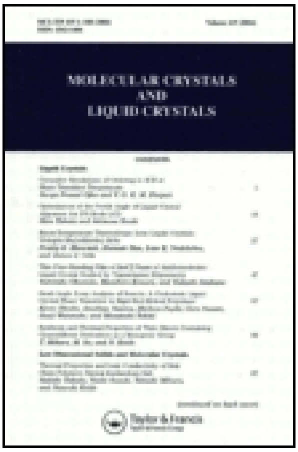

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Magnetic Properties of Organic Spin-Ladder Systems, (BDTFP) 2 X (PhCl) 0.5

Toshikazu Nakamura [a], Kazuko Takahashi [b], Toshi-Hiro Ise [c], Takashi Shirahata [c], Mikio Uruichi [a], Kyuya Yakushi [a] & Takehiko Mori [d]

[a] Institute for Molecular Science, Okazaki, 444-8585, Japan

[b] Center for Interdisciplinary Research, Tohoku University, Sendai, 980-8578, Japan

[c] Department of Chemistry, Tohoku University, Graduate School of Science, Sendai, 980-8577, Japan

[d] Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Tokyo, 152-8552, Japan

Version of record first published: 18 Oct 2010

To cite this article: Toshikazu Nakamura, Kazuko Takahashi, Toshi-Hiro Ise, Takashi Shirahata, Mikio Uruichi, Kyuya Yakushi & Takehiko Mori (2002): Magnetic Properties of Organic Spin-Ladder Systems, (BDTFP) 2 X (PhCl) 0.5, Molecular Crystals and Liquid Crystals, 376:1, 95-100

To link to this article: http://dx.doi.org/10.1080/713738390

Mol. Cryst. Liq. Cryst., Vol. 376, pp. 95-100

1058-725X/02 $12.00 + .00

Magnetic Properties of Organic Spin-Ladder Systems, $(BDTFP)_2X(PhCl)_{0.5}$

TOSHIKAZU NAKAMURA[a], KAZUKO TAKAHASHI[b], TOSHI-HIRO ISE[c], TAKASHI SHIRAHATA[c], MIKIO URUICHI[a], KYUYA YAKUSHI[a] and TAKEHIKO MORI[d]

[a]*Institute for Molecular Science, Okazaki 444-8585, Japan,*
[b]*Center for Interdisciplinary Research, Tohoku University, Sendai 980-8578, Japan,*
[c]*Department of Chemistry, Tohoku University, Graduate School of Science, Sendai 980-8577, Japan and*
[d]*Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Tokyo 152-8552, Japan*

Magnetic investigation was carried out for quasi-one-dimensional organic conductors, $(BDTFP)_2X(PhCl)_{0.5}$ (X=AsF_6, PF_6). They show Metal-Insulator transitions at low temperatures. To clarify the mechanism of the transitions, we performed ESR and NMR measurements. The low temperature electronic states of the title compounds are discussed by a microscopic point of view.

Keyword organic conductor; EPR; antiferromagnetic transition; spin singlet

INTRODUCTION

Recently there is significant interest in two-leg spin ladder systems because it may be a candidate of high-T_c superconductor. The BDTFP shown in Fig. 1 is an organic donor molecule recently synthesized by the Tohoku Univ. group [1]. Its cation radical salts, $(BDTFP)_2X(PhCl)_{0.5}$ (X=AsF_6, PF_6), are quasi-one-dimensional organic conductors with so-called two leg ladder structures; the inter-

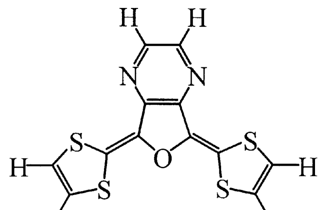

FIGURE 1 Molecular structure of BDTFP.

ladder interaction is one-order smaller than that in intra-ladder [1]. Since there is a considerable dimerization within the column, the upper band is a half-filled. They show metal to insulator transitions at low temperatures, but the mechanism of them is an open question. To clarify the low temperature electronic states, we performed ESR and NMR measurements. The low temperature electronic states of the spin-ladder systems, $(BDTFP)_2X(PhCl)_{0.5}$, are discussed by a microscopic point of view.

EXPERIMENTAL

Sample preparation and crystal structural data were shown in previous reports [1]. The ESR measurements were carried out for a single crystal using an X-band spectrometer, Bruker ESP-300E, with a rectangular cavity: TM110. The temperature range of the ESR measurements were between 300 K and 4 K. The ^{1}H-NMR measurements were performed by using a pulsed-NMR spectrometer operated at 104.33 MHz using a single crystal. The spin-lattice relaxation rate of ^{1}H-NMR, ^{1}H-T_1^{-1}, was measured by the recovery of the magnetization with the integration strength of the spin-echo signals. While the nuclear magnetic relaxation curves in the paramagnetic state showed single exponentials, those in the antiferromagnetic state did not show single exponentials. Hence we tentatively defined ^{1}H-T_1^{-1}

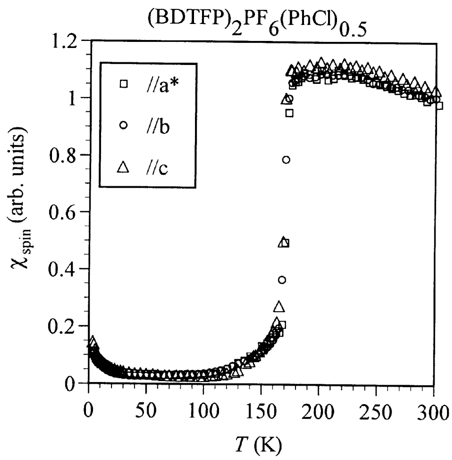

FIGURE 2 Temperature dependence of the spin susceptibility of the PF_6 salt determined by the EPR signal intensity of a single crystal.

as the initial slope of the relaxation curve as a weighted average of the relaxation rate. The ^{1}H-NMR absorption lines obtained by fast Fourier transform (FFT) of the spin-echo signals at different temperatures.

RESULTS AND DISCUSSION

We have performed ESR measurements of the BDTFP salts with counter anions of PF_6 and AsF_6. The low temperature properties of them are quite different from each other although those at R.T. are very similar.

Figure 2 shows the temperature dependence of the spin susceptibility of the PF_6 salt determined by the signal intensity of Electron Paramagnetic Resonance (EPR) for a single crystal. The result is in excellent agreement with that by SQUID measurements [1]. Between 170 and 300K, the spin susceptibility is almost temperature

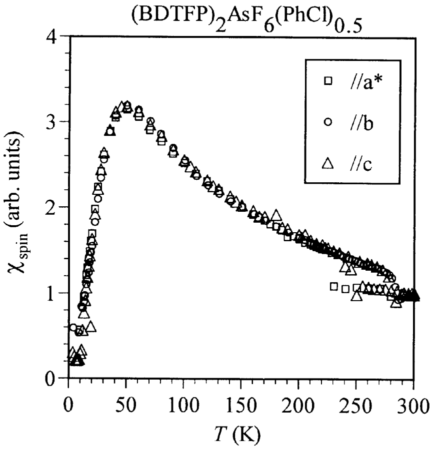

FIGURE 3 Temperature dependence of the spin susceptibility of the AsF_6 salt for a single crystal.

independent, but gradually increases as temperature decreases. The PF_6 salt is highly electrically conducting in this temperature region. The EPR signal intensity suddenly decreases below 170 K where the resistivity shows an abrupt jump. The energy gap determined by the intensities of residual EPR signals is evaluated as $E_g \sim 59$ K. The EPR linewidth also shows anomaly; it abruptly decreases around 170 K, suggesting an abrupt change of the relaxation mechanism of the electron spins. It probably corresponds with the sharp increase of the electric resistivity. Although the mechanism of the transition is still an open question, it is proved that the low temperature phase of the PF_6 salt is spin-singlet.

Figure 3 shows the temperature dependence of the spin susceptibility of the AsF_6 salt. In the case of the cooling process, the spin susceptibility abruptly increases around 230 K, suggesting the existence of a phase transition. Below 200K, the spin susceptibility of the AsF_6 salt shows a Curie-like enhancement. The temperature of

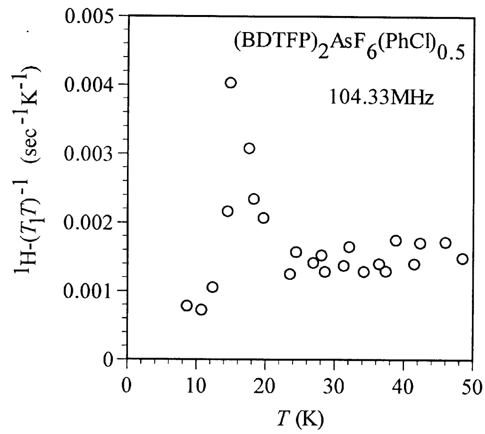

FIGURE 4 Temperature dependence of the [1]H-NMR spin-lattice relaxation rate, $(T_1T)^{-1}$ of the AsF_6 salt for a single crystal.

the spin susceptibility jump differs in the warming and cooling processes. This hysteresis phenomenon indicates that the transition is of first order. The EPR linewidth abruptly decreases associated with the transition; it also indicates an abrupt change of the relaxation mechanism as seen in the PF_6 salt. However the absolute value of the linewidth of the AsF_6 salt at low temperature phase is obviously larger than that of the non-magnetic PF_6 salt. Therefore the low temperature phases are undoubtedly different between the AsF_6 and PF_6 salts. Below 50 K, the spin susceptibility of the AsF_6 salt turns to decrease, indicating spin-gap behavior. It fits with Troyer's prediction for the undoped two-leg ladder [2]. However the EPR signal abruptly disappeared at 14 K, with line broadening.

Temperature dependence of the [1]H-NMR spin-lattice relaxation rate, $(T_1T)^{-1}$ of the AsF_6 salt for a single crystal exhibits a peak around 14 K as seen in Fig. 4. Taking into account the EPR results, the 14 K peak of the ^{1}H-$(T_1T)^{-1}$ is undoubtedly due to an antiferromagnetic transition. The linewidth of the ^{1}H-NMR absorption lines starts to deviate from the constant values and shows significant broadening below 14 K; it is a clear evidence of the onset of the additional local field. However the weak broadening suggests the small local magnetization. Detailed analysis of the NMR results will be discussed elsewhere.

In conclusion, we investigated the low temperature electronic state of the BDTFP salts by the ESR and ^{1}H-NMR measurements. Although the electronic states of the PF_6 and AsF_6 salts at R.T. are very similar, those at low temperatures are quite different: The PF_6 salt undergoes a spin-singlet transition around 170 K. On the other hand, the AsF_6 salt shows a drastic transition of first order around 230 K, associating with an abrupt jump of the spin susceptibility. Below 50 K, the spin susceptibility of the AsF_6 salt shows spin-gap behavior. However the ground state of the AsF_6 salt is not a spin-singlet one. Existing an antiferromagnetic transition suggests considerable inter-ladder interaction.

Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (B) of "Molecular Conductors and Magnets" (Area No. 730/11224213) from the Ministry of Education, Science, Sports and Culture of Japan.

References

1. T. Ise, T. Mori and K. Takahashi, J. Mater. Chem., (2001) in press.
2. M. Troyer, H. Tsunetsugu and D. Wurtz., Phys. Rev. , **B50**, 13515 (1994).