Magnetic Specific Heat of Anion-Radical Salt

[Ni(bipy)$_3$](TCNQ)$_4$·(CH$_3$)$_2$CO at Very Low Temperatures

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Thermodynamic studies of the anion-radical salt system [Ni(bipy)$_3$](TCNQ)$_4$·(CH$_3$)$_2$CO, where TCNQ is 7,7′,8,8′-tetracyano-quinodimethane, are reported. The anion-radical salt systems based on TCNQ belong to a material class in which the arrangement of the anion-radical salt has considerable impact on the charge transfer and magnetic properties. The crystal structure of the studied compound consists of [Ni(bipy)$_3$]$^{2+}$ cations containing Ni$^{2+}$ ions and four types of crystallographically independent anion-radicals TCNQ$^-$ (A, B, C and D). These TCNQ$^-$ radicals form two different types of TCNQ$^-$ stacks (AABB and CCDD), where a strong exchange interaction is expected. The temperature dependence of the specific heat of a single crystal was studied in magnetic fields up to 5 T and in the temperature range from 0.4 K to 30 K. The temperature dependence of specific heat displays a broad Schottky-like maximum above 0.4 K. Using a single-ion approximation, the analysis of the temperature dependence of the specific heat below 10 K yields values for the anisotropy parameters, $D/k_B = -1.95$ K and $E/k_B = 0.3$ K. These results suggest that the observed maximum in the specific heat originates from Ni$^{2+}$ ions while the exchange interaction between the transition metal ions and the TCNQ is negligible.

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1. Introduction

The anion-radical salt (ARS) systems based on TCNQ are distinguished by wide spectrum of magnetic, electric, and optical properties. These compounds are able to form low-dimensional magnets, and the arrangements of the ARS complexes have considerable impact on the charge transfer and magnetic properties. Materials formed by a connection of metal ions and organic radicals in a crystal structure can combine the properties of organic and inorganic components that can be used in various applications [1–6].

Herein, an investigation of the thermodynamic properties of the ARS system [Ni(bipy)$_3$](TCNQ)$_4$·(CH$_3$)$_2$CO, which contain Ni$^{2+}$ ions, are presented. The low-temperature specific heat is analyzed in the framework of a single-ion anisotropy approximation of Ni$^{2+}$ ions.

2. Crystal structure and experimental details

The compound [Ni(bipy)$_3$](TCNQ)$_4$·(CH$_3$)$_2$CO has a layered crystal structure (Fig. 1), which is formed by the [Ni(bipy)$_3$]$^{2+}$ cation, containing a Ni$^{2+}$ ion, and four types of anion-radicals of TCNQ$^-$ (A, B, C and D) with different bond lengths within the radicals and by the position in the unit cell. Subsequently, TCNQ$^-$ form two types of stacks (AABB and CCDD). Layers of anion-radical stacks alternate with cation sequences along crystallographic c-axis. The synthesis procedure of the compound and detailed crystal structure, including IR absorption and the Raman spectra studies, were reported previously [7].

Fig. 1. The crystal structure of [Ni(bipy)$_3$](TCNQ)$_4$·(CH$_3$)$_2$CO [7]. The text describes the TCNQ$^-$ notation of A, B, C, and D.

Needle-like shaped crystals of [Ni(bipy)$_3$](TCNQ)$_4$·(CH$_3$)$_2$CO with a maximum dimensions up to 2 mm were used in our investigation. The temperature dependence of the specific heat was investigated on a single crystal using a Quantum Design PPMS equipped with a $^4$He refrigerator that was...
operated in the temperature range from 0.38 K to 35 K and in magnetic fields from 0 T to 5 T. The magnetic field was applied parallel to the crystallographic c-axis.

3. Experimental results

The temperature dependence of specific heat of [Ni(bipy)₃]((TCNQ)₄·(CH₃)₂CO is shown in Fig. 2. In zero magnetic field, an increase with decrease of temperature is observed below 2 K, and no anomaly or maximum can be resolved. After the application of the magnetic field parallel to the c-axis, the specific heat displays a broad Schottky-like maximum below 10 K.

At the lowest temperatures, the total specific heat can be approximated by the sum of lattice and magnetic subsystem contributions. The lattice contribution to the total specific heat is usually approximated by a $T^3$ dependence at the low temperatures. Since the studied system has a quasi-one-dimensional crystal structure, the lattice contribution can be more accurately described by a relation

$$C_{\text{latt}} = \alpha T + \beta T^3,$$

where $\alpha$ and $\beta$ are fitting parameters. The high temperature approximation of the magnetic contribution can be described by a Maxwell relation which yields \cite{8,9}:

$$C_{\text{mag}} = \gamma T^2 \exp(-\delta T^2),$$

where $\gamma$ and $\delta$ are fitting parameters. The temperature dependence of specific heat in zero magnetic field was then fitted by

$$C_{\text{tot}} = C_{\text{latt}} + C_{\text{mag}}$$

(3)

in temperature range 2.5–6.5 K (see Fig. 3). Subsequently, the temperature dependence of the magnetic specific heat was obtained by subtracting the lattice contribution from the total specific heat, and the resulting values of the fitting parameters are presented in Table I.

Since the possible broad maximum in the temperature dependence of specific heat in zero magnetic field extends below our range of measurement, the magnetic entropy of the studied compound was calculated from the specific heat measured at 2 T. This analysis yielded 8.9 J/(mol K), and this value is in good agreement with theoretical magnetic entropy of a spin $S = 1$ system of $S_{\text{th}} = R \ln(2S + 1) = 9.1$ J/(mol K). This result suggests that only Ni²⁺ ions contribute to the low temperature magnetic specific heat. The magnetic contribution due to the $S = 1/2$ spins of TCNQ⁻ radical pairs is presumably shifted to very high temperatures due to the strong exchange coupling within the one-dimensional TCNQ stacks.

Subsequently, the temperature dependence of magnetic specific heat in zero magnetic field was used to estimate the single-ion anisotropy parameters $D/k_B = -1.95$ K and $E/k_B = 0.3$ K assuming isolated Ni²⁺ ions (Fig. 4). The sign of the single-ion anisotropy parameter $D$ is negative according to the analysis of magnetostructural correlations \cite{10}. To describe the magnetic field evolution of a broad maximum in magnetic specific heat, the mutual orientation of the magnetic-field vector

\[\text{TABLE I}\]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Standard error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>0.38</td>
<td>0.01</td>
</tr>
<tr>
<td>$\beta$</td>
<td>0.03</td>
<td>0.0003</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>1.56</td>
<td>0.29</td>
</tr>
<tr>
<td>$\delta$</td>
<td>0.43</td>
<td>0.03</td>
</tr>
</tbody>
</table>
and the easy-axis of the anisotropy needs to be taken into account. Therefore, the direction of the magnetic field, in agreement with magneto-structural correlations, was tilted 27° away from the easy axis of anisotropy. An excellent agreement with the experimental data in the low-field region up to 2 T was obtained using the same set of single-ion anisotropy parameters as used for the description of zero-field data (see Fig. 4).

Fig. 4. Temperature dependence of magnetic specific heat of [Ni(bipy)$_3$][TCNQ)$_4$·(CH$_3$)$_2$CO in fields up to 2 T applied parallel to the crystallographic c-axis. The experimental data points are given along with the results from the theoretical model described in the text.

4. Conclusions

The specific heat of a single crystal of the ARS system Ni(bipy)$_3$(TCNQ)$_4$·(CH$_3$)$_2$CO was measured and analysed. The experimental studies extended down to 0.38 K and in magnetic fields up to 5 T. The analysis suggests that the low-temperature data can be well-described by a model of isolated $S = 1$ ions with single-ion anisotropy parameters $D/k_B = -1.95$ K and $E/k_B = 0.3$ K in magnetic fields up to 2 T. These results provide an important basis for quantitative analysis of future magnetic measurements.

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References