Proceedings of the 15th Czech and Slovak Conference on Magnetism, Košice, Slovakia, June 17–21 2013

Spin-Peierls Transition in (N-Me-Tetra-Me-Pz)(TCNQ)$_2$

M. Kajňaková[a,*], M. Botko[a], V. A. Starodub[b], E. Čižmár[a] and A. Feher[a]

[a]Institute of Physics, Faculty of Sciences, P. J. Šafárik University, Park Angelinum 9, 041 54 Košice, Slovakia

[b]Institute of Chemistry, Jan Kochanowski University of Humanities and Sciences, Świętokrzyska 5G, 25-406 Kielce, Poland

The new organic anion-radical salt (N-Me-Tetra-Me-Pz)(TCNQ)$_2$, (Pz = pyrazine) was studied as a low dimensional magnetic system. Heat capacity and EPR studies were performed in the temperature range from 2 to 300 K. The magnetic susceptibility was measured in the temperature range from 2 to 300 K and in magnetic fields of 100 mT and 1 T. The magnetic properties of this new system can be described as a dimerized Heisenberg spin $S = 1/2$ chain possessing a spin-Peierls transition at 42 K.

DOI: 10.12693/APhysPolA.126.254

PACS: 64.60.i, 75.10.Jm, 75.50.Xx, 76.30.v

1. Introduction

The spin-Peierls (sP) transition occurs in systems of uniform low-dimensional Heisenberg antiferromagnets undergoing a transition to a spin-dimerized state [1]. The sP transition has a magneto-elastic origin, where the decrease of the magnetic free energy due to the formation of singlet spin pairs outweighs the increase in lattice free energy arising from the dimerization of the regular array of spins. The temperature dependences of both the magnetic susceptibility and the heat capacity of (N-Me-tetra-Me-Pz)(TCNQ) is described by a dimerized spin $S = 1/2$ Heisenberg chain model with the sP phase transition.

2. Experimental method

The temperature dependence of the susceptibility of a polycrystalline sample (32 mg) was investigated in a commercial Quantum Design MPMS apparatus in the temperature range from 2 K to 300 K and in applied magnetic fields of 100 mT and 1 T, zero-field cooling and field-cooling. Temperature dependence of the heat capacity of a pressed pellet (1.8 mg) was investigated in the temperature range from 2 K to 300 K in zero magnetic field using a commercial Quantum Design PPMS. The ESR spectra of a powder sample (0.3 mg) were measured in the temperature range from 2 K to 300 K using the X-band spectrometer Bruker ELEXSYS E500.

3. Crystal structure

The sample preparation method and the detailed crystallographical characterization of (N-Me-tetra-Me-Pz)(TCNQ)$_2$ are given elsewhere [2]. The crystal structure is formed by [N-Me-Tetra-Me-Pz]$^+$ cation columns and two types of TCNQ$^{\bullet-}$ anion-radicals (A and B), aligned along the c axis (Fig. 1). Whereas the cations are nearly planar, the anions are practically flat. In all the anion columns, A and B overlap in a slightly different manner, leading to a weak structural dimerization of the TCNQ molecules.

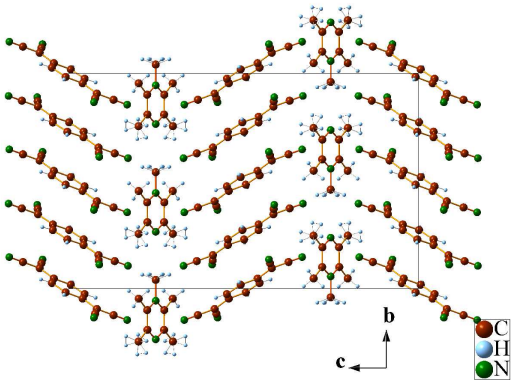

Fig. 1. The insight of the crystal structure of the radical salt (N-Me-tetra-Me-Pz)(TCNQ)$_2$ in bc-plane.

4. Results and discussion

The magnetic susceptibility shows a flat maximum at ~300 K (Fig. 2). At 42 K, the susceptibility bends abruptly and decreases exponentially to zero, whereas the low-temperature increase is attributed to free chain. Such an exponential decrease indicates a transition of the system from a magnetic state to the state with $S = 0$, typical for the presence of the sP transition.

According to the Bardeen-Cooper-Schrieffer type formula proposed by Orignac et al. [3] for the sP transiton

$$\frac{\Delta(T=0)}{T_{SP}} \approx 2.47,$$

where Δ is the energy gap due to the sP transition and T_{SP} is the transition temperature. The energy gap in the excitation spectra reaches to $\Delta \sim 108$ K ($T = 0$) [4] and $T_{SP} = 42$ K, then the ratio by Orignac's theory is 2.47. Consequently, we can consider studied system as a system in which the sP transition exists.

*corresponding author; e-mail: marcela.kajnakova@upjs.sk

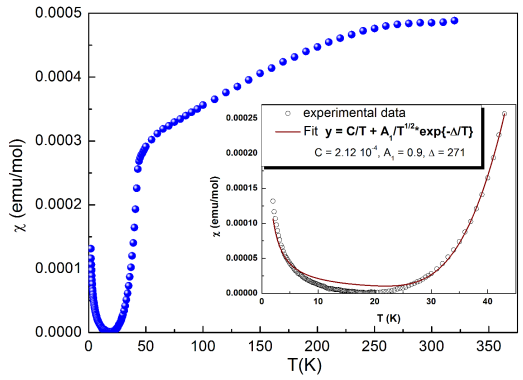

Fig. 2. The magnetic susceptibility of (N-Me-Tetra-Me-Pz)(TCNQ)$_2$. Inset: The low-temperature part of the magnetic susceptibility fitted by formula containing: paramagnetic impurities part and exponential part of sP transition [4].

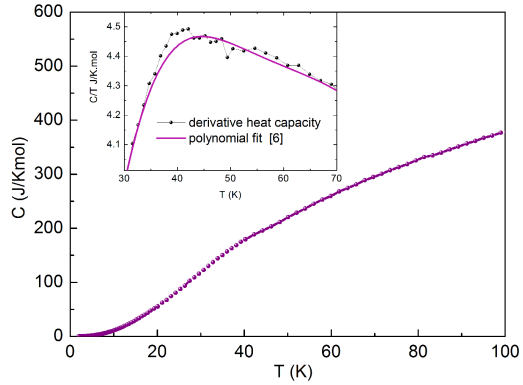

Fig. 3. The heat capacity measured in the temperature range from 2 K to 300 K. Inset shows C/T vs. T plot fitted by a polynomial function. The area over the fit (between the fit and the experimental data) is used for a calculation of the possible entropy gain due to the sP transition.

The temperature dependence of the heat capacity (Fig. 3) is characterized by of a small peak at $\sim$ 45 K, which coincides with the temperature of the sharp decrease in the magnetic susceptibility (inflection point in Fig. 2).

As shown by Nakazawa et al. [5], the sP transition can be detected and enhanced in the derivative of temperature dependence of the heat capacity, therefore the experimental data of C/T versus T was fitted by a polynomial function of temperature up to 9th order (Fig. 3 inset). In this way, we obtain an "excess" of the heat capacity ΔC_p around the transition peak. The height of the heat capacity peak (i.e. the peak area above the polynomial function fit) posses an entropy value of 2.08 J/K·mol, which yields 36% of total entropy of a system with the spin $S = 1/2$. The value of the entropy removal in the peak area is consistent with the sP image [5]. These features of the heat capacity allow us to identify our system as one undergoing a sP, because if it occurs, additional entropy, originating from the changes in the soft modes of lattice vibrations, should be considered [5].

The intensity of EPR signal decreases exponentially below 45 K (Fig. 4), which agrees with the susceptibility decrease and with the peak at $\sim$ 45 K in heat capacity. Such an exponential decrease indicates a transition to the state with magnetic excitations separated from the $S = 0$ (singlet) ground state by an energy gap typical for the sP transition [6]. The intensity of EPR transitions observed below the transition temperature is described by thermally activated behavior with the formula in the Fig. 4.

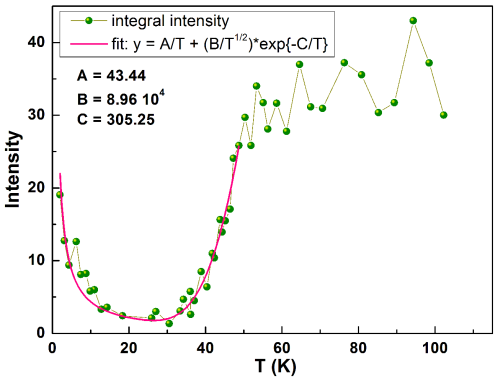

Fig. 4. The temperature dependence of the integral intensity of EPR signal.

5. Conclusions

The new organic magnetic system studied in this work has been identified as a dimerized Heisenberg spin $S = 1/2$ chain that possesses a spin-Peierls transition. This description was observed experimentally by the temperature dependences of magnetic susceptibility, heat capacity, and EPR, and was confirmed by comparison with the predicted theoretical expectation.

Acknowledgments

This work was supported by the Slovak Research and Development Agency under the contract No. APVV-0132-11 and by the Slovak Grant Agency VEGA 1/0145/13.

References

[1] E. Pyte, *Phys. Rev. B* **10**, 4637 (1974).

[2] O.N. Kazheva, D.V. Ziolkovskiy, G.G. Alexandrov, A.N. Chekhlov, O.A. Dyachenko, V.A. Starodub, A.V. Khotkevich, *Synthetic Metals* **156**, 1010 (2006).

[3] E. Orignac, R. Chitra, *Phys* **70**, 214436 (2004).

[4] I.S. Jacobs, J.W. Bray, H.R. Hart, Jr., L.V. Interrante, J.S. Kasper, G.D. Watkins, D.E. Prober, J.C. Bonner, *Phys. Rev. B* **14**, 3036 (1976).

[5] Y. Nakazawa, A. Sato, M. Seki, K. Saito, K. Hiraki, T. Takahashi, K. Kanoda, M.Sorai., *Phys. Rev. B* **68**, 085112 (2003).

[6] S.A. Zvyagin, J. Krzystek, P.H.M. van Loosdrecht, G. Dhalenne, A. Revcolevschi, *Physica B: Condensed Matter* **346-347**, 1 (2004).