Structural phase transition in one-dimensional bond-alternating antiferromagnet F$_5$PNN

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Abstract. A structural phase transition of pentafluorophenyl nitronyl nitroxide (F$_5$PNN) single crystals with $S = 1/2$ bond-alternating Heisenberg antiferromagnetic chains has been studied by ac magnetic susceptibility measurements. At the transition around 3 K in zero field, the bond-alternating ratio changes from 0.7 to 0.4 at low temperatures. Thus, the transition is considered to be one of processes from uniform magnetic chain at room temperature to the low-temperature bond-alternating state. The structural transition is likely to have a crystal-size dependence, and in powder sample, continuous deformation is substituted for it. As the applied fields increases until the lower critical field of gapped bond-alternating chains, the transition temperature slightly decreases, which suggests competition between the lattice energy and decreasing internal magnetic energy.

1. Introduction

Recently gapped quantum spin chains have attracted much attention because of the rich field-induced effects. In the gapless region between two critical fields $H_{c1}$ (closing of the spin gap) and $H_{c2}$ (magnetization saturation), purely one-dimensional (1D) systems do not have any long-range ordered phase. Instead, they have short-range ordering, which can be interpreted as the spin Tomonaga-Luttinger liquid (TLL). The nature has become examined in recent experimental studies, especially on 2-leg spin-ladder systems [1]. Pentafluorophenyl nitronyl nitroxide (F$_5$PNN) is a pure organic magnet regarded as $S = 1/2$ bond-alternating Heisenberg antiferromagnetic chains with interactions $J_1$ and $J_2$ ($< J_1$) at low temperatures, which also has a spin gap due to dimering of spins in zero field [2]. Between $H_{c1} = 3$ T and $H_{c2} = 6.5$ T, heat capacity [3] and NMR [4] experiments have partially suggested consistency with the TLL picture, above temperatures of the field-induced 3D long-range ordering via small interchain interaction. In addition, our recent ac susceptibility measurements have determined the short-range ordered region in a more distinct form, which is in preparation to be published.

Though F$_5$PNN has bond-alternating chains at low temperatures, the magnetic chains are uniform at room temperatures. Unlike the spin-Peierls materials, however, the bond alternation is considered to appear at much higher temperatures than the dimering temperature. In this article, we report a structural phase transition observed in F$_5$PNN single crystals by the ac magnetic susceptibility, which should closely relate to formation of the bond-alternating chains at low temperatures.
2. Experimentals
The ac magnetic susceptibility $\chi$ of the $F_5$PNN single crystal was measured down to 50 mK by an ordinary mutual inductance bridge circuit of which operating frequency is 520 Hz. In addition, for zero field, a SQUID magnetometer was also used as the null detector of the bridge to obtain better resolution, where the frequency lowers to 175 Hz. The sensitivity and offset for zero-field data of the bridge circuits were calibrated against the high-temperature data measured by a commercial susceptometer. The offsets for measurements in applied fields were fitted to the derivative of the magnetization curve at 1 K measured by Takahashi et al. [2].

The sizes of $F_5$PNN single crystal samples are about a few mm, of which masses are 2 and 11 mg. Since the large stress effect due to the use of grease has been reported for this magnet [5], to fix the sample, a minimum amount of Apiezon N grease was used only between one crystal surface and a Ag thermal link. It assures the stress-free condition for the sample crystal. For measurements in applied fields where $F_5$PNN has rather large heat capacities at low temperatures [5], the sample and thermal link were capsuled into a Stycast 1266 cell filled with $^4$He gas. Thus, at low temperatures, the thermal conduction of superfluid film provides sufficiently fast thermal relaxation.

3. Results and Discussion
The ac susceptibility $\chi$ of a $F_5$PNN single crystal (2 mg) measured using SQUID at zero field is shown in Fig. 1, where the Curie-Weiss component due to free spins was subtracted, assuming that they are 0.12% of total spins with the Weiss temperature of $-25$ mK. The exponential decrease at low temperatures clearly indicates existence of a spin gap in bond-alternating antiferromagnetic chains. As the temperature is raised, $\chi$ suddenly increases at 3.4 K. When the temperature lowers, however, no anomalies are observed at 3.4 K. Instead, another discontinuous jump of $\chi$ appears at lower temperature 2.1 K, and then $\chi$ agrees with the observed in the warming process. The temperature hysteresis indicates that the $F_5$PNN crystal has a first-order phase transition around 3 K. Though the similar transition was also reported from measurements of the susceptibility and heat capacity [6], it has not been observed in past magnetization measurements [2]. It suggests that appearance of the structural transition is very sensitive to the sample quality.

![Figure 1. ac Magnetic susceptibility of a $F_5$PNN single crystal in zero field. The Curie-Weiss component was subtracted (0.12% of total spins, the Weiss temperature $\theta = -25$ mK). Solid and open symbols are for warming and cooling processes, respectively. Arrows indicate the structural transitions. Solid and dashed lines are fittings to theoretical curves (see text). Inset: dc Susceptibility of a small grain of crushed crystal. The Curie-Weiss term (4.2%, $\theta = -25$ mK) was subtracted. No transitions or temperature hysteresis are observed.]

The precise measurement shown here enables us to estimate changes of interactions through the transition. The high-temperature and low-temperature $\chi$ were individually fitted to the approximate susceptibilities for bond-alternating antiferromagnetic chains, which were calculated by Johnston et al. [7]. The fittings are indicated by dashed and solid lines in Fig. 1, respectively. The alternating ratio $\alpha = J_2/J_1$ and intrachain interaction $2|J_1|/k_B$ for
the low-temperature $\chi$ are estimated to be 0.35 ± 0.1 and 5.7 ± 0.1 K, respectively. For the high-temperature $\chi$, $\alpha = 0.7 ± 0.1$ and $2|J_1|/k_B = 4.85 ± 0.1$ K. The parameters for low temperatures agree with $\alpha = 0.4$ and 5.6 K reported in the previous measurements [2]. Thus, the observed transition is indicated to be a structural transition where the alternating ratio decreases at low temperatures, which causes increase of the spin gap energy and lowering of the total magnetic energy. It should be noted, however, that even at the higher-temperature side, the alternating ratio is considerably less than unity, apart from uniform chains at room temperatures. It indicates that the transition is one of processes to the low-temperature bond-alternating state. We also made the same analyses for two samples in different batches. The obtained parameters were considered to be the same within the fitting uncertainties.

Next, we have done measurements applying the magnetic fields for a larger crystal (11 mg) of the same batch as the crystal shown in Fig. 1, where the ordinary bridge circuit without SQUID was used. A part of results are shown in Fig. 2. For this sample, the transition temperature in warming process was always observed clearly, e.g. in zero field it is at 3.25 K which is almost the same temperature as in Fig. 1. However, the transition in cooling process looks rather broad or multi-stepped, as typically seen in Fig. 2(b), which suggests that the sample has been broken into a few crystals by stress from thermal shrinking. Therefore, the multi-stepped transition implies that the transition temperature in cooling process has a crystal-size dependence in contrast with that in warming process, and also that the temperature hysteresis of the transition is determined by supercooling rather than superheating. For a reference, the susceptibility of one small grain picked up from a F$_5$PNN crystal crushed into powder is shown in the inset of Fig. 1, which was measured as magnetization at 10 Gauss. In such a small sample, the structural transition or temperature hysteresis was not observed, indicating that the continuous deformation is substituted for the structural transition. Absence of the transition is consistent with the dielectric constant measurement for powder [8].

![Figure 2](image-url)

**Figure 2.** ac Magnetic susceptibilities of a F$_5$PNN single crystal in applied fields. (a) At 1 Tesla (b) At 2 Tesla. Symbols are similar to those in Fig. 1.

The transitions observed in applied fields are summarized in Fig. 3. As shown in Fig. 3(a) and also seen in Fig. 2, the changes of $\chi$ above 0.5 T are reverse to that in zero field. It is considered to be because the temperature of $\chi$ maximum following the spin-gap energy becomes lower than the transition temperature, with increasing the field. As the applied field increases up to $H_{c1} = 3$ T, the transition temperature slightly decreases as shown in Fig. 3(b). It suggests competition between internal magnetic energy and lattice energy, where the energy gain due to dimerization decreases with increasing the field. Above $H_{c1}$, the structural transition was not clearly observed by $\chi$. It is probably due to the small temperature dependence of $\chi$ in the gapless region, since the dielectric constant in powder sample has shown lattice deformation even in this region [9].
Figure 3. Field dependences of (a) the change in $\chi$ at the structural transition and (b) transition temperature, observed in a F$_5$PNN single crystal. In (b), for a reference, the region where field-induced magnetic orderings appear [3] are plotted by solid and dashed lines. They lie at much lower temperature regions, compared with the structural transition.

4. Summary
By ac magnetic susceptibility measurements, we have observed a structural phase transition of F$_5$PNN single crystals with $S = 1/2$ bond-alternating Heisenberg antiferromagnetic chains, which is one process from uniform magnetic chain to the low-temperature bond-alternating state. In zero field, the bond-alternating ratio decreases from 0.7 to 0.4 at the transition temperature. The structural transition is likely to have a crystal-size dependence, and seems sensitive to the sample quality. In powder sample, it changes to continuous deformation. With increasing fields up to the lower critical field of gapped bond-alternating chains, the transition temperature was observed to decrease, suggesting that the origin is competition between magnetic and lattice energies. At fields in the gapless region, the transition was not observed, probably because of the small temperature dependence of $\chi$. In this region, measurements such as the heat capacity will provide the additional information about the transition.

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