Bose–Einstein condensation of semi-hard bosons in the $S = 1$ dimerized organic compound F$_2$PNNNO

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Received 24 August 2009, in final form 28 October 2009
Published 16 December 2009
Online at stacks.iop.org/JPhysCM/22/036001

Abstract
An analysis of the energy spectrum and magnetization curve of the two-dimensional organic antiferromagnet F$_2$PNNNO with a spin-one dimerized structure shows that the behavior of the compound in an external magnetic field can be explained within a lattice boson model with an extended Pauli exclusion principle, i.e. no more than two bosons per dimer. The unusual magnetization curve observed experimentally in the compound reflects a sequence of phase transitions intrinsic for a lattice boson system with strong on-site and inter-site repulsions due to a tuning of magnon density by the applied magnetic field.

1. Introduction
The possibility of studying Bose–Einstein condensation (BEC) with low-dimensional magnetic materials predicted theoretically twenty years ago [1] gave rise to intense experimental research in the field. The analogy between the spins and the bosons becomes evident for antiferromagnets where spins form dimers with a spin-singlet ground state [2]. Originally, the attention was mainly focused on spin-1/2 systems where excitations inside each dimer (triplons) were regarded as bosons with hard-core repulsion, i.e. no more than one boson was presented on a single dimer. The analogy enables the treatment of spin systems as interacting bosons whose ground state is determined by the balance between kinetic energy and repulsive interactions [3]. If the repulsion dominates, the bosons form a superlattice and a finite energy cost is needed to create an additional particle. This is exhibited as a jump in the chemical potential versus boson number, in spin language, as a plateau in the magnetization curve versus magnetic field at a rational fraction of the saturated magnetization.

The field induced condensation of magnons has been experimentally observed in coupled quantum ($s = 1/2$) dimer systems based on Cu$^{2+}$ ions such as TlCuCl$_3$, BaCuSi$_2$O$_6$ [4–6] and the compound Ba$_2$Cr$_2$O$_8$ [7] which are adequately described by the BEC theory.

Recently, the magnetic weakly coupled dimer system Ba$_3$Mn$_2$O$_8$ with $S = 1$ moments has attracted a lot of attention [8, 9]. The field behavior of magnetization in the system of antiferromagnetically weakly coupled $S = 1$ dimers can be described as BEC of magnons by mapping the spin-1 system into a gas of semi-hard-core bosons [10]. Considering the example of a simple two-dimensional (2D) $S = 1$ isotropic Heisenberg model with a dimerized structure and frustrating interactions, it was suggested that an emergence of the spin supersolid state (a long-range mixing of superfluid and charge-ordered phases) was induced by a magnetic field [11]. The organic compound F$_2$PNNNO is another example of a spin-one dimer based magnetic insulator. This is a 2D Heisenberg system with a singlet ground state, in which $S = 1$ dimers interact antiferromagnetically [12, 13]. The lattice of the system is equivalent to the honeycomb one (figure 1). The field magnetization process shows a two-step saturation behavior that is a rare example of observing a plateau in a two-dimensional system. The intermediate plateau corresponds to the half value of saturation magnetization. The consistent calculation of susceptibility and magnetization for the finite-size cluster with imposed periodic conditions yields the following estimations of antiferromagnetic exchange couplings, $2J_0 = 67.5$ K, $2J_1 = 7.5$ K, i.e. the system can be regarded as a real 2D dimerized spin-one system.

Apparently, the quantum antiferromagnet F$_2$PNNNO offers an opportunity to verify the relevance of the semi-

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2. The model

The Hamiltonian of weakly interacting spin-one dimers on the 2D lattice depicted in Figure 1 is given by

\[ H_S = J_0 \sum_i \vec{S}_i \cdot \vec{S}_j + J_1 \sum_{(\alpha, \beta)} \vec{S}_\alpha \cdot \vec{S}_\beta, \]  

where \( J_0 \) is the coupling inside the \( i \)-th dimer, \( J_1 \) is the strength of the exchange interaction between the dimers located on the bonds \((i, j)\). The indices \( \alpha, \beta \) mark \( S = 1 \) spins that enter into the interacting dimers, namely, \( \alpha = 1, 2, \) provided \( \alpha = 2, 1 \), respectively. Both types of interactions are antiferromagnetic \( J_{0,1} > 0 \), and the regime of weakly interacting dimers, \( |J_0| \gg |J_1| \), is considered. The Heisenberg model has been previously suggested to explain some thermodynamical properties of \( \text{F}_{2}\text{PNNNO} \) [12]. Numerical calculations based on the Hamiltonian (1) via exact diagonalization of small clusters and their comparison with experimental data prove its relevance for the ratio \( |J_1/J_0| \ll 1 \). The dimerization caused by the anisotropy of interactions on a lattice is somewhat analogous to the situation in two-leg spin-1 antiferromagnetic ladders in a strong antiferromagnetic rung-coupling regime, when the ladder ground state is well approximated by the tensor product of singlet rung-dimers [16].

To get the energy spectrum, finite-size clusters composed of \( N = 10 \) and 18 sites are selected. In a choice of the cluster, care should be taken to ensure that the lattice point group symmetry holds. Since intra-dimer interactions are the strongest, the cluster should contain whole dimers and not break them into parts. To mark sites inside the cluster, chessboard-like notations will be used, where site positions along the \( x \)-axis are denoted by numbers whereas positions along the \( y \)-axis are denoted by Latin letters.

The Hamiltonian of the central dimer has the form \( H_c = J_0 \vec{S}_{c3} \vec{S}_{c3} \), whereas the interaction between the center and its environment is given by

\[ V_{ec} = J_1 \vec{S}_{c3} (\vec{S}_{c2} + \vec{S}_{c4}) + J_1 \vec{S}_{c3} (\vec{S}_{c2} + \vec{S}_{c4}). \]  

The environment consists of four parts, namely of two dimers, left (l) and right (r) ones, with the Hamiltonians

\[ H_l = J_0 \vec{S}_{c1} \vec{S}_{c1}, \quad \text{and} \quad H_r = J_0 \vec{S}_{c5} \vec{S}_{c5}, \]  

respectively, as well as two fork-like parts, i.e. the down and up ones, with the corresponding Hamiltonians

\[ H_{down} = J_0 (\vec{S}_{c2} \vec{S}_{c2} + \vec{S}_{c3} \vec{S}_{c3} + \vec{S}_{c4} \vec{S}_{c4}) + J_1 \vec{S}_{c3} (\vec{S}_{c2} + \vec{S}_{c4}), \]  

\[ H_{up} = J_0 (\vec{S}_{c2} \vec{S}_{c2} + \vec{S}_{c3} \vec{S}_{c3} + \vec{S}_{c4} \vec{S}_{c4}) + J_1 \vec{S}_{c3} (\vec{S}_{c2} + \vec{S}_{c4}). \]  

The interaction between the left/right dimers and the fork-like parts is presented as

\[ V_{env} = J_1 (\vec{S}_{c2} \vec{S}_{c1} + \vec{S}_{c2} \vec{S}_{c1} + \vec{S}_{c4} \vec{S}_{c5} + \vec{S}_{c4} \vec{S}_{c5}). \]  

The Hamiltonian of the entire cluster gathers all the above terms

\[ H = H_c + V_{ec} + \{H_l + H_r + H_{down} + H_{up} + V_{env}\}. \]  

There are three states of dimer, an elementary block of the cluster, with total spin \( S_{dm} = 0 \) (singlet), \( S_{dm} = 1 \) (triplet), and \( S_{dm} = 2 \) (quintuplet). The energies of the states are
where \([ \cdots ]\) is the Clebsch–Gordan coefficient. To increase the size of cluster, reduced matrix elements (RME) of the operators \(S(1)\) and \(S(2)\), that constitute the dimer, calculated within the basis (8), are needed

\[
\langle \delta_{S_{1m}}|S(1)|\delta_{S_{2m}}\rangle = (-1)^{1+S_2n+2S_2'}\sqrt{(2S_{dm}+1)(2S_{dm}'+1)} \sum_{\sigma_1\sigma_2} \left(\begin{array}{c} S_1 \end{array}\right)|\sigma_1|1\sigma_2),
\]

\[
\langle \delta_{S_{1m}}|S(2)|\delta_{S_{2m}}\rangle = (-1)^{1+S_2n+2S_2'}\sqrt{(2S_{dm}+1)(2S_{dm}'+1)} \sum_{\sigma_1\sigma_2} \left(\begin{array}{c} S_1 \end{array}\right)|\sigma_1|1\sigma_2),
\]

where \([ \cdots ]\) is the Clebsch–Gordan coefficient.

The reduced matrix elements of spin operators required to build the Hamiltonian of the environment are shown in appendix A (see equations (A.2)–(A.5)). Note, that the number of states (14) is too great to avoid the truncation procedure (see section 3).

The matrix elements of the environment Hamiltonian

\[
H_{env} = H_1 + H_2 + H_{down} + H_{up} + V_{env}
\]

are listed below

\[
\langle \langle (i_{up}\delta_{S_{up}}\delta_{S_{down}})S_{ud}, (S_iS_i')S_{lr}, S_{env}M_{env}\rangle \rangle
\]

where \(\delta_{S_{up}}\delta_{S_{down}}\) is too great to avoid the truncation procedure (see section 3).

The terms in \(\cdots\) include the product of the reduced matrix elements given by equations (A.2) and (A.3) for spins that enter into the left/right dimers and by equations (A.4) and (A.5) for the constituents of the fork-like parts.

After finding the environment eigenvalues \(E_{i_{up},S_{ud}}\) and eigenfunctions

\[
|\delta_{S_{up}}\delta_{S_{down}}(S_{ud})\rangle = \sum_{S_1S_2S_{ud}} \alpha_{\langle S_1S_2|S_{ud}\rangle} |S_1S_2\rangle |S_{ud}\rangle,
\]

where \(\delta_{S_{up}}\delta_{S_{down}}\) index distinguishes basic functions with the same total spin \(S_{ud}\). The results for the upper fork-like part can be obtained the same way provided the site \(c4\) is substituted for \(d2\), and \(c2\) is changed for \(d4\) etc. The assembly of the cluster part is completed by calculations of the reduced matrix elements (see equation (A.1) in appendix A).

In the next step, we construct spin functions of the non-interacting parts, i.e. of the left and of the right dimers

\[
|S_iS_i', S_{lr}M_{lr}\rangle = \sum_{S_1S_2} \left(\begin{array}{c} S_1 \end{array}\right)|S_1M_1\rangle \left(\begin{array}{c} S_2 \end{array}\right)|S_2M_2\rangle |S_1S_2\rangle |S_{lr}M_{lr}\rangle,
\]

where \(S_i = 0, 1, \ldots, 4\), and upper and lower fork-like parts

\[
|i_{up}\delta_{S_{up}}\delta_{S_{down}}(S_{ud})\rangle = \sum_{S_{1M_1}} \left(\begin{array}{c} S_{ud} \end{array}\right)|S_{ud}M_{ud}\rangle |S_1S_1\rangle |S_{up}M_{up}\rangle |i_{up}\delta_{S_{up}}(S_{down})\rangle |S_{ud}M_{ud}\rangle.
\]
the Hilbert space of the entire cluster, one should pick out only
the target spectrum $E_iS$ either by simply controlling a number of vectors retained in the
'tfork'-like parts, but the former is easier to perform. One can truncate the basis of the environment after combining
lattice segments. This is not the only way to do so, for example
of two 'fork'-like parts before combining them into a larger

$$\langle iSM \rangle = \sum S_{SM} m_{SM} S_{SM} S_{SM}.$$

(18)

3. The truncation procedure

The classification of eigenstates of the parts we used to gather
the total cluster according to irreducible representations of the
$SU(2)$-group enables us to organize the truncation procedure
inside sectors of Hilbert space that arise at consecutive steps of
the algorithm. A possibility to carry out calculations within a
reduced basis is a feature of the algorithm that relates it with
other renormalization group methods.

We hold the following strategy of the truncation procedure
to build target states that are obtained after combining two parts
of the lattice. For a given spin-$S$ sector a certain amount of
states having the lowest energies are kept. Thus each group of
$\{iS\}$ states is presented in a reduced basis. We truncate the basis
of two of 'fork'-like parts before combining them into a larger
lattice segment. This is not the only way to do so, for example
one can truncate the basis of the environment after combining
the 'fork'-like parts, but the former is easier to perform.

We tested several realizations of the truncation procedure,
either by simply controlling a number of vectors retained in the
reduced basis, or by monitoring a genealogy of the target spin-$S$
state through the triangle rule, i.e. only states that contribute
to the target state are taken into account. The last approach
gives an opportunity to keep more vectors in the basis due to
omitting of redundant states. Moreover, the highest-spin
cluster states, i.e. those with $S \geq 15$ in our problem, are treated
exactly. The size of the truncated basis was chosen equal to
either 64 or 121 for the scheme without taking genealogy of the
target state into account, and it varies from 12 up to 352, being
dependent on the total spin $S$, for the 'genealogical' scheme.

The accuracy of the truncation procedure is controlled by
monitoring the energy of the lowest state within each spin
sector. The variation of this observable, computed through both
the schemes, does not normally exceed 1–2% (a maximum
discrepancy of the order 6% is reached only in the S-8 sector); this
provides evidence for the correctness of the constructed basis, which exhibits almost no dependence on the used
truncation procedure. The results that we present below are
obtained within the 'genealogical' scheme.

Another feature of the algorithm is combining the central
unit (one site or dimer) with its environment at the final
step. The procedure does not depend on the structure of the
environment and looks similar for any cluster. However, the
information about quantum numbers of the environment states
enables us to simplify the calculations substantially at this
stage of the algorithm. Indeed, for a given spin-$S$ sector of the
Hilbert space of the entire cluster, one should pick out only
those environment eigenfunctions for which the spins $S_a$ obey the rule
$|S_a - S_i| \leq S \leq S_a + S_i$.

Using the truncation procedure results in bases composed
from a maximum of 4–5 thousand states. To control the accuracy of the procedure, results obtained for the 18-site system
are compared with those for the 10-site system. The
smaller cluster enables us to handle the complete basis without
any truncation. The 10-site system is embedded into a bigger
cluster and consists of the following parts: the central dimer
c3, d3 and neighbor dimers b2, c2, b4, c4, d2, e2, e2, d2, d4, e4. Apparently, the construction of the environment requires two
consecutive steps (i) addition of dimers b2, c2 and b4, c4 as
well as d2, e2 and d4, e4 ones according to equation (12),
followed by calculation of the reduced matrix elements
according to equation (A.2) and (A.3); (ii) construction of the
environment states from the upper and lower parts built
previously and the calculation of the RME of the environment
spins that interact directly with the central dimer. The entire
cluster Hamiltonian is obtained through (17). The biggest
Hilbert space dimension $(2053 \times 2053)$ is reached in the
$S$-2 sector. Numerical results for the supplementary cluster
are listed in table 1 for comparison. Note that one should
compare energy values with the same magnetization per dimer
(see figure 2).

4. The energy spectrum and magnetization curve

The results of the energy spectrum calculation for two $N = 10$ and
18 clusters are listed in table 1, where the minimal energy
$E_{min}$ within each spin-$S$ sector along with energy per dimer
$\tilde{e} = 2E_{min}/N$ are given. The magnetization per dimer is
determined by $m = 2S/N$. Both $N = 10$ and 18 dependences
$\tilde{e}(m)$ are shown together in figure 2. Points for both clusters lay
on the same curve, i.e. finite-size effects can be ignored, which

| $S$ | $E_{min}$ $(N = 10)/J_0$ | $\tilde{e}$ $(N = 10)$ | $E_{min}$ $(N = 18)/J_0$ | $\tilde{e}$ $(N = 18)$ |
|-----|--------------------------|---------------------|--------------------------|---------------------|
| 0   | −10.0334                | −2.0067             | −18.0356                 | −2.0037             |
| 1   | −9.8583                 | −1.8371             | −17.1431                 | −1.9048             |
| 2   | −8.2123                 | −1.6425             | −16.2529                 | −1.8059             |
| 3   | −7.1978                 | −1.4396             | −15.2935                 | −1.6993             |
| 4   | −6.1430                 | −1.2286             | −14.3205                 | −1.5912             |
| 5   | −5.9344                 | −0.9869             | −13.3164                 | −1.4796             |
| 6   | −2.9278                 | −0.5957             | −12.2745                 | −1.3638             |
| 7   | −0.9610                 | −0.1922             | −11.1879                 | −1.2431             |
| 8   | 1.0849                  | 0.2170              | −10.0260                 | 1.1140              |
| 9   | 3.1588                  | 0.6318              | −8.8335                  | 0.9815              |
| 10  | 5.4418                  | 1.0883              | −6.8807                  | −0.7645             |
| 11  | −4.8994                 | −0.4444             |                         |                     |
| 12  | −2.8795                 | −0.3199             |                         |                     |
| 13  | −0.8172                 | −0.0908             |                         |                     |
| 14  | 1.2815                  | 0.1424              |                         |                     |
| 15  | 3.4533                  | 0.3837              |                         |                     |
| 16  | 5.6844                  | 0.6316              |                         |                     |
| 17  | 7.960                   | 0.8844              |                         |                     |
| 18  | 10.3254                 | 1.1473              |                         |                     |
is expected for the regime of a small dimer–dimer interaction $J_1 \ll J_0$.

A remarkable feature of the curve is the cusp in the middle, i.e. at $m = 1$. Independent fitting of both parts by the quadratic form $\varepsilon(m) = \varepsilon_0 m^2 + \varepsilon_1 m + \varepsilon_0$ joined in the point yields $\varepsilon_2 = 0.190 \pm 0.018$, $\varepsilon_1 = 0.828 \pm 0.019$, and $\varepsilon_0 = -2.0073 \pm 0.0040$ for lower part of the curve ($0 < m < 1$) together with $\varepsilon_2 = 0.200 \pm 0.058$, $\varepsilon_1 = 1.4578 \pm 0.018$, and $\varepsilon_0 = -2.629 \pm 0.014$ for upper part ($1 < m < 2$).

Based on $N = 18$ case data we build a dependence of jumps $E_{\text{min}}$ when the total spin $S$ changes from 0 up to 18, or the dimer magnetization varies from 0 up to 2 (figure 3). One can see that the values of jumps are approximately $J_0$ for $S \leq 9$ and they increase by a factor of 2 as $S \geq 10$. It means that the energy of the total system of weakly interacting dimers changes with an increase of magnetic field, due to local excitations inside separate dimers. Indeed, for the single $S = 1$ dimer the spectrum consists of a singlet, a triplet, and a quintuplet. The energy difference between the singlet and the triplet is $J_0$, while the difference between the quintuplet and the triplet is $2J_0$ (see the discussion in section 5).

A standard way to describe the magnetization process at $T = 0$ is to define $E_{\text{min}}^{(S)}(N)$ as the lowest energy of the Hamiltonian (1) in the spin-$S$ subspace for the finite system of $N$ elementary dimers. Applying a magnetic field $B$ leads to the Zeeman splitting of the energy levels $E_{\text{min}}^{(S)}(B) = E_{\text{min}}^{(S)} + SB$, and therefore, the level crossing occurs at values $B_S = E_{\text{min}}^{(S)}(B) - E_{\text{min}}^{(S)}$. These level crossings correspond to jumps of value $1/N$ in magnetization at zero temperature, until the fully polarized state with magnetization per dimer $m_{\text{sat}} = 2N/N = 2$ is reached at a value of the magnetic field $B_{\text{sat}} = E_{\text{min}}^{(S)}(B) - E_{\text{min}}^{(S)}$. The calculation performed for $N/2 = 9$ dimers yields the magnetization points presented in figure 4 and reveals the appearance of the ground state plateau as well as the plateau at one-half of the saturation value.

To guarantee the validity of the magnetization curve we use the approach developed by Sakai and Takahashi [17] to recover the $m(B)$ dependence in the thermodynamic limit. In this case the condition for crossover fields transforms into $B = \varepsilon'(m)$, where $\varepsilon$ is the energy per dimer. The plateau boundaries are determined by the derivatives at the special points: (i) $B_1 = \varepsilon'(0)$ is related with the end of the ground state plateau; (ii) $B_2 = \varepsilon'(1-0)$ and $B_3 = \varepsilon'(1+0)$ correspond to the beginning and the end of intermediate plateau, respectively; (iii) $B_4 = \varepsilon'(2-0)$ marks an emergence of saturation magnetization.

Treating the energy spectrum results in linear dependences relevant to the sectors between plateaus

\[
\begin{align*}
\varepsilon'(m) &= 0.83 + 0.38m, \quad 0 < m < 1, \\
\varepsilon'(m) &= 1.46 + 0.40m, \quad 1 < m < 2,
\end{align*}
\]

that yields immediately $B_1 = 0.83J_0$, $B_2 = 1.21J_0$, $B_3 = 1.86J_0$, and $B_4 = 2.26J_0$. Values normalized to the saturation field $B_{\text{sat}}$ are listed in table 2 and exhibit a reasonable agreement with the experimental data for the $F_2\text{PNNNO}$ system. A comparison of finite cluster calculations with those of the thermodynamic limit (19) is given in figure 4. One can see that both methods come to close results.

Note that the method we used for numerical calculations is intrinsically a two-dimensional one, whereas the previous numerical study of the system [12] dealt with an essentially one-dimensional ‘folded chain’ cluster. The regions between the plateaus of the magnetization curve exhibit a behavior closer to a linear one instead of the S-shape forms obtained earlier.
Hamiltonian (1) is reached through representation [11] (see 2D case (see appendix B). The algebra of the operators is a transmutation of statistics that complicates calculations in a realized via parafermion language, but its description requires algebra, \( n_i \) and \( \mu \) with the extended Pauli exclusion principle \( g_i^{13} = 0 \), i.e. more than two bosons per site are forbidden. Note that this principle may be realized via parafermion language, but its description requires a transmutation of statistics that complicates calculations in a 2D case (see appendix B). The algebra of the operators is \( [g_i, g_j] = [g_i, g_j^\dagger] = 0 \), and \( [g_i, g_i^\dagger] = \delta_{ij}(1 - F_i) \), where \( F_i = (3/2)n_i(n_i - 1) \) is deformation of the canonical boson algebra, \( n_i = g_i g_i^\dagger \) is the number operator [10].

The boson Hamiltonian in terms of operators is written as

\[
H = \frac{1}{2} \sum_{\langle ij \rangle} (g_i^\dagger g_j + g_j^\dagger g_i)(h_1 + h_2 + h_3) - \mu \sum_i n_i + \frac{U}{2} \sum_i n_i(n_i + 1) + V \sum_{\langle ij \rangle} (n_i - 1)(n_j - 1),
\]

where the hopping terms

\[
h_1 = t_1(n_{ij} - 2)(n_{ij} - 3), \quad h_2 = 2t_2(n_{ij} - 1)(3 - n_{ij}),
\]

\[
h_1 = t_1(n_{ij} - 1)(n_{ij} - 2)
\]

depend on the number of particles \( n_{ij} = n_i + n_j \) on the bonds \( i,j \).

The map between the bosonic (20) and the spin Hamiltonian (1) is reached through representation [11] (see figure 5)

\[
n_i = S_i^z = S_{i1}^z + S_{i2}^z,
\]

where (1, 2) marks two spins on each dimer, and

\[
g_i^\dagger = \frac{1}{\sqrt{2}}(S_i^2 - S_i^1) \left[ \frac{\sqrt{3}}{2\sqrt{2}} + \left(1 - \frac{\sqrt{3}}{2\sqrt{2}}\right)\ S_i^1 \right].
\]

This establishes the relationship between the spin and the bosonic parameters \( U = J_0, V = J_1/2, \mu = B - 4J_1, \) and \( t_i = -\frac{a_i}{2}a^\dagger J_1 \), where \( a = \frac{J_1}{\sqrt{2}}(i = 1, 2, 3) \). Thus, the bosonic model includes a strong on-site boson repulsion \( U \) as well as a noticeable repulsive inter-site interaction \( V \). The magnetic field \( B \) plays the role of the chemical potential \( \mu \).

Table 2. Values of the magnetic field special points compared with the experimental data.

| \( B_i/B_{sat} \) | \( i = 1 \) | \( i = 2 \) | \( i = 3 \) | \( i = 4 \) |
|------------------|-----------|-----------|-----------|-----------|
| Theory           | 0.37      | 0.53      | 0.82      | 1         |
| Experiment [12]  | 0.33      | 0.53      | 0.89      | 1         |

5. The semi-hard-core boson model

Here we introduce the boson picture based on data presented in figure 3. For \( J_1 \ll J_0 \) the low energy subspace of the spin Hamiltonian (1) consists of the singlet, the \( S^z = 1 \) component of the triplet, and the \( S^z = 2 \) component of the quintuplet. It is convenient to identify the triplet state with the presence of a bosonic particle (triplon), the quintuplet state as a pair of bosons (quintuplon), and the singlet state as an absence of bosons. Then, the boson model is formulated via the semi-hard-core bosonic operators \( g_i \) and \( g_i^\dagger \) with the extended Pauli exclusion principle \( g_i^{13} = 0 \), i.e. more than two bosons per site are forbidden. Note that this principle may be realized via parafermion language, but its description requires a transmutation of statistics that complicates calculations in a 2D case (see appendix B). The algebra of the operators is \( [g_i, g_j] = [g_i, g_j^\dagger] = 0 \), and \( [g_i, g_i^\dagger] = \delta_{ij}(1 - F_i) \), where \( F_i = (3/2)n_i(n_i - 1) \) is deformation of the canonical boson algebra, \( n_i = g_i g_i^\dagger \) is the number operator [10].

The boson Hamiltonian in terms of operators is written as

\[
H = \frac{1}{2} \sum_{\langle ij \rangle} (g_i^\dagger g_j + g_j^\dagger g_i)(h_1 + h_2 + h_3) - \mu \sum_i n_i + \frac{U}{2} \sum_i n_i(n_i + 1) + V \sum_{\langle ij \rangle} (n_i - 1)(n_j - 1),
\]

where the hopping terms

\[
h_1 = t_1(n_{ij} - 2)(n_{ij} - 3), \quad h_2 = 2t_2(n_{ij} - 1)(3 - n_{ij}),
\]

\[
h_1 = t_1(n_{ij} - 1)(n_{ij} - 2)
\]

depend on the number of particles \( n_{ij} = n_i + n_j \) on the bonds \( i,j \).

The map between the bosonic (20) and the spin Hamiltonian (1) is reached through representation [11] (see figure 5)

\[
n_i = S_i^z = S_{i1}^z + S_{i2}^z,
\]

where (1, 2) marks two spins on each dimer, and

\[
g_i^\dagger = \frac{1}{\sqrt{2}}(S_i^2 - S_i^1) \left[ \frac{\sqrt{3}}{2\sqrt{2}} + \left(1 - \frac{\sqrt{3}}{2\sqrt{2}}\right)\ S_i^1 \right].
\]

This establishes the relationship between the spin and the bosonic parameters \( U = J_0, V = J_1/2, \mu = B - 4J_1, \) and \( t_i = -\frac{a_i}{2}a^\dagger J_1 \), where \( a = \frac{J_1}{\sqrt{2}}(i = 1, 2, 3) \). Thus, the bosonic model includes a strong on-site boson repulsion \( U \) as well as a noticeable repulsive inter-site interaction \( V \). The magnetic field \( B \) plays the role of the chemical potential \( \mu \).

The boson Hamiltonian (20) constitutes a low energy effective model of the spin Hamiltonian (1) that emerges from restricting \( H_2 \) to the subspace of the semi-hard-core bosonic operators. The map is valid in the limit \( J_1 \ll J_0 \), or in the boson language \( t_i/U, V/U \ll 1 \), when the main physics is governed by a competition between one-site repulsion and chemical potential.

The quantum phase diagram of the boson Hamiltonian (20) was built in [11] by using the stochastic series expansion quantum Monte Carlo method (see their figure 4). It has been found that a Bose condensate fraction appears in the regions of the chemical potential (magnetic field) between the plateaus of the g-particles density (magnetization curve). In contrast, the charge density wave (Ising-like charge order (CO) phase) forms around the intermediate plateau. There are regions, where a supersolid phase, a mixing of the charge order and the Bose-superfluid (BS), emerges. According to this study, the magnetization curve shown in figure 4 can be interpreted as tuning of boson density by an applied magnetic field. At a small chemical potential, the lowest energy is achieved by empty states, i.e. those where all dimers are in the singlet state (boson vacuum). For \( B > B_1 \), a finite density of bosons (triplons) emerges in the ground state and contributes to the BS phase. The triplon excitations are mobile due to weak inter-dimer coupling. The density (magnetization) increases monotonically as a function of magnetic field until \( B_2 \), where a transition to the CO-phase occurs. This corresponds to the boson concentration \( n = 0.5 \), when the triplons crystallize in a superstructure pattern (figure 5). The fractional plateau requires strong boson interactions in comparison to the kinetic energy. At \( B > B_3 \), the filling increases monotonically in the resulting BS phase (quintuplon condensation) until the ground state transforms into a Mott insulating (MI) phase with two bosons per dimer at \( B > B_4 \). The boson concentration in the MI phase is \( n = 1 \). The reasonings are easily reproduced if one analyzes the boson Hamiltonian (20) by neglecting the inter-site terms.
6. Conclusions

Quantum dimer antiferromagnetic systems are a good field for studying the BEC of interacting particles. Along with ultracold atomic gases in optical lattices [18, 19] they offer an opportunity to observe transitions predicted by lattice boson models. In many cases, the boson picture is more transparent physically than the original spin language. Based on the analysis of the finite cluster energy spectrum for the two-dimensional spin-1 organic antiferromagnet F$_3$PNNNO with dimerized structure, we prove the relevance of semi-hard-core phases change each other subsequently with field increases. The unusual magnetization curve observed in F$_3$PNNNO is nothing but a manifestation of the fine tuning of the density of bosons by an applied magnetic field, when a low-density Bose-superfluid, charge ordering with one boson per dimer, and a high-density Bose-superfluid phases change each other subsequently with field increases.

Acknowledgments

We would like to thank T. Sakai, J. Kishine and N. V. Baranov for discussions. VES would like to acknowledge the support of the US Civilian Research & Development Foundation (CRDF) and the Ministry of Education and Science of the Russian Federation (MinES) under the ‘Basic Research and Higher Education’ (BRHE) program.

Appendix A

The reduced matrix elements for spins on c2 and c4 sites computed in the basis of eigenfunctions of the Hamiltonian $H_{\text{down}}$ are given by the $14 \times 141$ matrix

$$
\langle S_{\text{down}}S_{\text{c2(c4)}}||S_{\text{up}}S_{\text{c2(c4)}}\rangle = \sum_{S_x} \langle S_x S_{\text{c2(c4)}}||S_{\text{up}}S_{\text{c2(c4)}}\rangle = \langle S_x S_{\text{c2(c4)}}||S_{\text{up}}S_{\text{c2(c4)}}\rangle = \text{constant},
$$

The reduced matrix elements that enter into the expression are calculated according to the rules

$$
\langle S_{\text{up}} S_{\text{c2(c4)}}||S_{\text{down}}S_{\text{c2(c4)}}\rangle = \langle S_{\text{up}} S_{\text{c2(c4)}}||S_{\text{down}}S_{\text{c2(c4)}}\rangle = \text{constant},
$$

where $S_x = (2S + 1)$.

The reduced matrix elements for spins on the sites c1 (d1) are given by the $19 \times 19$ matrix built in the basis of functions, which are constructed from the ‘left’ and the ‘right’ dimers equation (12)

$$
\langle S_x S_y; S_{\text{up}}||S_{\text{c1(d1)}}||S_x S_y; S_{\text{up}}\rangle = \langle S_x S_y; S_{\text{up}}||S_{\text{c1(d1)}}||S_x S_y; S_{\text{up}}\rangle = \text{constant},
$$

The RME for spins on the c5 (d5) sites are calculated as follows:

$$
\langle S_x S_y; S_{\text{up}}||S_{\text{c5(d5)}}||S_x S_y; S_{\text{up}}\rangle = \langle S_x S_y; S_{\text{up}}||S_{\text{c5(d5)}}||S_x S_y; S_{\text{up}}\rangle = \text{constant},
$$

Quantum statistics is based on two principles. The first one is exchange statistics, when a permutation of two identical
particles causes an appearance of a phase factor in the total wave function. The second one is exclusion statistics, which reflects an ability to accommodate \( p \) particles in the same single-particle quantum state. Whereas the first concept depends on the space dimensionality of the system, the second one does not \[20\].

The exclusion statistics algebra obeying the generalized Pauli exclusion principle can be formulated in terms of the bond \( g \) operators that have been used in the main text. Another variant of the exclusion statistics can be realized, for example, via Green’s parafermion statistics \[21, 22\]. According to common formalism based on Burnside’s theorem of group theory (see \[10\] for details), both algebraic approaches are related to each other.

Indeed, let us introduce two modes (\( \alpha = 1, 2 \)) for each \( i \)th bond
\[
\{d_i^\alpha, d_j^\beta\} = \{\overline{(d_i^\alpha)^\dagger}, (d_j^\beta)^\dagger\} = 0, \quad \{d_i^\alpha, (d_j^\beta)^\dagger\} = \delta_{ij}.
\]
(B.1)

with the condition \( d_i^\alpha \) [vacuum] \( = 0 \). For \( \alpha \neq \beta \) the modes satisfy non-standard relations
\[
\{d_i^\alpha, d_j^\beta\} = \{\overline{(d_i^\alpha)^\dagger}, (d_j^\beta)^\dagger\} = 0, \quad \{d_i^\alpha, (d_j^\beta)^\dagger\} = 0.
\]
(B.2)

Parafermion creation and annihilation operators are determined as
\[
d_i^\dagger = (d_i^\dagger)^\dagger + (d_i^\dagger)^\dagger, \quad d_j = d_j^\dagger + d_j^\dagger.
\]
(B.3)

They satisfy commutation relations
\[
[[d_i^\dagger, d_j], d_l] = -2\delta_{ij}d_l, \quad [[d_i, d_j], d_l] = 0.
\]
(B.4)

The parafermion number operator \( n_i^\alpha = (d_i^\dagger)(d_i^\dagger)^\dagger \) can be written as
\[
n_i^\alpha = \frac{1}{2}(n_i + 1).
\]
(B.5)

and obeys the commutation rule
\[
[n_i^\alpha, d_j] = \delta_{ij}d_j.
\]
(B.6)

From the property \( (n_i^\alpha)^2 = n_i^\alpha \) one can conclude that \( n_j^\dagger \) varies from 0 to 2. Moreover,
\[
(d_i^\dagger)^2 = 2(d_i^\dagger)^\dagger(d_i^\dagger)^\dagger,
\]
(B.7)

that means \( (d_i^\dagger)^3 = 0 \). Therefore, the parafermion representation provides the extended Pauli exclusion principle.

To establish a connection between the bond \( g \)-algebra and the parafermion statistics, we note that the local Hilbert space related with a bond has the dimension \( D = 3 \). Therefore, one can map the \( g \)-particles onto the algebra of \( S \)-1 operators
\[
S_i^+ = \sqrt{2}g_i^+ \left[ 1 + \left( \frac{1}{\sqrt{2}} - 1 \right) n_i^\dagger \right],
\]
\[
S_i^- = \sqrt{2} \left[ 1 + \left( \frac{1}{\sqrt{2}} - 1 \right) n_i^\dagger \right] g_i, \quad S_i^0 = n_i^\dagger - 1.
\]
(B.8)

These spin operators are connected with two-flavor hard-core bosons via the generalization of the Jordan–Wigner transformation \[23, 24\]
\[
S_i^+ = \sqrt{2}(b_{i1} + b_{i2}), \quad S_i^- = \sqrt{2}(b_{i1} + b_{i2}^\dagger), \quad S_i^0 = b_{i1} + b_{i2}^\dagger - b_{i2}b_{i2}^\dagger
\]
(B.9)

with the imposed constraint \( b_{i1}^\dagger b_{i1} + b_{i2}^\dagger b_{i2} = 1 \), and the spin state \( S^0 = 0 \) is taken as a vacuum. The commutation relations for the hard bosons are
\[
[g_{ia}, g_{ib}] = \{b_{ia}^\dagger, b_{ib}^\dagger\} = 0, \quad [g_{ia}, b_{ib}^\dagger] = \delta_{ij}\delta_{ab}(1 - n_{ia}^\dagger), \quad [n_{ia}^\dagger, b_{ib}^\dagger] = \delta_{ij}\delta_{ab}b_{ia}^\dagger.
\]
(B.10)

where \( n_{ia}^\dagger = b_{ia}^\dagger b_{ia} \) \( (\alpha = 1, 2) \) is the number operator for the hard bosons.

A transition from the hard-core bosons to the parafermions is related with a transmutation of statistics. In the two-dimensional case, the change of statistics is based on a generalization of the conventional Jordan–Wigner transformation [25, 26]. In the following, for simplicity, we will illustrate the connection on an example of dimerized one-dimensional \( S \)-1 chain.

The parafermion modes are converted into the canonical two-flavor canonical fermions \( c_{ia} \) \( (\alpha = 1, 2) \) determined on the \( i \)th bond of the chain through the partial non-local transmutators
\[
(d_i^\dagger)^\dagger = c_{i1}^\dagger \exp \left[ i\pi \sum_{j<i} n_{j2} \right],
\]
\[
(d_i^\dagger)^\dagger = c_{i2}^\dagger \exp \left[ i\pi \sum_{j<i} n_{j1} + n_{j1} \right],
\]
(B.11)

where
\[
\{c_{ia}, c_{bj}\} = \{c_{ia}^\dagger, c_{bj}^\dagger\} = 0, \quad \{c_{ia}, c_{bj}^\dagger\} = \delta_{ij}\delta_{ab},
\]
(B.12)

and \( n_{ia} = c_{ia}^\dagger c_{ia} \) is the number operator for the fermions.

A map between the hard-core bosons and the two-flavor fermions is established by the total non-local transmutators
\[
b_{i1}^\dagger = c_{i1}^\dagger \exp \left[ i\pi \sum_{j<i} (c_{j1}^\dagger c_{j1} + c_{j2}^\dagger c_{j2}) \right],
\]
\[
b_{i2}^\dagger = c_{i2}^\dagger \exp \left[ i\pi \sum_{j<i} (c_{j1}^\dagger c_{j1}^\dagger c_{j2}^\dagger c_{j2}) \right] e^{i\pi c_{i1}^\dagger c_{i1}}.
\]
(B.13)

Relations (B.8), (B.9), (B.11), (B.13) provide the mapping between the parafermions and the \( g \)-particles.

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