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Exchange Interactions in a Low-Dimensional Magnetic System $Cu(H_2O)_2(en)SO_4$

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We report a theoretical *ab-initio* investigation of the exchange interaction between Cu atoms in $Cu(H_2O)_2(en)SO_4$, en=$C_2H_8N_2$(ethylenediamine), an insulating magnetic material. Unlike previous experimental studies which describe the system as a quasi-two-dimensional antiferromagnet, our results, based on the mapping of the system onto an effective Heisenberg model, suggest a quasi-one-dimensional character of magnetism, with the exchange coupling between the Cu atoms being propagated along a zigzag line, lying in the crystal's *bc* plane and connecting the Cu atoms through the N atoms. Furthermore, we report the calculated positions of the H atoms that have not been provided in experimental papers.

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1. Introduction

Low-dimensional magnets with low critical temperatures feature a wealth of experimentally accessible quantum-mechanical phenomena, which are not blurred by temperature-related effects. Below we give a brief theoretical account of magnetic exchange coupling in $Cu(H_2O)_2(en)SO_4$, supposedly an insulating antiferromagnet with the Néel temperature of $T_N = 0.9$ K [1]. Our results approve both the material being an insulator (calculations yield a gap of about 1 eV) and the antiferromagnetic order as a candidate for the ground state. Nonetheless our results also imply the system's effective magnetic coupling paths are different from those previously considered in [1] and form zigzag chains. This quasi-one-dimensional character makes the system appealing since explanation and quantification of phase transitions in such systems is not easy [2, 3].

2. Computational methodology

The calculations were performed using the VASP code [4, 5] within the density functional theory, using the projector-augmented-wave pseudopotential method with the generalized gradient approximation parameterized by Perdew, Burke, and Ernzerhof. The Brillouin zone was sampled on a k-point mesh with $5 \times 3 \times 4$ points (for supercells doubling the unit cell along the a, or b, or a and c directions, used when we considered more complicated antiferromagnetic orderings, this was $2 \times 2 \times 3$, $5 \times 1 \times 4$, and $3 \times 3 \times 2$, respectively). We used the conjugate gradient energy minimization scheme for geometry optimization and relaxed the structure until the forces on individual atoms were smaller than 5×10^{-3} eV Å^{-1} and the external pressure was below 0.1 kbar. All the calculations presume collinear magnetism and ignore the spin-orbit coupling.

3. Geometric structure

The $Cu(H_2O)_2(en)SO_4$ possesses a monoclinic symmetry, space group $C2/c$ (no. 15), and four chemical formula units ($Z = 4$) in the unit cell, which thus contains 96 atoms [6]. The Cu and S atoms have the Wyckoff positions 4e, all the others are at general 8f positions. The structure is formed by stacking, along the c axis, of hydrogen-bonded ab planes of mutually hydrogen-bonded linear chains running along the a axis of covalently-bonded $Cu(H_2O)_2(en)SO_4$ complexes. Experimental lattice parameters together with our optimized ones are given in Tab. 1. The calculated constants are larger by +5, +2, and −1 % in the a, b, c dimensions, respectively.

TABLE I

Experimental [6] and optimized lattice parameters.

	a [Å]	b [Å]	c [Å]	β [°]	V [Å^3]
exp.	7.232	11.725	9.768	105.5	798
cal.	7.597	11.964	9.675	104.0	853

Equilibrium atomic positions are given in Tab. 2, and are in a good agreement (to within 2 % of the lattice vectors) with the X-ray diffraction values [6].

4. Magnetic order

For the optimized geometry we have evaluated the total energies of the system with ferromagnetically (FM) ordered Cu ions as well as for several antiferromagnetic (AF) configurations. The calculations show that magnetic moments exist only on the Cu atoms, of 0.6 μ_B (Bohr magneton), and on N atoms, of 0.1 μ_B, the latter

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being always ferromagnetically ordered with respect to the closest Cu atom. These moments are stable between all the different investigated magnetic orderings. This allows us to map the system's energy differences onto an effective Heisenberg model, described by the Hamiltonian $H = -\frac{1}{2}\sum_{i\neq j} J_{ij}\boldsymbol{e}_i \cdot \boldsymbol{e}_j$, where i, j count the Cu sites, J_{ij} represent effective exchange couplings, and $\boldsymbol{e}_i$ denotes the site-i magnetization direction, $\boldsymbol{e}_i\boldsymbol{e}_j = \pm 1$ for a FM and AF ordering, respectively. Hereafter, instead of $J_{ij}/2$ we use Jn to label different exchange couplings.

TABLE II

Calculated equilibrium atomic positions given as fractional coordinates x, y, z with respect to the (relaxed) a, b, c lattice vectors. Only inequivalent positions are listed. In parentheses the experimental values [6] are given (these are, strictly speaking, with respect to the experimental lattice parameters).

	x	y	z
Cu	0	0.279 (0.2718)	0.75
N	0.004 (−0.0165)	0.156 (0.1486)	0.609 (0.6079)
C	0.045 (0.0576)	0.051 (0.0395)	0.829 (0.8270)
S	0.5	0.191 (0.1938)	0.75
O1	0.052 (0.0482)	0.394 (0.3905)	0.903 (0.8990)
O2	0.365 (0.3551)	0.259 (0.2642)	0.799 (0.7902)
O3	0.402 (0.4050)	0.115 (0.1179)	0.629 (0.6281)
H1	−0.009	0.387	0.984
H2	0.060	0.475	0.879
H3	0.078	0.173	0.990
H4	−0.137	0.152	0.899
H5	−0.009	0.387	0.984
H6	0.060	0.475	0.879

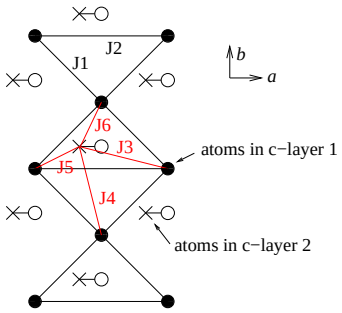

Fig. 1. Considered neighbours and exchange couplings of a Cu atom. Full circles represent atoms in one c layer, crosses then atoms in the next c layer, whose positions would be empty circles if β were 90°. The distances corresponding to $J1$–$J6$ are 7.1, 7.6, 6.9, 8.2, 5.4, 7.2 Å, respectively.

For each Cu atom, guided by the geometric distances, we considered its 14 Cu neighbours, see Fig. 1. There are 6 neighbours in the same c plane: 2 along the a direction, within the same covalently-bonded chain, described by the exchange $J2$, and 4 $(2+2)$ in the two neighbouring chains, described by $J1$. Each Cu atom further has 8 neighbours in the c planes above and below itself $(4+4)$, described by constants $J3$ to $J6$.

All of the considered exchange couplings with the exception of $J3$ are antiferromagnetic, but most importantly only the $J4$ constant is sizeable, of the order -5×10^{-4} eV, whereas the others being at least an order of magnitude smaller. Namely, $J1 \approx -8\times10^{-6}$ eV, $J2 \approx -7\times10^{-7}$ eV, $J3 \approx +6\times10^{-6}$ eV, $J5 \approx -6\times10^{-6}$ eV, and $J6 \approx -7\times10^{-5}$ eV. $J4$ corresponds to the coupling via the N atoms, spans the longest distance, and forms a zigzag chain in the bc plane.

5. Conclusions

Using first-principle calculations we determined exchange couplings in a low-dimensional antiferromagnetic insulator $Cu(H_2O)_2(en)SO_4$. The magnetic ordering is rather one-dimensional (along a zigzag chain within the bc plane) than two-dimensional (in the ab plane) as supposed previously [1]. Further, the calculation shows the gap of about 1 eV indicating the true one can be expected at about 2 eV, in accord with a preliminary UV-VIS-spectroscopy measurement (measured with Cintra 303 spectrometer at VSB-TUO Ostrava, Czech Republic). Finally, the positions of the H atoms that have not been reported before are given.

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