Interlayer Dzyaloshinskii–Moriya Interactions in a Quasi-Two-Dimensional Spin 1/2 Antiferromagnet Cu(en)(H₂O)₂SO₄

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We present a theoretical study of magnetic interlayer exchange couplings in a quasi-two-dimensional quantum antiferromagnet Cu(en)(H₂O)₂SO₄ (en = C₂H₈N₂) (CUEN). We use symmetry arguments to construct the most general form of interlayer spin exchange interactions, and discuss the significance of individual terms. Particular attention is paid to the antisymmetric Dzyaloshinskii–Moriya spin anisotropy, allowed for the interlayer interactions in the ab-planes. We argue that it should not lead to weak ferromagnetism of neither conventional nor hidden type. Instead, such canting is usually produced by antisymmetric Dzyaloshinskii–Moriya spin interactions (DMI), which are allowed for the interlayer couplings [1]. The study of the interlayer interactions is accentuated by the recent antiferromagnetic-resonance (AFMR) experiments on CUEN [7] which confirmed the existence of the two q = 0 magnon gaps, but also observed a small splitting of both branches. Invoking a small isotropic interlayer coupling [8] could explain the splitting, but not its actual observation in a collinear antiferromagnet (AF), because the two of the eigenmodes do not couple to the rf-field and should not be excited.

Our goal is to analyse interlayer spin interaction in CUEN and elucidate the role of the individual terms. We argue that the DMI in CUEN should not lead to the spin canting, and emphasize the need for an alternative explanation of the experiment.

1. Introduction

Cu(en)(H₂O)₂SO₄ (en = C₂H₈N₂) (CUEN) was originally identified as a quasi-two-dimensional (2D) easy-plane Heisenberg antiferromagnet (HAF) with spin S = 1/2 on the spatially anisotropic triangular lattice [1], which becomes magnetically ordered below Tₙ = 0.91 K. Recent experimental and theoretical study established CUEN as a representative of the S = 1/2 HAF on a zigzag square lattice [2] within the magnetic bc-layers. This picture, suggested by ab-initio calculations [3], was corroborated by finite-temperature quantum Monte-Carlo simulations and single-crystal measurements of the specific heat, susceptibility, and magnetization. Symmetry analysis of magnetic layers indicated only the presence of symmetric spin exchange anisotropies (SEA) and anticipated an easy-axis within the easy plane. The easy-axis was identified experimentally through the observation of a spin-flop transition in a magnetic field 200 mT applied along the b-axis.

The emerging picture of a collinear HAF with two intralayer SEA is mostly consistent with the data, but some issues remain unexplained. More specifically, the differences in the susceptibility measured in the field-cooling and zero-field-cooling regimes, the susceptibility peak below the Néel temperature [2], and the observed hysteresis in a field along the b-axis [4] suggest the presence of hidden spin canting of unknown origin. On the other hand, such canting is usually produced by antisymmetric Dzyaloshinskii–Moriya spin interactions (DMI), which are allowed for the interlayer couplings [1]. The study of the interlayer interactions is accentuated by the recent antiferromagnetic-resonance (AFMR) experiments on CUEN [7] which confirmed the existence of the two q = 0 magnon gaps, but also observed a small splitting of both branches. Invoking a small isotropic interlayer coupling [8] could explain the splitting, but not its actual observation in a collinear antiferromagnet (AF), because the two of the eigenmodes do not couple to the rf-field and should not be excited.

Our goal is to analyse interlayer spin interaction in CUEN and elucidate the role of the individual terms. We argue that the DMI in CUEN should not lead to the spin canting, and emphasize the need for an alternative explanation of the experiment.

2. Crystal symmetry and the intralayer spin interactions

CUEN crystallizes in the monoclinic symmetry with the space group C2/c which is preserved at least down to 0.4 K [1]. The room-temperature lattice parameters are a = 7.23 Å, b = 11.73 Å, c = 9.77 Å, β = 105.5°, and Z = 4 [9]. The four translationally inequivalent Cu atoms within the unit cell are denoted as A, B, C, and D. In the following, the spins S = 1/2 located on the Cu atoms are denoted by their standard symbol S, or by A, B, C, D.
when a distinction between the four sublattices becomes necessary. The major spin interactions suggested by \textit{ab initio} studies [3] occur within the basal (A, B spins) and middle bc-layers (C, D spins) where the symmetry precludes the existence of DMI [2] (Fig. 1).

The isotropic exchange interaction between the nearest neighbors within the bc-layer takes a single value \( J \), whereas the SEA is described by four (symmetric) matrices. Assuming the spins to be spatially uniform on each sublattice, most of the off-diagonal elements average out to zero. The rest can be diagonalized by a suitable rotation around the \( b \)-axis [2]. This rotation defines the new orthogonal axes 1, 2, 3, with 1 ≠ 2 ≠ 3, with 1, 3 \parallel \text{out-of-plane} \( \tilde{G}_{\text{out}} \) anisotropies. The energy per spin in a magnetic field \( H \) is then given as

\[
W_S = J \mathbf{A} \cdot \mathbf{B} - \frac{1}{2} g \mu_B H (\mathbf{A} + \mathbf{B}) - \tilde{G}_{\text{in}} A_3 B_3 - \tilde{G}_{\text{out}} A_1 B_1,
\]

where \( g \) is the usual g-factor, \( J > 0 \), and \( \mu_B \) is the Bohr magneton. The components of \( \mathbf{A} \) (B spins) along the axes 1, 3, respectively, are denoted as \( A_1 \) and \( A_3 \) (\( B_1 \) and \( B_3 \)), respectively. Consistency with the experiment requires \( \tilde{G}_{\text{out}} > \tilde{G}_{\text{in}} > 0 \). The values \( \tilde{G}_{\text{in}}, \tilde{G}_{\text{out}} (\approx 10^{-3} J) \) are directly related to the field \( g = 0 \) magnon gaps [2, 7].

Spin interactions in the middle bc-layers are completely isomorphic. The corresponding energy is obtained from (1) by \( \mathbf{A} \rightarrow \mathbf{C}, \mathbf{B} \rightarrow \mathbf{D} \). For \( H = 0 \), above equation is minimized by the collinear spins \( \mathbf{A}, \mathbf{B} \). Even more transparent formulation of (1) can be obtained in terms of the “uniform magnetization” \( \mathbf{m} = (\mathbf{A} + \mathbf{B})/(2s) \), and the “staggered magnetization” \( \mathbf{n} = (\mathbf{A} - \mathbf{B})/(2s) \). If \( g \mu_B S \ll J \), weak anisotropies imply \( |m| \ll |n| \). Here, \( m \) can be treated as small quantity of order \( \epsilon \).

Then, to leading order, \( m \cdot n = 0, n^2 = 1 \). It is useful to introduce rescaled (dimensionless) parameters

\[
g_{\text{in}} = 2 \tilde{G}_{\text{in}}/\epsilon^2 J, g_{\text{out}} = 2 \tilde{G}_{\text{out}}/\epsilon^2 J, \quad \text{and magnetic field parameter} \quad h = g \mu_B H/(2s \epsilon J), \quad \text{which are all of the order of unity. Then, the rescaled energy per spin} \quad w_S \quad (\text{in units of} \quad s^2 \epsilon^2 J), \quad \text{and} \quad m \quad \text{can be expressed entirely in terms of} \quad n, \quad \text{namely}
\]

\[
w_S = \frac{g_{\text{out}} n_1^2 + g_{\text{in}} n_3^2 + (n \cdot h)^2}{2},
\]

3. Interlayer interactions

3.1. Interlayer couplings along the ab-planes

We now discuss the interlayer interactions between the nearest neighbors (NN) within the ab-planes, (i.e., the spin pairs A, C, and B, D in Fig. 2). We assume the modification of the 2D interactions introduced in Sect. 2 to be of the form

\[
W_\perp = \sum_{\langle kl \rangle} [J_{kl} (S_k \cdot S_l) + D_{kl} \cdot (S_k \times S_l)]
\]

\[
+ \sum_{i,j} K_i^{ij} \left( S_i S_j + S_j S_i \right),
\]

where \( \langle \langle kl \rangle \rangle \) is an interlayer NN spin pair. We assume our results in the aforementioned coordinate frame 1, 2, 3 of Sect. 2. The isotropic exchange takes a single value \( J_{kl} = J_\perp \) for all NN neighbors in the ab-planes. The SEA is described by two symmetric matrices \( K_I \) and \( K_{II} \), whose distribution over the lattice is shown in Fig. 2:

\[
K_I = \begin{pmatrix}
K_{11} & K_{12} & K_{13} \\
K_{12} & K_{22} & K_{23} \\
K_{13} & K_{23} & K_{33}
\end{pmatrix},
\]

\[
K_{II} = \begin{pmatrix}
K_{11} & -K_{12} & K_{13} \\
-K_{12} & K_{22} & -K_{23} \\
K_{13} & -K_{23} & K_{33}
\end{pmatrix}.
\]

Finally, DMI are indeed present, as anticipated in [1], and are restricted to the two vectors, see Fig. 2:

\[
D_I = (D_1, D_2, D_3),
\]

\[
D_{II} = (D_1, -D_2, D_3).
\]

Note that the sign of the DMI vectors is opposite for the A, C, and B, D spins.

The isotropic exchange contributes to the total energy as \( J_\perp (\mathbf{A} \cdot \mathbf{C} + \mathbf{B} \cdot \mathbf{D}) \). Using the interlayer staggered magnetization defined in Sect. 2, this contribution can be, lead to leading order, rewritten as \( J_\perp (n_L \cdot n_U) \).
The lattice. In contrast, strong interaction of, say, the DMI for unlikely to occur when limagnetism — the collective rotation of spins, but it is of such alternation indicates a possible occurrence of hetero alternate in sign on opposite bonds [10]. The lack fact that weak ferromagnetism requires the DMI vector no weak-ferromagnetism. This is also supported by the lattice, the DMI contribution is actually zero, with it clear that, for the spins uniform on each sub-

3.2. Interlayer couplings along the ac-planes

We have also examined the interactions between the nearest and the next-nearest neighbors along the ac-planes. Our symmetry analysis revealed that only symmetric exchange anisotropies are present, and DMI is precluded by symmetry. However, the structure of SEA is similar to those already explicitly presented, and does not bring in any new qualitative elements.

4. Conclusions

We have studied the interlayer spin interactions in the antiferromagnet CUEN. We have confirmed the presence of antisymmetric interlayer exchange interactions, and examined them in detail. We found that the Dzyaloshinskii–Moriya interactions do not lead to weak-ferromagnetism of any type. Instead, they admit the existence of helimagnetism, whose actual occurrence, however, is not favored by the system parameters. Similarly, the structure of symmetric exchange interactions does not indicate any obvious spin canting mechanism. The explanation of the experimental results thus requires additional effort.

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