Crystal dependence of the magnetic properties of an antiferromagnetic alternating chain compound F5PNN

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Abstract. An \( S = \frac{1}{2} \) organic radical F₅PNN forms a uniform chain structure at room temperature and the magnetic properties at low temperature is described by the Heisenberg antiferromagnetic alternating chain model with \( 2J/k_B = -5.6 \) K and \( \alpha = 0.4 \). The structural change occurring below 5 K is studied by magnetic measurements. The structural change occurs at different temperatures depending on the condition of the crystal growth. The behaviour is discussed from the aspect of the homogeneity of crystals. The deuterated sample F₅PNN-d₁₂ was also synthesized and the magnetic properties are described. The exchange coupling and alternating ratio is estimated to \( 2J/k_B = -4.9 \) K and \( \alpha = 0.65 \).

1. Introduction

Recently, spin-gapped quantum spin systems have attracted much attention from the experimental and theoretical aspects. Pentafluorophenyl nitronyl nitroxide radical (F₅PNN) has an \( S = \frac{1}{2} \) which distributes mainly on the O-N-C-N-O moiety. The crystal structure at room temperature involves a uniform chain constructed by the close spacing between NO groups. However, nonmagnetic ground state with the energy gap \( \Delta = 3T \) was confirmed by the magnetic measurement. The magnetic behaviour is explained by the Heisenberg antiferromagnetic alternating chain model,

\[
H = -2J \sum_{i=1}^{N_A/2-1} (S_{2i} \cdot S_{2i-1} + \alpha S_{2i} \cdot S_{2i+1}) .
\]  

(1)

The temperature dependence of the susceptibility above 0.5 K and magnetization curves above 1.0 K are well reproduced by the parameter sets of \( 2J/k_B = -5.6 \) K and \( \alpha = 0.4 \)[1, 2]. The distortion of the lattice below 5 K is suggested by the heat capacity and single crystal ESR experiments. Structural distortion at such a low temperature suggests the interrelation between the lattice and magnetic interactions. In fact, in the dielectric measurements in magnetic fields, the competition of the magnetic energy and lattice energy was observed [3]. The properties of the gapped ground state is examined by the heat capacity in magnetic fields at very low temperatures, and the field induced magnetic ordering and the low-energy excitation in the Tomonaga-Luttinger liquid was observed [4]. For understanding the thermodynamics, possibility of the competing magnetic interaction is pointed out [5]. The magnetic property of F₅PNN is sensitive to pressure, and even the stress in the powdered sample affects the ground state [2, 6, 7]. The phase boundary of the field induced ordered phase is different in the powdered sample and possibility of the pressure-enhanced frustration is suspected [8].
As is summarized above, the ground state properties of $F_5PNN$ is quite interesting but the nature of the structural change below 5 K is not clear yet. The quality of the crystal is an essential factor to study the ground state properties. In this report, the crystal dependent behavior of the structural change is described. The magnetic properties of deuterated crystal are also presented.

2. Experimental

$F_5PNN$ and its deuterated compound $F_5PNN$-$d_{12}$ were synthesized through a conventional method. Crystals of $F_5PNN$ were grown by recrystallization of concentrated solutions. Recrystallization from the mixed solvent of Et$_2$O-hexane at 10°C or -10°C yielded crystals with 1~20 mg. We tried several kinds of the mixing ratio of the solvents and each batch of the crystals are labeled by #A(serial number). Recrystallization from hexane solutions at 20°C was also done (crystals of #B). Evaporation from the Et$_2$O solution at 300 mbar in water bath of 40°C gives fine crystals with 0.03~0.1 mg (#C). Temperature dependence of susceptibility ($\chi(T)$) and field dependence of magnetization ($M(B)$) were measured on a Quantum Design MPMS-XL SQUID magnetometer in the temperature range of 2-300 K and an applied field up to 5 T. Measurements of $\chi(T)$ below 10 K were made in 50 mT and at 0.1 K intervals with settling each temperature in cooling and warming processes. The magnetic properties were measured for 26 crystals. Among them, three typical examples are shown in this report for the single crystals of #A7 (11.562 mg) and #B3 (8.554 mg), and fine crystals of #C1 (0.1 mg each). Single crystals of $F_5PNN$-$d_{12}$ were grown from the solution of Et$_2$O-hexane and recrystallization from Et$_2$O solution gave fine crystals. A single crystal (3.026 mg) and fine crystals were measured $\chi(T)$ and $M(B)$.

3. Result and discussion

In Fig.1(a), $\chi(T)$’s in the cooling and warming processes of crystals of #B3(▲) and #C1(□) are compared. Although the behaviours above 5 K is identical each other, below this temperature crystal dependence is seen. The behaviour of the #C1 crystal in the whole temperature range obeys the calculation for the alternating chain with $2J/k_B = -5.6$ K and $\alpha = 0.4$ which is shown by a solid curve, as is reported previously [1]. On the other hand, the #B3 crystal shows abrupt change at 3.4 K in the warming process. Thermal hysteresis suggests that this is the first order transition possibly related to the structural change. Below the transition temperature, the behaviour of #B3 crystal is the same as that of #C1. Since the behaviour of the uniform chain with $2J/k_B = -4.1$ K which is shown by a dashed curve is not distinguishable from the alternating chain above 4 K, the structural change of #C1 occurring above this temperature is not detectable by $\chi(T)$. Fig.1(b) shows $M(B)$’s with increasing and decreasing fields measured at 2 K for the crystals of #B3 and #C1. The concave curve of the #C1 crystal means the singlet ground state of this material.

Fig. 1. (a) Temperature dependence of magnetic susceptibilities of the crystals of #B3(▲) and #C1(□). Arrows indicate the sweeping direction. Solid, dotted, and dashed curves represent the calculation for the alternating chain with $2J/k_B = -5.6$ K and $\alpha = 0.4$, with $2J/k_B = -5.1$ K and $\alpha = 0.55$, and for the uniform chain with $2J/k_B = -4.1$ K, respectively. (b) Magnetization curves at 2 K of #B3(▲) and #C1(□). Solid lines are guide for eye. Arrows indicate the sweeping direction.
Although $M(B)$ of the #B3 crystal in the up sweep is almost identical with the one of #C1, $M(B)$ of #B3 in the down sweep shows discrepancy. The tendency of the linear field dependence above 1.5 T in the down sweep suggests the gapless behaviour of a uniform chain. In spin-Piers materials, the transition from a gapped state to a gapless one by applying magnetic fields is reported [9].

Figure 2 shows the magnetic behaviour of the #A7 crystal by open circles. The transition temperature is 2.9 K in the warming process accompanied by larger hysteresis than that in #B3. In the magnetization curve also, we can see larger hysteresis than that in #B3. The measurements were made repeatedly and several thermal cycles did not affect the transition temperature and field. We measured the magnetic properties of #A7 after grinding to microcrystals. The behaviour is compared in Fig. 2.

$\chi(T)$ of the grinded microcrystals (▽) is reproduced by the alternating chain with $2J/k_B = -5.8$ K and $\alpha = 0.5$. No hysteresis was observed, which suggests the enhancement of the transition temperature.

In the temperature range between 2-4 K, $\chi(T)$ shows crystal dependence as well as the transition temperature. For example, #B3 or #A7 obeys the alternating chain with $2J/k_B = -5.1$ K and $\alpha = 0.55$, or the one with $2J/k_B = -4.7$ K and $\alpha = 0.7$. Seemingly the values of $J$ and $\alpha$ are changeable, but the calculated curves with these parameters are identical with the calculation for the uniform chain with $2J/k_B = -4.1$ K above 3.5 K. We consider that the high temperature phase is a uniform chain and just above the transition temperature, growth of the inhomogeneous domains gives the discrepancy from the uniform chains. The different transition temperature is also related to the effect of the inhomogeneous domains formed in the crystal growth. This compound is very sensitive to pressure and even the stress when it is coated with grease works as pressure. This comes from the pressure enhances the potential barrier of some kinds of structural change in organic materials [6].

![Figure 2](image1.png)

**Fig. 2.** Comparison of the magnetic behaviour of the #A7 crystal (○) and grinded microcrystals of #A7 (▽). (a) Temperature dependence of magnetic susceptibilities. Arrows indicate the sweeping direction. Solid, dot-dashed, dotted, and dashed curves represent the calculation for the alternating chain with $2J/k_B = -5.6$ K and $\alpha = 0.4$, with $2J/k_B = -5.8$ K and $\alpha = 0.5$, with $2J/k_B = -4.7$ K and $\alpha = 0.7$, and for the uniform chain with $2J/k_B = -4.1$ K, respectively. (b) Magnetization curves at 2 K. Solid lines are guide for eye. Arrows indicate the sweeping direction.

![Figure 3](image2.png)

**Fig. 3.** Temperature dependence of the magnetic susceptibility of F$_5$PNN-d$_{12}$. Observed data for single crystal (◇) and fine crystals (+) are shown. Solid, dot-dashed, and dashed curves represent the calculation for the alternating chain with $2J/k_B = -5.6$ K and $\alpha = 0.4$, with $2J/k_B = -4.9$ K and $\alpha = 0.65$, and for the uniform chain with $2J/k_B = -4.0$ K, respectively.
When the single crystal of #A7 was grinded, it is considered that the stress by the inhomogeneity is released and the transition temperature is enhanced. \( \chi(T) \) of the grinded microcrystal obeys the calculation for the alternating chain with \( 2J/k_B = -5.8 \) K and \( \alpha = 0.5 \). The larger magnetic interactions may come from the compression of the lattice when grinded.

The magnetic properties of \( F_5PNN-d_{12} \) are also studied. Figure 3 shows \( \chi(T) \) of \( F_5PNN-d_{12} \) and no thermal hysteresis was observed. Crystal dependence was checked by two independent measurements for a single crystal and fine crystals grown in different batches, and no crystal dependence was observed. In both cases, \( \chi(T) \) obeys the calculation for the alternating chain with \( 2J/k_B = -4.9 \) K and \( \alpha = 0.65 \). The values of \( \alpha \) and \((1+\alpha)J\) of \( F_5PNN-d_{12} \) are larger than the ones of \( F_5PNN \). This is the same tendency to the pressure effects on \( F_5PNN \) [7]. The possibility of the deuteration working as pressure is pointed out. Due to the larger \( \alpha \) value, the smaller energy gap above the singlet ground state is expected for \( F_5PNN-d_{12} \) than the one for \( F_5PNN \).

4. Conclusion
Several conditions of the crystal growth of \( F_5PNN \) were tried and the crystal dependence of the structural change was studied by magnetic measurements. Some crystals show the structural change at about 3 K, which is detected by the sudden change of the temperature dependence of the susceptibility. The crystal which undergoes the structural change at lower temperature shows larger thermal and field hysteresis. The inhomogeneity of the crystal may lower the structural change. Good crystals having no hysteresis were also obtained. The magnetic properties of \( F_5PNN-d_{12} \) was studied and explained by the antiferromagnetic alternating chain model with \( 2J/k_B = -4.9 \) K and \( \alpha = 0.65 \). Deuteration is considered to work as pressure.

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