+1} \equiv \boldsymbol{S}_1 \quad , \tag{1}$$

and they calculated the susceptibility numerically for values of N from 2 to 11. Since the exact value of the susceptibility at T=0K for an infinite chain, $\chi(0) \approx 0.05066\, g^2 \mu_B{}^2 / |J|$, had already been reported[2], they estimated the temperature dependence of the susceptibility for the infinite chain by extrapolation. The susceptibility shows a broad maximum, $\chi_{max} \approx 0.07346 g^2 \mu_B{}^2 / |J|$, at a temperature, $T_{max} \approx 1.282\,|J|/k$, and approaches the exact value at T=0K, $\chi(0)$, with the slope of $d\chi/dT \approx 0$. To the contrary, Eggert *et al.*[3] have calculated more accurately the susceptibility for the S=1/2 Heisenberg AFM infinite chain. According to their theory, the susceptibility approaches the limiting value, $\chi(0)$, with infinite slope of $d\chi/dT$, which is definitely different from the results by Bonner-Fisher.

From the experimental point of view to examine the critical behavior of χ for $T \rightarrow 0$, it is indispensable to start with an isotropic S=1/2 magnet in purely one dimension, because χ is sensitive to the anisotropy and the dimension of the system. Recently, the magnetic properties of two substances[4,5] have been reported in connection with the theory by Eggert *et al.* One is an inorganic magnet[4], Sr_2CuO_3, of which exchange interaction is rather large , J/k=-1100K. The critical behavior seems to be successfully observed beyond the anisotropy inherent to the electronic state of Cu^{2+} ion, and independently of the three-dimensional(3-D) long range AFM ordering below 5K. Another is one of the organic ion-radical salts[5], [3,3'-dimethyl-2,2'-thiazolinocyanine]-[7,7',8,8'-tetracyanoquinodimethane] (DMTzNC-TCNQ). Originally, magnetic behaviors in the purely organic compounds are described with the Heisenberg model for isotropic spins of unpaired electrons. The temperature dependence of the spin-susceptibility of the salt, DMTzNC-TCNQ, shows a broad maximum around 40K. The susceptibility above 10K is quantitatively explained by the Bonner-Fisher curve with J/k=-32.5K, whereas it seems that the susceptibility below 10K shows the characteristic slope reported by Eggert *et al.*[3] rather than the

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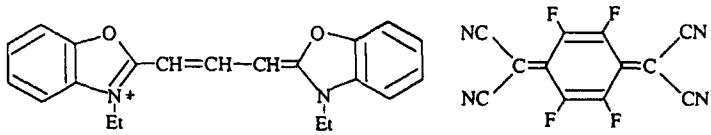
Bonner-Fisher curve[1]. The salt may be one of the substances of which susceptibility follows the theoretical results by Eggert *et al.*[3] The salt, however, seems to show an AFM phase transition below 2.0K which results from non-negligible interchain interaction.

In order to reduce the interchain interaction in such ion-radical salts, it is necessary to combine a large cation molecule with TCNQ. The large cation is expected to separate effectively TCNQ columns each other on which unpaired electrons with S=1/2 exist.

In this paper the experimental results on the susceptibility, electron-spin-resonance(ESR) and heat capacity as well as the crystal structure of an organic ion-radical salt are reported. The salt consists of 3,3'-diethyl-2,2'-oxacarbocyanine$^+$(DEOCC$^+$) and 2,3,5,6-tetrafluoro-7,7',8,8'-tetracyanoquinodimethane$^-$(TCNQF$_4^-$) (see Figure 1). The cation, DEOCC$^+$, is much larger than the cation, DMTzNC$^+$. The results show that the salt seems to be a typical S=1/2 Heisenberg antiferromagnetic chain.



(a) DEOCC$^+$ (b) TCNQF$_4$

FIGURE 1. Molecular structure of (a) DEOCC$^+$ and (b) TCNQF$_4$

The cation, DEOCC$^+$, is one of the cyanine dyes and makes 1:1 and 1:2 salt with TCNQ: DEOCC-TCNQ and DEOCC-[TCNQ]$_2$. The 1:1 salt shows typical paramagnetism of which susceptibility obeys Curie law, whereas the 1:2 salt is a low dimensional antiferromagnet with two-dimensional spin correlation at high temperatures[6]. The cation, DEOCC$^+$, also forms a 1:1 salt with TCNQF$_4$: DEOCC-TCNQF$_4$. The TCNQF$_4$ molecule is obtained by replacing the four hydrogen atoms of TCNQ with four fluorine atoms and then is a little larger than TCNQ molecule. The chemical structure of the two elements of the salt are shown in Figure 1.

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EXPERIMENTAL PROCEDURES

The salt, DEOCC-$TCNQF_4$, was synthesized by the standard method and crystallized by slow cooling of an acetonitrile solution. The crystals were crushed into powder and the powder specimen was used for the measurement of magnetic susceptibility. The susceptibility was measured in the temperature range of 1.5-300K and at the magnetic field of 7.22kOe using a Faraday-type magnetic balance with a conventional cryostat[7]. The crystal structure of the salt was determined using an X-ray automatic diffractometer (RIGAKU RASA7). The ESR measurements were carried out for a single crystal of the salt down to 1.4K using a standard ESR spectrometer (JEOL JES-RX2X) with a conventional cryostat. A conventional adiabatic calorimeter was employed to measure the heat capacity in the temperature range of 1.1-10K.

EXPERIMENTAL RESULTS AND DISCUSSION

The crystal of the present salt is monoclinic with the space group $P2_1/n$ and lattice constants a=11.568(3), b=15.469(4), c=16.964(2) Å, β=103.57(1), U=2951.0(9) $Å^3$ and Z=4. For the convenience, a'-axis is defined to be perpendicular to the bc-plane. Fractional atomic coordinates and thermal factors are provided for request.

The crystal structure viewed along the a-axis is shown in Figure 2. There are four DEOCC and $TCNQF_4$ molecules in a unit cell. The planer DEOCC and $TCNQF_4$ molecules are stacked separately along the a-axis making columns. As the cation, $DEOCC^+$, is rather large, the $TCNQF_4$ columns are significantly separated each other by the cation columns. Only one $TCNQF_4$ column is shown in Figure 3 to demonstrate the column structure. Since unpaired electrons are supposed to be on $TCNQF_4$ molecules, the salt is magnetically approximated as an S=1/2 Heisenberg AFM chain.

The paramagnetic susceptibility of the salt is shown in Figure 4 as a function of temperature. The low temperature region of the susceptibility is enlarged and inset in the figure. The diamagnetic susceptibility of each

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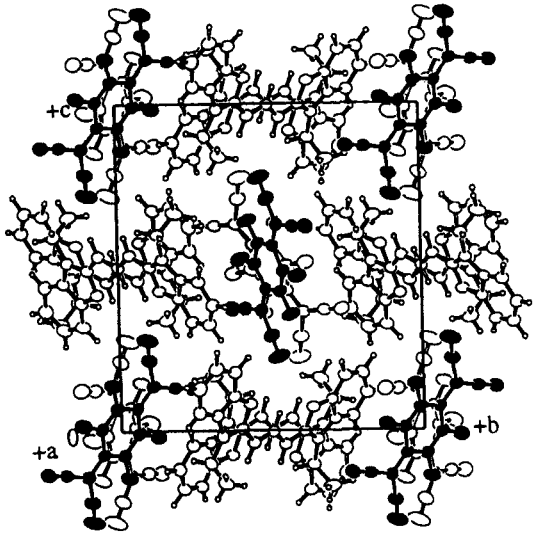

FIGURE 2. Crystal structure viewed along the *a*-axis

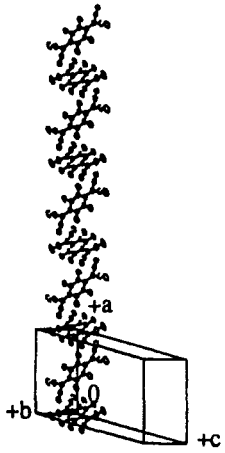

FIGURE 3. $TCNQF_4$ column

component has been corrected. The small increase of the susceptibility below 10K is attributable to the small amount of paramagnetic impurities. The susceptibility shown in the inset is corrected for the paramagnetic impurities of 0.05% mole. Passing through a maximum around 70K, the susceptibility decreases monotonically with decreasing temperature down to 1.5K. The dotted curve is the Bonner-Fisher curve with J/k=-55K, while the solid curve shows the theoretical results with J/k=-55K reported by Eggert *et al.* Above 15K, the susceptibility is quantitatively explained by these theoretical curves. Below 15K, however, it begins to deviate from the Bonner-Fisher curve and seems to give the infinite slope of d χ/dT at lower temperatures as reported by Eggert *et al.*[3] The inflection point of χ is expected to be at T=0.174 | J | /k from the theory[3], which corresponds to 9.6K for the present salt with J/k=-55K. It is found in the inset in Figure 4 that the slope of χ starts to increase below 3K.

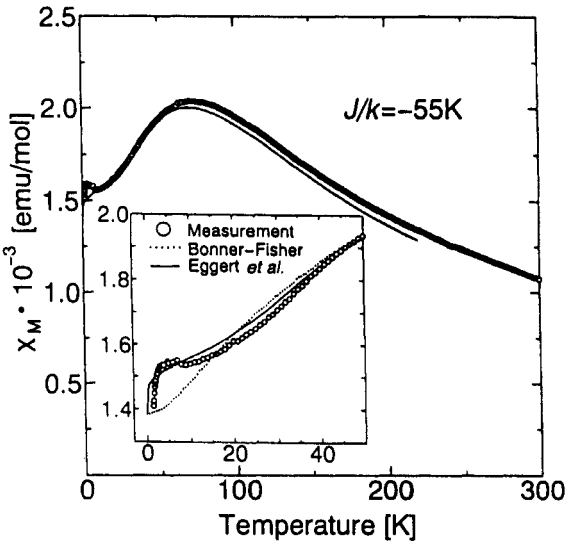

FIGURE 4. Temperature dependence of the paramagnetic susceptibility of the salt. The low temperature region of the susceptibility is enlarged and inset in the figure.

A single-line ESR absorption is observed from room temperature down to 1.4K. Although the linewidth depends on the temperature and the orientation of the single crystal, the g-factor of the crystal hardly depends on the temperature and the anisotropy of the g-factor is less than 10^{-3}. The angular dependence of the ESR linewidth in the b-plane is shown in Figure 5, where θ is the angle between the a'-axis and the direction of the external magnetic field. The linewidth goes through minima at approximately $\pm 50^{\circ}$ with relative maxima at 0° and $\pm 90^{\circ}$. Namely, it shows a typical W-shaped angular dependence which is observed for low-dimensional magnets[8,9]. Though the linewidth decreases with decreasing temperature, the W-shaped angular dependence remains unchanged even at 4.2K.

According to the theory of the ESR for one-dimensional magnets[8], the angular dependence of the linewidth, $\Delta H(\theta)$, is described by an expression,

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$$\Delta H(\theta) = A\left|3\cos^2\theta - 1\right|^{4/3} \qquad (2)$$

, where A is a constant and θ is the angle between the magnetic chain axis and the direction of external magnetic field. The $TCNQF_4$ molecules are not stacked along the a'-axis but along the a-axis in the salt. Since the angle between the a- and a'-axis is 13.6°, the expression (2) should be modified as follows to be compared with the experimental results:

$$\Delta H(\theta) = A\left|3\cos^2(13.6^\circ)\cdot\cos^2\theta - 1\right|^{4/3}$$

$$\approx A\left|2.8\cos^2\theta - 1\right|^{4/3}. \qquad (3)$$

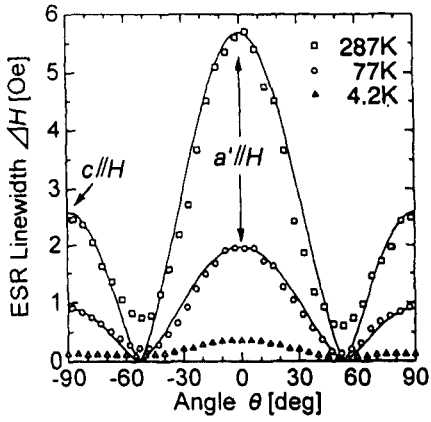

FIGURE 5. Angular dependence of the ESR linewidth in the b-plane.

The solid lines in Figure 5 show the linewidth described by the expression (3), where the constant A was determined to be 0.9 Oe at 77K and 2.6 Oe at 287K, respectively. The angular dependence of the linewidth can be well described by the expression (3) which is based on the spin-diffusion theory for one-dimensional magnets.

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Figure 6 shows the results of the heat capacity measurements on the salt. There is no anomaly down to 1.1K. The residual entropy below 1.1K is estimated to be 0.124J/(K • mol) including the lattice contribution, which corresponds to only 2.15% of total magnetic entropy $Nk \cdot \ln(2S+1)$. Considering the absence of the 3-D long range ordering down to 1.1K, we estimate the permissible maximum value of effective interchain interaction zJ', if any, to be $| zJ'/J | < 2 \times 10^{-3}$ from the mean field theory which gives a relation $kT_c \cong 2S^2 \sqrt{| zJ'J |}$. In this theory, however, quantum fluctuations are not taken into consideration. Since the spin value is S=1/2 in the salt, quantum fluctuations in the salt seems to become dominant at lower temperatures. Therefore, it seems that the 3-D long range ordering no longer occurs in the salt even below 1.1K.

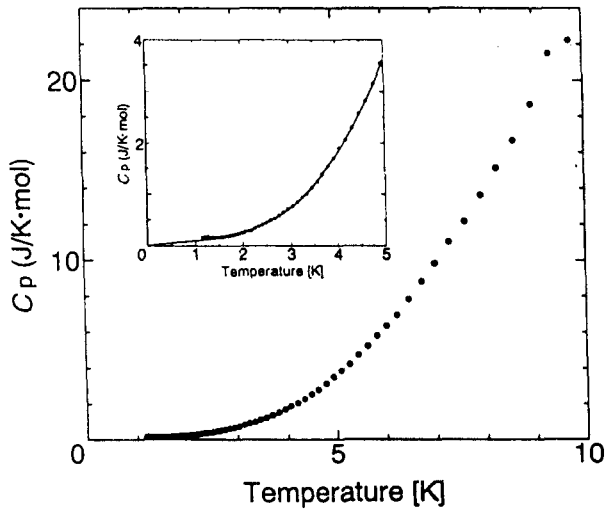

FIGURE 6. Low-temperature heat capacity of the salt. The inset shows the overall results up to 5K.

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CONCLUSION

In conclusion, the organic salt, DEOCC-TCNQF$_4$, is a typical S=1/2 Heisenberg AFM chain where the one-dimensional critical behavior of the susceptibility predicted by Eggert *et al.* is observed as well as the characteristic ESR linewidth expected for 1-D Heisenberg antiferromagnets. The 3-D long range ordering is not detected down to 1.1K below which quantum fluctuations are expected to overwhelm weak interchain interactions.

Acknowledgments

The X-ray crystal analysis and ESR measurements were carried out at The Center for Instrumental Analysis, Kyushu Institute of Technology. This work was partially supported by The C.O.E. Research Fund of Kyushu Institute of Technology.

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