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Magnetic interactions in the $S = 1/2$ square-lattice antiferromagnets Ba$_2$CuTeO$_6$ and Ba$_2$CuWO$_6$: parent phases of a possible spin liquid

The isostructural double perovskites Ba$_2$CuTeO$_6$ and Ba$_2$CuWO$_6$ are shown by theory and experiment to be frustrated square-lattice antiferromagnets with opposing dominant magnetic interactions. This is driven by differences in orbital hybridisation of Te$^{6+}$ and W$^{6+}$. A spin-liquid-like ground state is predicted for Ba$_2$Cu(Te$_{1-x}$W$_x$)O$_6$ solid solution similar to recent observations in Sr$_2$Cu(Te$_{1-x}$W$_x$)O$_6$.

Magnetic frustration can stabilise novel quantum ground states such as quantum spin liquids or valence bond solids. Frustration occurs when not all of the magnetic interactions in a material can be satisfied simultaneously as a result of lattice geometry or competing interactions. We have recently shown that a quantum-spin-liquid-like state forms in the double perovskite solid solution Sr$_2$Cu(Te$_{1-x}$W$_x$)O$_6$ with a square lattice of Cu$^{2+}$ (3d$^9$, $S = 1/2$) cations. This was the first observation of a spin-liquid-like state in a square-lattice compound after 30 years of theoretical predictions.

The parent compounds Sr$_2$CuTeO$_6$ and Sr$_2$CuWO$_6$ are frustrated square-lattice (FSL) antiferromagnets. The FSL model (Fig. 1) has two interactions: nearest-neighbour $J_1$ and next-nearest-neighbour $J_2$, and a quantum spin liquid state has been predicted for $J_2/J_1 = 0.5$ where magnetic frustration is maximised.

The two compounds have a tetragonal $I4/m$ double perovskite structure with nearly identical bond distances and angles. The magnetism becomes highly two-dimensional as a result of a Jahn-Teller distortion as the only unoccupied Cu orbital $3d_z^2$-$y^2$ is in the $ab$ plane square. The major differences in dominant magnetic interactions are due to the diamagnetic Te$^{6+}$ $d^{10}$ and W$^{6+}$ $d^{3}$ cations located in the middle of the Cu$^{2+}$ square (Fig. 1c), which hybridise differently with O 2p allowing different superexchange paths between the Cu$^{2+}$ cations. The spin-liquid-like ground state forms when these two perovskites are mixed into a Sr$_2$Cu(Te$_{1-x}$W$_x$)O$_6$ solid solution. Muon spin relaxation experiments revealed the absence of magnetic order or static magnetism in a wide composition range of $x = 0.1$-
The specific heat displays $T$-linear behaviour suggesting gapless excitations in a similar composition range. The ground state has been proposed to be a random-singlet state with a disordered arrangement of non-magnetic valence bond singlets.

Motivated by these exciting findings in the Sr$_2$Cu(Te$_{1-x}$W$_x$)O$_6$ system, we have investigated the magnetic interactions of the isostructural barium analogues Ba$_2$CuTeO$_6$ and Ba$_2$CuWO$_6$. Ba$_2$CuWO$_6$ is known to have columnar magnetic order, but little is known about Ba$_2$CuTeO$_6$ as the perovskite phase requires high pressures to synthesise. Here we use density functional theory (DFT) calculations and high-temperature series expansion (HTSE) fitting of experimental susceptibility data to show that these compounds are FSL antiferromagnets with opposite dominant interactions similar to Sr$_2$CuTeO$_6$ and Sr$_2$CuWO$_6$. We predict a quantum-spin-liquid-like state in Ba$_2$Cu(Te$_{1-x}$W$_x$)O$_6$ with strong antiferromagnetic interactions.

Magnetic interactions and electronic structure in Ba$_2$CuTeO$_6$ and Ba$_2$CuWO$_6$ were calculated using the DFT+$U$ framework, where an on-site Coulomb repulsion term $U$ was used to model electron correlation effects of localised Cu $3d$ orbitals. Interactions up to the fourth-nearest neighbour were evaluated, see Fig. 1b. $J_1$ and $J_2$ are the square plane interactions of the FSL model, and $J_3$ and $J_4$ are additional out-of-plane interactions. Energies of different spin configurations were mapped onto a Heisenberg Hamiltonian to obtain $J_1$-$J_4$. We have previously shown this approach works well for Sr$_2$CuWO$_6$. The $J_1$ and $J_2$ interactions were also determined from experimental magnetic susceptibility data using high-temperature series expansion fitting. Ba$_2$CuTeO$_6$ was prepared by high-pressure synthesis and Ba$_2$CuWO$_6$ by conventional solid state synthesis. Details of the DFT calculations, sample synthesis and characterisation are available in the ESI.

Table 1. Exchange constants of Ba$_2$CuTeO$_6$ and Ba$_2$CuWO$_6$ obtained by density functional theory using different on-site Coulomb $U$ terms and by high-temperature series expansion fitting of magnetic susceptibility data. Negative (positive) values correspond to antiferromagnetic (ferromagnetic) interactions.

|          | $U = 7 \text{ eV}$ | $U = 8 \text{ eV}$ | $U = 9 \text{ eV}$ | HTSE |
|----------|--------------------|--------------------|--------------------|------|
| $J_1$ (meV) | -23.65             | -20.22             | -17.22             | -16.54(3) |
| $J_2$ (meV) | 0.13               | 0.23               | 0.06               | -0.04(3) |
| $J_3$ (meV) | 1.28               | 0.83               | 0.67               | -      |
| $J_4$ (meV) | -0.30              | 0.01               | 0.05               | -      |
| $J_4/J_2$ | -0.01              | -0.01              | -0.003             | 0.002 |

Table 1. Exchange constants of Ba$_2$CuTeO$_6$ and Ba$_2$CuWO$_6$ obtained by density functional theory using different on-site Coulomb $U$ terms and by high-temperature series expansion fitting of magnetic susceptibility data. Negative (positive) values correspond to antiferromagnetic (ferromagnetic) interactions.

The calculated magnetic interactions of Ba$_2$CuTeO$_6$ and Ba$_2$CuWO$_6$ are presented in Table 1. The calculated values depend on the Coulomb $U$ term as is typical with DFT+$U$, but the same trends are observed for reasonable values of $U$. Despite being isostructural, the magnetic interactions in Ba$_2$CuTeO$_6$ and Ba$_2$CuWO$_6$ are very different. Ba$_2$CuTeO$_6$ has a very dominant antiferromagnetic $J_1$ interaction with weak $J_2$, $J_3$, and $J_4$ interactions. It is a near-ideal FSL Néel antiferromagnet. Ba$_2$CuWO$_6$, in contrast, has a dominant antiferromagnetic $J_2$ interaction slightly frustrated by an antiferromagnetic $J_1$ interaction with negligible $J_3$ and $J_4$ interactions. The strong $J_2$ interaction is consistent with the known columnar magnetic structure of this compound. Due to the weakness of the out-of-plane $J_3$ and $J_4$ interactions, magnetism in both compounds is highly two-dimensional and well described by the FSL model.

The significant differences in the magnetic interactions of Ba$_2$CuTeO$_6$ and Ba$_2$CuWO$_6$ can be explained by their electronic structures. We have plotted total and partial densities of states for both compounds in Fig. 2. Ba$_2$CuTeO$_6$ and Ba$_2$CuWO$_6$ are antiferromagnetic insulators: the band gaps open between the occupied Cu $3d$ states hybridised with O $2p$ (valence band) and the unoccupied Cu $3d_{x^2-y^2}$ states hybridised with O $2p$ (conduction band). In Ba$_2$CuWO$_6$ the conduction band is further
hybridised with unoccupied W 5d states. The W 5d states also hybridise with the Cu 3d/O 2p states in the valence band, which allows a 180° Cu-O-W-Cu superexchange pathway resulting in a strong antiferromagnetic J2 interaction. This hybridisation does not occur in Ba2CuTeO6 and therefore J2 is negligible. In Ba2CuTeO6 the Te 5p states hybridise to a lesser degree with the Cu 3d/O 2p states in the conduction band, which could explain the strong antiferromagnetic J1 interaction. However, the role of Te in the J1 superexchange in Sr2CuTeO6 is under debate. Overall, the electronic structures of Ba2CuTeO6 and Ba2CuWO6 are similar to their strontium analogues Sr2CuTeO6 and Sr2CuWO6, and the differences in magnetic interactions are driven by the same orbital hybridisation mechanism.

The magnetic susceptibilities were fitted to a high-temperature series expansion (HTSE) or by inelastic neutron scattering (INS). The data for Ba2CuTeO6 and Ba2CuWO6 are from this work unless specified otherwise. The model has four parameters: J1, J2, g and ΘCW. Open symbols represent experimental data and the lines are HTSE fits with the parameters J1 = -16.54(3) meV, J2 = -0.04(3) meV, g = 2.2(1) and ΘCW = 210 K for Ba2CuTeO6 and Ba2CuWO6 respectively. The ZFC and FC curves overlap and therefore only ZFC data is shown.

**Table 2.** Magnetic properties of Ba2CuTeO6, Sr2CuTeO6, Ba2CuWO6 and Sr2CuWO6.

| Interaction | Ba2CuTeO6 | Sr2CuTeO6 | Ba2CuWO6 | Sr2CuWO6 |
|-------------|-----------|-----------|----------|----------|
| J1 (meV)    | -16.54(3) | -16.54(3) | -16.54(3) | -16.54(3) |
| J2 (meV)    | -0.04(3)  | -0.04(3)  | -0.04(3)  | -0.04(3)  |
| ΘCW (K)     | -2911     | -2820     | -2413     | -2413     |
| T0 (K)      | 2911      | 2820      | 2413      | 2413      |
| f=ΘCW/T0    |           |           |           |           |
| k            | [0 1/2 1/2] | [0 1/2 1/2] | [0 1/2 1/2] | [0 1/2 1/2] |

*predicted based on magnetic interactions

The magnetic properties of Ba2CuTeO6, Ba2CuWO6, Sr2CuTeO6 and Sr2CuWO6 are summarised in Table 2. Magnetic interactions in Ba2CuTeO6 and Ba2CuWO6 are notably stronger than their strontium analogues. This is due to the smaller Te 5p states hybridise to a lesser degree with the Cu 3d/O 2p states in the conduction band, which could explain the strong antiferromagnetic J1 interaction. However, the role of Te in the J1 superexchange in Sr2CuTeO6 is under debate. Overall, the electronic structures of Ba2CuTeO6 and Ba2CuWO6 are similar to their strontium analogues Sr2CuTeO6 and Sr2CuWO6, and the differences in magnetic interactions are driven by the same orbital hybridisation mechanism.

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and Sr$_2$CuWO$_6$ have been observed at temperatures higher than $2T_J$ driven by the two-dimensional magnetic interactions.\textsuperscript{9,10} The stronger in-plane $J_1$ and $J_2$ interactions of the barium phases indicate the excitations survive to even higher temperatures.

Since Ba$_2$CuTeO$_6$ has a dominant $J_1$ interaction and Ba$_2$CuWO$_6$ has a dominant $J_2$ interaction, we predict a spin-liquid-like state will form in the Ba$_2$Cu(Te$_{1-x}$W$_x$)O$_6$ solid solution similar to Sr$_2$Cu(Te$_{1-x}$W$_x$)O$_6$. In the Sr$_2$Cu(Te$_{1-x}$W$_x$)O$_6$ system the Néel order is destabilised already at $x = 0.1$, and spin-liquid-like state exist in the composition region $x = 0.1-0.6$. Columnar order is observed for $x = 0.7-1$. Since the $J_1$ interaction of Ba$_2$CuTeO$_6$ is so strong even compared to $J_2$ in Ba$_2$CuWO$_6$, we predict the Néel order remains more stable against W substitution. For the same reason, the columnar order near $x = 1$ is likely to be less stable in Ba$_2$Cu(Te$_{1-x}$W$_x$)O$_6$. The extent of the spin-liquid-like region depends also on disorder, and is difficult to predict from the properties of the end phases. Finally, the stronger antiferromagnetic interactions in the barium phases indicate that the quantum disordered ground state will remain stable up to higher temperatures.

The previous discussion concerns a double perovskite Ba$_2$Cu(Te$_{1-x}$W$_x$)O$_6$ solid solution, which near $x = 0$ will require high-pressure synthesis to form. The ambient pressure form of Ba$_2$CuTeO$_6$ is triclinic with a tolerance factor higher than 1.03.\textsuperscript{24} Therefore, a Ba$_2$Cu(Te$_{1-x}$W$_x$)O$_6$ solid solution prepared in ambient pressure will have a triclinic to tetragonal structural change at some composition. Triclinic Ba$_2$CuTeO$_6$ is a spin ladder system close to a quantum critical point,\textsuperscript{25} and we propose Te-for-W substitution could drive the system from magnetic order to a spin singlet state.

In conclusion, we have investigated the magnetic interactions of the tetragonal double perovskites Ba$_2$CuTeO$_6$ and Ba$_2$CuWO$_6$ by DFT calculations and by HTSE fitting. Both compounds are well described by the frustrated square-lattice model as out-of-plane interactions are very weak. In Ba$_2$CuTeO$_6$ the antiferromagnetic nearest-neighbor $J_1$ interaction dominates ($|J_1|/|J_2| < 0.02$), whereas in Ba$_2$CuWO$_6$ the antiferromagnetic next-nearest neighbor interaction $J_2$ dominates ($|J_1|/|J_2| < 0.12$). The Ba$_2$Cu(Te,$W$)O$_6$ system is the second known FSL system where isostructural compounds have opposite magnetic interactions. This is driven by differences in orbital hybridisation of Te 5$p$/5$s$ and W 5$d$ with O 2$p$. A spin-liquid-like ground state is predicted for the Ba$_2$Cu(Te$_{1-x}$W$_x$)O$_6$ solid solution similar to the recent findings in the Sr$_2$Cu(Te$_{1-x}$W$_x$)O$_6$ system.

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Conflicts of interest

There are no conflicts to declare.

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