Thermodynamic properties of the coupled dimer system \( \text{Cu}_2(\text{C}_5\text{H}_{12}\text{N}_2)_2\text{Cl}_4 \)

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(Dated: August 20, 2018)

We re-examine the thermodynamic properties of the coupled dimer system \( \text{Cu}_2(\text{C}_5\text{H}_{12}\text{N}_2)_2\text{Cl}_4 \) under magnetic field in the light of recent NMR experiments [Clémançon et al., Phys. Rev. Lett. 97, 167204 (2006)] suggesting the existence of a finite Dzyaloshinskii-Moriya interaction. We show that including such a spin anisotropy greatly improves the fit of the magnetization curve and gives the correct trend of the insofar unexplained anomalous behavior of the specific heat in magnetic field at low temperature.

PACS numbers: 75.40.Cx, 75.10.Jm

The molecular solid \( \text{Cu}_2(\text{C}_5\text{H}_{12}\text{N}_2)_2\text{Cl}_4 \) is of particular interest due to the formation of dimers between the two copper (\( S=1/2 \)) spins of each molecule. It was long believed that the coupling between those dimers were quasi-one dimensional hence realizing the physics of a two-leg spin ladder [1]. Later, it was emphasized that the magnetic coupling between molecules might be more three-dimensional (3D) [2]. In a recent Letter, Clémançon et al. [3] proposed that including Dzyaloshinskii-Moriya (DM) interactions is essential to explain its experimental behavior under magnetic field. From simple symmetry considerations, the lack of inversion centers at the middle of the dimers enables \textit{a priori} the existence of such a DM term which can lead to experimentally observable effects such as the appearance of a uniform transverse magnetization [4] as shown by \( T=0 \) numerical calculations. However, a theoretical investigation of physical properties at \textit{finite} \( T \) in the presence of such a DM interaction has not been done so far.

Following [3] we consider an anisotropic spin ladder under a magnetic field \( h \) along \( z \) with a staggered DM term along \( y \),

\[
\mathcal{H} = J_{\perp} \sum_i \mathbf{S}_{i,1} \cdot \mathbf{S}_{i,2} + J_{\parallel} \sum_i (\mathbf{S}_{i,1} \cdot \mathbf{S}_{i+1,1} + \mathbf{S}_{i,2} \cdot \mathbf{S}_{i+1,2}) + D \sum_i (-1)^i \hat{y} \cdot (\mathbf{S}_{i,1} \times \mathbf{S}_{i,2}) + g \mu_B h \sum_i (S_{i,1}^z + S_{i,2}^z),
\]

where the last term corresponds to the field Zeeman energy. Our aim here is to show that the thermodynamic properties of the above-mentioned molecular system can be partly explained within this model without invoking more complicated three-dimensional couplings.

Specific heat measurements done on the same compound could not be satisfactorily explained with a SU(2)-invariant Heisenberg interaction i.e. \( D = 0 \) [5, 6, 7]. Indeed, despite a fairly good agreement at low fields, a large discrepancy occurs for fields around 10 T for which a strong anomalous low-temperature peak around 1 K is seen experimentally and not reproduced theoretically. In contrast, we show here that the inclusion of the finite DM interaction of [3] provides a more quantitative agreement with the experimental data. We take parameters of previous literature, \( J_{\perp} = 13.1 \) K, \( J_{\parallel} = J_{\perp}/5 \) and \( g = 2.1 \), and use Exact Diagonalisations (ED) to compute the magnetization curve and the specific heat \( C_{mag}(T, h) \). Interestingly, a finite \( D \) strongly reduces finite-size effects so that accurate estimates can be obtained on 16-site systems (see later).

We start by computing the zero-temperature uniform magnetization per site \( m_z \) vs magnetic field \( h \) (in Tesla) for various cluster sizes. (a) \( D = 0 : \) \( m_z \) exhibits finite-size plateaus at rational values multiple of \( 1/N \) that disappear in the thermodynamic limit. (b) Finite \( D \) : we obtain continuous curves (since \( S_z \) is not conserved any more) which show very small finite-size effects. The square root singularity disappears and the magnetization curves become smooth.

![FIG. 1: (Color online) Uniform magnetization per site \( m_z \) vs magnetic field \( h \) (in Tesla) for various cluster sizes. (a) \( D = 0 : \) \( m_z \) exhibits finite-size plateaus at rational values multiple of \( 1/N \) that disappear in the thermodynamic limit. (b) Finite \( D \) : we obtain continuous curves (since \( S_z \) is not conserved any more) which show very small finite-size effects. The square root singularity disappears and the magnetization curves become smooth.](https://example.com/fig1.png)
quantum number, the magnetization has to be computed for each $h$ value, which makes the problem harder. Fortunately, as shown on Fig. 1(b), the absence of $SU(2)$ symmetry makes the finite-size effects almost negligible for any finite $D$. Moreover, we observe that the absence of singularities at $h_{C1}$ and $h_{C2}$ is well reproduced by any finite $D$ as noticed in Ref. 4.

Prior to the calculation of $C(T, h)$, we estimate $D$ from a fit of the experimental magnetization curve at low temperature. On Fig. 2, we plot the numerical uniform magnetization for various $D$. By comparing to experimental data, we find that $D \simeq 0.05J_\perp$ gives an excellent fit with no other adjustable parameter. Remarkably, our estimate of $D$ is exactly the numerical value obtained in Ref. 3.

We show on Fig. 3 the main results of our specific heat calculations and compare it to the experimental data of Ref. 6. First, at low magnetic field up to 6 T ($h < h_{c1}$), $D$ has almost no effect due to the very large spin gap (the $D = 0$ and $D = 0.05J_\perp$ curves are indistinguishable in Fig. 3(a)) and the agreement is very good. However, above this magnetic field, we observe, in addition to the large broad maximum around 6 K, another peak around 1 or 2 K. In our results, this low-temperature peak has the largest magnitude around $h \sim 10$-11 T, as seen in experiment. By taking our previous value, $D/J_\perp = 0.05$, we clearly observe a significant increase of its intensity that translates into a better comparison with experiments.

It is of interest to see whether a larger $D$ value could give rise to a better agreement for the heat capacity (at the price of worsening the magnetization fit). However, as indicated on Fig. 4, we observe that increasing the DM interaction has two important effects: first, it leads to an increase of the height of the low-temperature peak but, secondly, to a shift of its position in temperature with little influence on the second (broad) maximum. As a consequence, the minimum between the two peaks increases too with $D$.

Therefore, a small DM term can partly account for the anomalous experimental height of the low-temperature peak. Note that small sources of discrepancy between theory and experiment should still remain like the exper-
imental uncertainty (due to the subtraction of the phonon contribution), the deviation of the compound from a real ladder system, the small finite size effects in our calculation, etc...

Lastly, we would like to discuss briefly the finite size effects at finite T on e.g. $C_{\text{mag}}(T)$ by comparing data obtained on clusters with 12 and 16 spins. As shown in Fig. 5(a), in the absence of a magnetic field, finite size effects are invisible on the scale of the plot. Moreover, the specific heat is almost unsensitive to a small finite DM term. This contrasts to the case of intermediate $h$ where, as shown above on Fig. 4, the data are greatly sensitive to the value of $D$. In addition, Fig. 5(b) clearly shows that, fortunately, finite size effects are reduced when $D = 0.05 J_\perp$ (compared to $D = 0$), the two curves for $N = 12$ and $N = 16$ being almost superposed. This provides a great deal of confidence on our previous analysis.

To conclude, we have shown that the proposal of Ref. 3 of a finite (small) DM interaction gives the correct trend of the insofar unexplained anomalous behavior of the specific heat in magnetic field of Cu$_2$(C$_5$H$_9$N$_2$)$_2$Cl$_4$. From magnetization measurements, our considerations provide an estimate of $D$ around 0.05 $J_\perp$ in agreement with the value extracted from other recent measurements [3].

We thank S. Miyahara and F. Mila for fruitful discussions.

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