Direct three-dimensional ordering of quasi-one-dimensional quantum dimer system near critical fields

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Dimensionalities of XXZ spin orderings or degenerate hard-core bosons in a quasi-one-dimensional (1D) dimer system are examined by the ac susceptibility and specific heat of antiferromagnetic bond-alternating chains in pentafluorophenyl nitronyl nitroxide (F5PNN). At intermediate fields in the gapless region, the 1D short-range order (SRO) corresponding to the Tomonaga-Luttinger liquid and three-dimensional (3D) long-range order (LRO) BEC at lower temperatures are separately observed, as expected from the small interchain interaction. In contrast, a definite region around the critical field was established where 3D LRO occurs without the development of 1D SRO at higher temperatures.

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In their lattice liquid model for the superfluid transition of 4He, Matsubara and Matsuda showed that hard-core bosons can be mapped to an XXZ spin system, where the chemical potential corresponds to the applied magnetic field [1]. The three-dimensional (3D) long-range ordering (LRO) of the spins is thus regarded as the Bose-Einstein condensation (BEC). On the other hand, BEC does not exist in one dimension (1D). Therefore, the short-range ordered (SRO) state of the XXZ spin chain, which corresponds to 1D hard-core bosons or, equivalently, spinless fermions, is described as a Tomonaga-Luttinger liquid (TLL) instead. Such equivalences between bosons and spins have attracted much interest recently, because they have been realized in spin systems, especially as field-induced orderings in antiferromagnetic (AF) dimer systems. As the applied field increases, the lower branch of the triplet states in a dimer goes down to the energy of the singlet state, and then the spin gap is closed at a field $H_c$. For interacting dimers, the lower two states around $H_c$ are regarded as $S = \frac{1}{2}$ XXZ pseudospins under an effective field $h_{\text{eff}}$, where $h_{\text{eff}} = 0$ at $H \approx H_c$ [2]. The pseudospins have LRO at the small $h_{\text{eff}}$ region between two critical fields $H_{c1}$ and $H_{c2}$. Thus, in these systems, the triplet dimers act as bosons (often referred to as triplons) and cause BEC as LRO. Indeed, it was shown in a 3D dimer system that the field-induced magnetic order is well explained by BEC of triplons rather than the order simply derived from a mean-field analysis [3]. The BEC of spin systems nowadays has been studied and recognized in various materials [4]. For 1D systems, properties consistent with the TLL picture have been intensively studied by dimer chain systems [5,6], including the observation of the spinon continuum characteristic of TLL [7].

Since real “1D” dimer systems are always quasi-1D materials with a weak interchain interaction, they provide an opportunity to study the dimensional crossover of the order from 1D to 3D. In applied fields between $H_{c1}$ and $H_{c2}$, these systems show 1D SRO (TLL) below the temperature corresponding to the interdimer interaction within chains, and then, at lower temperatures where the interchain interaction cannot be ignored, 3D LRO (BEC) occurs. This scenario for the dimensional crossover of field-induced orderings has been generally accepted and experimentally confirmed in intermediate fields in the gapless region [6,8]. However, considering the field dependences of boundaries for these ordered states, the scenario is inconsistent around the critical fields. As shown in Fig. 1(a), the 1D SRO crossover temperature to the TLL regime has a linear dependence on the applied field [9,10], reflecting that the crossover temperature and field correspond to the Fermi temperature and chemical potential, respectively.

In contrast, the 3D LRO (BEC) transition temperature $T_C$ has a convex shape as a function of fields, i.e., $\lim_{T \rightarrow 0} dH/dT_C = 0$ by thermodynamical requirements. Therefore, a 1D SRO crossover temperature should coincide with the 3D LRO temperature at a crossover field near to but different than the critical field. In these critical regions the picture with high-$T$ 1D SRO and low-$T$ 3D LRO does not hold. This dimensionality paradox, 3D behavior around critical fields, has been theoretically suggested [11] and claimed partially from the measured magnetization curve [5]. However, conclusive results have not been obtained so far, though they are also an important issue for recent studies on the quantum criticality around critical fields [12,13]. In this Rapid Communication, we show field-induced orderings of bond-alternating AF chains in pentafluorophenyl nitronyl nitroxide (F5PNN), where the 1D SRO crossover and 3D LRO transition are determined by the ac susceptibility and specific heat, respectively, around the upper critical field and at sufficiently low temperatures. This study concentrates on the dimensionality of the order in a quasi-1D dimer system at fields close to the critical fields. The results clearly show that around the critical field, 3D LRO directly occurs without 1D SRO development, even though the 1D intrachain interaction is sufficiently larger than the interchain one.

F5PNN is a genuine organic compound with $S = \frac{1}{2}$ Heisenberg AF chains of unpaired electrons in radicals. Around zero fields, the susceptibility shows an exponential decrease at low temperatures, by the spin gap of dimers due to the AF bond alternation [14]. The larger intrachain AF interaction $J_1$ causing the dimerization was estimated to be 5.6 K, and the alternation ratio $\alpha = J_2/J_1$ for AF interactions in chains was observed to be 0.4–0.5, depending on the applied field. Field-induced 3D LRO was observed between 3 and 6 T by
specific-heat peaks [15]. Above the transition temperatures, the specific heats qualitatively agree with theoretical calculations for the two-leg ladder [16], which suggests that a TLL-like 1D SRO region exists at higher temperatures, together with NMR results [17]. In addition, single sharp peaks observed in powder samples indicate the highly isotropic nature of this spin system. 

In this study, two collections of small F5PNN single crystals (maximum $\sim 1 \times 1 \times 1$ mm) were used for specific-heat ($\sim 10$ crystals, total 1.3 mg) and ac magnetic susceptibility ($\sim 10$ crystals, total 4.9 mg) measurements, respectively. These crystals were simultaneously extracted from the same solution, which indicates the good quality of our samples and the very small sample dependence among crystals. The transition temperatures indicated by $C_{\text{T}}$ are critical fields for the gapless region, where field-induced orderings are observed. Characteristic temperatures $T_{g}(\text{max})$ of 1D SRO are observed by a broad maximum of the ac susceptibility $\chi_{ac}$ in the relatively small $h_{\text{eff}}$ region below $H_{c1} = 5.8$ T. $T_{g}(\text{kink})$ are kink temperatures of $\chi_{ac}$. $T_{c}$ are 3D transition temperatures indicated by the specific heat. A hysteretic behavior of $T_{c}$ seen around $H_{c1}$ is due to a field-induced structural transition.

considered to be caused by a structural transition around $H_{c1}$, which also explains the apparent change of the alternation ratio $\alpha$ reported previously [14]. The field-induced structural transition is out of the scope of this Rapid Communication and should be published elsewhere. Thus, we examine the behavior around the upper critical field $H_{c2}$ far from the structural-transition field.

Figure 2(a) shows the specific heats $C$ of F5PNN observed between 4.5 T, where the effective field $h_{\text{eff}} \approx 0$ for the $XXZ$ pseudospins, and the upper critical field $H_{c2}$. In all fields in the gapless region between $H_{c1}$ and $H_{c2}$, typical sharp $\lambda$-type peaks are observed at $T_{c}$, indicating the second-order transition to the 3D LRO state of spins. The observed transition peaks are sharper and higher than those reported previously [15, 19], which indicates the good quality of our samples and the very small sample dependence among crystals. The transition temperatures $T_{c}$ are plotted by solid inverse triangles in Fig. 1(b), including data around $H_{c1}$, which definitely determines a 3D LRO region on the $H$-$T$ phase diagram. Critical fields $H_{c1}$ and $H_{c2}$ were observed to be about 2.8 and 6.35 T, respectively, close to those reported previously [14, 15]. As shown in Fig. 2(b), a characteristic behavior is observed in the peak heights. Here, the highest peak appears around a field $H_{X} = 5.8$ T, which contrasts with the fact that the peak height for simple 3D magnetic orderings is the highest at the highest $H_{c2}$ where $h_{\text{eff}} \approx 0$ [21]. The reason will be discussed later.

Figure 3(a) shows the ac susceptibilities $\chi_{ac}$ between 4.8 and 5.4 T under relatively small $h_{\text{eff}}$ in the gapless region. In the figure, the development of 1D SRO is observed by typical broad maxima at $T_{g}$ (max), which are indicated by solid arrows. In the 1D SRO state of $XY$ spin chains at $T = 0$, $\chi_{ac}$ shows divergent behavior at the critical field, which is a hallmark of 1D SRO, as shown theoretically [9, 16, 22]. Therefore, the $\chi_{ac}$ maximum which indicates the 1D SRO crossover becomes higher as the field approaches the critical field. The increase of $\chi_{ac}$ seen in the figure is thus consistent with the 1D SRO property. $T_{g}$ (max) are plotted by solid inverse triangles in Fig. 1(b). With increasing the field, $T_{g}$ (max) approaches the linear field dependence. It agrees as expected for the TLL

FIG. 1. (a) Schematic drawing of boundaries of the field-induced order phases expected in quasi-1D dimer chains. (b) Field-temperature phase diagram of F5PNN. $H_{c1} \approx 2.8$ T and $H_{c2} = 6.35$ T are critical fields for the gapless region, where field-induced orderings are observed. Characteristic temperatures $T_{g}(\text{max})$ of 1D SRO are observed by a broad maximum of the ac susceptibility $\chi_{ac}$ in the relatively small $h_{\text{eff}}$ region below $H_{c1} = 5.8$ T. $T_{g}(\text{kink})$ are kink temperatures of $\chi_{ac}$. $T_{c}$ are 3D transition temperatures indicated by the specific heat. A hysteretic behavior of $T_{c}$ seen around $H_{c1}$ is due to a field-induced structural transition.

FIG. 2. (a) Temperature dependences of specific heats $C$ of F5PNN in the gapless region below the upper critical field $H_{c2}$. Dashed arrows indicate 3D LRO transition temperatures $T_{c}$. (b) Field dependence of the transition peak heights in (a). The highest peak appears around $H_{X} = 5.8$ T. The dashed line is a guide for the eyes extending the field dependence around $H_{c2}$.
From 5.6 to 6.3 T near F$_5$PNN at various applied fields. (a) At a relatively small $T\chi$ around 5 T. Solid arrows indicate broad maxima due to 1D SRO. Dashed arrows are the 3D ordering temperatures $T_C$ observed by C. From 5.6 to 6.3 T near $H_c2$. Temperatures of kinks observed above 5.65 T are indicated as $T_f$(kink).

picture of 1D SRO, though the slope is about a half of that from the free-fermion theory [10]. In Fig. 3(a), the 3D LRO transition temperatures $T_C$ observed in Fig. 2(a) are also indicated by dashed arrows, which show that $T_C$ is significantly lower than $T_f$(max). Thus in this region, first 1D SRO develops at high temperatures, and then the 3D transition occurs at lower temperatures by the weak interchain interaction, as usually expected for quasi-1D dimer systems. Up to about 5.2 T, $\chi_{ac}$ show no clear signatures at $T_C$, which indicates that the magnetization does not change much through the 3D transition. It is explained by considering that the LRO transition is of XY spin components perpendicular to the field which are fluctuating in the 1D SRO state.

At higher fields toward $H_c2$, a different behavior appears in $\chi_{ac}$, which is shown in Fig. 3(b). Above 5.65 T, a kink becomes clear at $T_C$ below $T_f$(max). Then, the broad maximum merges with the kink into a cusp around 5.8 T, which we define as a crossover field $H_X$. When the field further increases above $H_X$, the cusp becomes a kink, as shown in the figure. We refer to the temperature of the kink or cusp as $T_f$(kink), which is plotted in Fig. 1(b) by open inverse triangles. As seen in the phase diagram, the field dependence of $T_f$(kink) is different from that of $T_f$(max). $T_f$(kink) coincides with $T_C$, so that the sharp anomaly of $\chi_{ac}$ at $T_f$(kink) is an indication of the 3D LRO transition. Above $H_X$, $T_f$(kink) is higher than the extrapolation of $T_f$(max) at the same field. Consequently, an increase of $\chi_{ac}$ indicating 1D SRO development looks to be interrupted by the 3D transition which occurs at higher temperatures, resulting in the observed kink of $\chi_{ac}$. The absence of a broad maximum above $H_X$ clearly indicates that the 1D SRO does not develop above the 3D LRO temperature.

In Fig. 4, the phase boundaries around $H_c2$ are replotted by the log-log form to see the field dependences in detail. As seen in the figure, $T_f$(kink) are observed to be the same as $T_C$ of the 3D LRO transition and obey the same power law, $T_f$(kink) $\propto |H - H_c2|^\nu$. The apparent exponent of the power law is estimated to be $\nu = 0.52 \pm 0.04$ using both $H_c2$ and $\nu$ as fitting parameters. The $\nu$ does not change within errors when the lower limit of the fitting range is varied from $H_X$ to 6 T. Although the value $\nu$ is smaller than $\frac{1}{3}$ expected theoretically [3,11], it is close to those observed in materials recognized to show BEC [4]. Below $H_X$, i.e., $H \geq H_c2 > H_c1 - H_X$, where the linear field dependence of $T_f$(max) is observed, $T_C$ is lower than the extension of the above power law near $H_c2$. It is consistent with the fact that 1D SRO develops only below $H_X$, since 1D SRO reduces the internal energy gain through the 3D transition and leads to a lowering of $T_C$.

Finally, we discuss the $C$ results shown in Fig. 2 in terms of dimensionality of the magnetic order. In the relatively small $h_{eff}$ region, humps of $C$ corresponding to $\chi_{ac}$ maxima at $T_f$(max) have been reported in previous measurements [15]. Thus, the development of 1D SRO should reduce the magnetic entropy above $T_C$ and results in the suppression of the 3D transition peak height. In Fig. 2(b), the highest C peak is observed around $H_X$, which indicates that such suppression occurs only below $H_X$ and that entropy reduction due to 1D SRO is negligibly small above $H_X$. The highest peak appearing at $H_X$ is clear evidence that the 3D transition directly occurs without 1D SRO above $H_X$ up to $H_c2$. 
Thus, it has been experimentally established for quasi-1D dimer chains that, in a definite field region between $H_K$ and $H_{c2}$, 3D LRO occurs without passing through the 1D SRO region at high temperatures, even when the interchain interaction is sufficiently small compared to the intrachain one. Qualitatively, this paradoxical dimensionality reversal can be explained by the relatively increasing significance of the interchain interaction around the critical field where the 1D intrachain interaction competes with the Zeeman energy. In the boson picture [23], the interchain transfer cannot be ignored around $H_{c2}$ where bosons become dilute in chains, which is likely to bring the 3D BEC. On the other hand, interestingly, the present results reveal that the 3D ordered state has a nature different from that of typical BEC. In existing theories, where the system near critical fields is essentially treated as an isotropic 3D one by a rescaling of the anisotropy, $\chi_{ac}$ is independent of the applied field [3,11]. As shown in Fig. 3(b), however, $\chi_{ac}$ below $T_{\chi}(kink)$ continuously increases with fields even in the 3D region above $H_K$; $\chi_{ac}$ around $H_{c2}$ is more than two times larger compared to that at $H_K$. It is noted that, at 6.25 T just below $H_{c2}$, the large $\chi_{ac}$ is recovered when 3D LRO occurs at $T_{\chi}(kink)$, although $\chi_{ac}$ above $T_{\chi}(kink)$ is small, indicating the absence of 1D SRO. It suggests that the $\chi_{ac}$ increasing with fields is characteristic of the present 3D ordered state itself. In addition, if the $\chi_{ac}$ increase toward $H_{c2}$ is attributed to the density dependence of the boson interaction parameter in the BEC framework [3,11], the exponent $\nu$ for the phase boundary is reduced from $2/3$. Such an effect is likely to be implied by the smaller $\nu = 0.52$ shown in Fig. 4. These behaviors suggest that a theoretical analysis beyond simple anisotropy rescaling is necessary.

To conclude, using bond-alternating chains in F$_3$PN, we have studied the dimensionality of field-induced orders in a quasi-1D dimer system or degenerate hard-core bosons, and the phase boundaries corresponding to the chemical potential dependences. A direct 3D transition without 1D SRO was confirmed at the critical field region between $H_K$ and $H_{c2}$ by the absence of broad maxima in $\chi_{ac}$ and the field dependence of $C$ peak heights. It contrasts with the fact that 1D SRO develops from significantly higher temperatures than 3D LRO transition temperatures under the small effective fields $h_{eff}$ below $H_K$. In the boson picture, when bosons are dense under relatively small $h_{eff}$, the TLL state at high temperatures is suggested by the boundary which linearly depends on the chemical potential (field). In contrast, above $H_K$, BEC-like 3D LRO with higher transition temperatures occur prior to TLL formation. The dimensionality reversal around the critical field itself is commonly expected for quasi-1D TLL materials. A similar phase diagram can be found in the literature for the other bond-alternating chains [24]. It is interesting to examine it in other quasi-1D systems such as two-leg ladders or Haldane chains.

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[23] Here, the boson is a hole or singlet dimer instead of the triplon, because the magnetization is large around the saturation field $H_{c2}$.