



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

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(Received 10 March 2016; published 12 January 2017)

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 (F_5PNN). 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.

DOI: [10.1103/PhysRevB.95.020408](https://doi.org/10.1103/PhysRevB.95.020408)

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_{eff} , where $h_{\text{eff}} = 0$ at $H \approx H_c$ [2]. The pseudospins have LRO at the small h_{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., $\lim_{T_C \rightarrow 0} dH/dT_C = 0$ 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 (F_5PNN), 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.

F_5PNN 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

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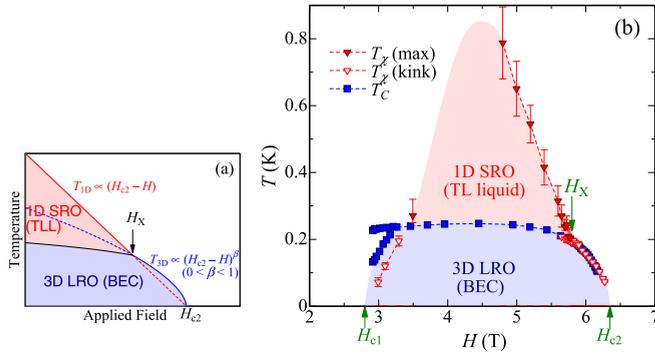


FIG. 1. (a) Schematic drawing of boundaries of the field-induced order phases expected in quasi-1D dimer chains. (b) Field-temperature phase diagram of F_5PNN . $H_{c1} \approx 2.8$ T and $H_{c2} = 6.35$ T are critical fields for the gapless region, where field-induced orderings are observed. Characteristic temperatures $T_\chi(\text{max})$ of 1D SRO are observed by a broad maximum of the ac susceptibility χ_{ac} in the relatively small h_{eff} region below $H_X = 5.8$ T. $T_\chi(\text{kink})$ are kink temperatures of χ_{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.

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 F_5PNN single crystals (maximum $\sim 1 \times 1 \times 1$ mm) were used for specific-heat (~ 10 crystals, total 1.3 mg) and ac magnetic susceptibility (~ 10 crystals, total 4.9 mg) measurements, respectively. These crystals were simultaneously extracted from the same solution, in the synthesis described in Ref. [18]. Since it has been suggested that a possible stress effect may occur in this material due to the thermal shrinkage of added grease [19], measurements presented here were done in completely stress-free conditions. For the specific heat C , F_5PNN crystals were enclosed in a Ag cell with 1 atm ^4He gas at room temperature. The ^4He gas forms a superfluid film at low temperatures, which offers sufficiently good thermal contact for C measurements even without any grease. C was measured by the adiabatic heat pulse method below 0.6 K, where the latent heat of ^4He vaporization becomes negligible. For the ac susceptibility χ_{ac} ($=\partial M/\partial H$), sample crystals were placed on a Kapton tray fixed on a Ag foil, and then encapsulated into a Stycast 1266 epoxy cell, similarly with ^4He gas for thermal contact and no fixing by grease. χ_{ac} was measured by a mutual inductance bridge circuit at a frequency of 215 Hz. The absolute value was determined referring to higher-temperature data and assuming that χ_{ac} agrees with the 1 K magnetizations shown in Ref. [14]. In F_5PNN , a temperature-induced structural transition has been observed below the lower critical field H_{c1} [20]. As shown later in the phase diagram [Fig. 1(b)], 3D transition temperatures indicated by C show a hysteresis against the applied field around H_{c1} , and, correspondingly, the observed χ_{ac} are irreproducible between 3.5 and 4.8 T. They are

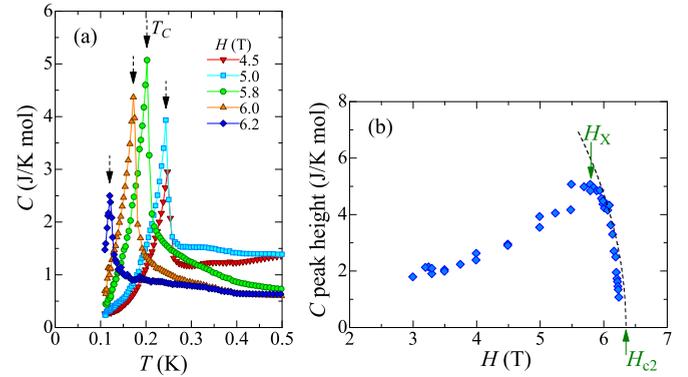


FIG. 2. (a) Temperature dependences of specific heats C of F_5PNN in the gapless region below the upper critical field H_{c2} . Dashed arrows indicate 3D LRO transition temperatures T_C . (b) Field dependence of the transition peak heights in (a). The highest peak appears around $H_X = 5.8$ T. The dashed line is a guide for the eyes extending the field dependence around H_{c2} .

considered to be caused by a structural transition around H_{c1} , which also explains the apparent change of the alternation ratio α 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 F_5PNN 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 λ -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 squares 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 T_C where $h_{\text{eff}} \approx 0$ [21]. The reason will be discussed later.

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

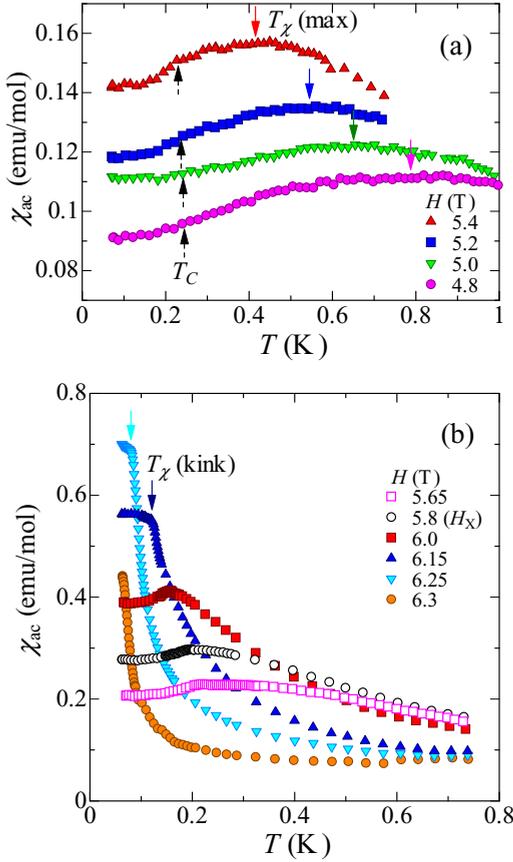


FIG. 3. Temperature dependences of the ac susceptibilities χ_{ac} of F_5PNN at various applied fields. (a) At a relatively small h_{eff} region around 5 T. Solid arrows indicate broad maxima due to 1D SRO. $T_\chi(\max)$ was determined by the parabola fitting around the maximum. Dashed arrows are the 3D ordering temperatures T_C observed by C . (b) From 5.6 to 6.3 T near H_{c2} . Temperatures of kinks observed above 5.65 T are indicated as $T_\chi(\text{kink})$.

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 $T_\chi(\max)$. 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, χ_{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 χ_{ac} , which is shown in Fig. 3(b). Above 5.65 T, a kink becomes clear at T_C below $T_\chi(\max)$. 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 $T_\chi(\text{kink})$, which is plotted in Fig. 1(b) by open inverse triangles. As seen in the phase diagram, the field dependence of $T_\chi(\text{kink})$ is different from that of $T_\chi(\max)$. $T_\chi(\text{kink})$ coincides with T_C , so that the

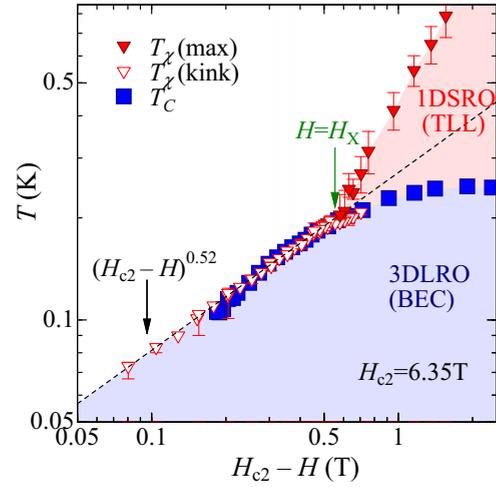


FIG. 4. Logarithmic plot of phase boundaries for magnetic orderings in F_5PNN around H_{c2} . The dashed line indicates the power law of the kink temperature $T_\chi(\text{kink})$ in χ_{ac} and 3D LRO transition temperature T_C at $H_X < H < H_{c2}$.

sharp anomaly of χ_{ac} at $T_\chi(\text{kink})$ is an indication of the 3D LRO transition. Above H_X , $T_\chi(\text{kink})$ is higher than the extrapolation of $T_\chi(\max)$ at the same field. Consequently, an increase of χ_{ac} indicating 1D SRO development looks to be interrupted by the 3D transition which occurs at higher temperatures, resulting in the observed kink of χ_{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, $T_\chi(\text{kink})$ are observed to be the same as T_C of the 3D LRO transition and obey the same power law, $T_\chi(\text{kink}) \propto |H - H_{c2}|^\nu$. The apparent exponent of the power law is estimated to be $\nu = 0.52 \pm 0.04$ using both H_{c2} and ν as fitting parameters. The ν does not change within errors when the lower limit of the fitting range is varied from H_X to 6 T. Although the value ν is smaller than $\frac{2}{3}$ expected theoretically [3,11], it is close to those observed in materials recognized to show BEC [4]. Below H_X , i.e., $H_{c2} - H > H_{c2} - H_X$, where the linear field dependence of $T_\chi(\max)$ 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 χ_{ac} maxima at $T_\chi(\max)$ 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_X 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, χ_{ac} is independent of the applied field [3,11]. As shown in Fig. 3(b), however, χ_{ac} below T_χ (kink) continuously increases with fields even in the 3D region above H_X ; χ_{ac} around H_{c2} is more than two times larger compared to that at H_X . It is noted that, at 6.25 T just below H_{c2} , the large χ_{ac} is recovered when 3D LRO occurs at T_χ (kink), although χ_{ac} above T_χ (kink) is small, indicating the absence of 1D SRO. It suggests that the χ_{ac} increasing with fields is characteristic of the present 3D ordered state itself. In addition, if the χ_{ac} increase toward H_{c2} is attributed to the density dependence of the boson interaction parameter in the BEC framework [3,11], the exponent ν for the phase boundary is reduced from $\frac{2}{3}$. 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_2PNN , 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_X and H_{c2} by the absence of broad maxima in χ_{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_X . 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_X , 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.

We thank M. Oshikawa for pointing out the possibility of this dimensionality paradox around critical fields to us and M. Tsuchiizu for useful comments. This research is partly supported by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science.

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