Magnetic interactions in the $S = 1/2$ square-lattice antiferromagnets Ba$_2$CuTeO$_6$ and Ba$_2$CuWO$_6$

Otto Mustonen,$^{a,b}$ Sami Vasala,$^{c,d}$ Heather Mutch,$^{b}$ Chris I. Thomas,$^a$ Gavin B. G. Stenning,$^e$ Elisa Baggio-Saitovitch,$^c$ Edmund J. Cussen$^b$ and Maarit Karppinen$^a$

Electronic Supporting Information

Density functional theory calculations

Density functional theory was used to calculate the magnetic exchange constants in Ba$_2$CuTeO$_6$ and Ba$_2$CuWO$_6$. The calculations were carried out with the full potential linearized augmented plane wave code ELK.$^1$ We used the generalized gradient approximation functionals by Perdew, Burke and Ernzerhof.$^2$ Five different spin configurations with $2 \times 2 \times 1$ ($1 \times 1 \times 2$) supercells were needed to calculate the exchange constants (Fig. 1).$^3,4$ A $k$ point grid of $4 \times 4 \times 6$ ($8 \times 8 \times 3$) was used. A plane-wave cutoff of $|G + k|_{\text{max}} = 8/\text{R}_{\text{MT}}$ a.u.$^1$ was used, where $\text{R}_{\text{MT}}$ was the average muffin tin radius. Electron correlation effects of the localized Cu$^{2+}$ 3$d$ orbitals were included within the DFT+$U$ framework with the on-site coulombic repulsion $U$ and Hund exchange term $I$ as parameters.$^5$ The on-site coulombic $U$ term was varied from 7 to 9 eV, which are typical values for Cu 3$d$ orbitals. The Hund term $I$ was fixed at 0.9 eV for all calculations.

Fig. 1. The five different spin configurations used in the density functional theory calculations. Only the magnetic Cu$^{2+}$ cations and their spins are shown. The energies are calculated in $2 \times 2 \times 1$ (and one $1 \times 1 \times 2$) supercells.

In order to obtain the exchange constants $J_1$-$J_4$ we mapped the energies of the different spin configurations to a simple Heisenberg Hamiltonian:

$$H = - \sum_{i<j} J_{ij} S_i \cdot S_j$$

where $J_{ij}$ is the exchange constant for the interaction between spins $i$ and $j$. The spin configurations are presented in Fig. 1. Using the Hamiltonian, the energies of the spin configurations$^3$ can be written as:

$$E_{FM} = E_0 + (-4J_1 - 4J_2 - 8J_3 - 2J_4)S^2$$
$$E_{AFM1} = E_0 + (-4J_1 - 4J_2 + 8J_3 - 2J_4)S^2$$
\[ E_{AFM2} = E_0 + (4J_1 - 4J_2 - 2J_4)S^2 \]
\[ E_{AFM3} = E_0 + (4J_2 - 2J_4)S^2 \]
\[ E_{AFM4} = E_0 + (-4J_1 - 4J_2 + 2J_4)S^2 \]

The exchange constants \( J_1 \) to \( J_4 \) can then be obtained from:

\[ J_3 = \frac{(E_{AFM1} - E_{FM})}{16S^2} \]
\[ J_1 = \frac{(E_{AFM2} - E_{FM} - 8J_3S^2)}{8S^2} \]
\[ J_2 = \frac{(E_{AFM3} - E_{FM} - 4J_1S^2 - 8J_3S^2)}{8S^2} \]
\[ J_4 = \frac{(E_{AFM4} - E_{FM} - 8J_3S^2)}{4S^2} \]

The calculated energies and exchange constants for \( U = 7-9 \) eV are presented in Table 1.

<table>
<thead>
<tr>
<th>( E_{FM} ) (meV/2f.u.)</th>
<th>( E_{AFM1} ) (meV/2f.u.)</th>
<th>( E_{AFM2} ) (meV/2f.u.)</th>
<th>( E_{AFM3} ) (meV/2f.u.)</th>
<th>( E_{AFM4} ) (meV/2f.u.)</th>
<th>( J_1 ) (meV)</th>
<th>( J_2 ) (meV)</th>
<th>( J_3 ) (meV)</th>
<th>( J_4 ) (meV)</th>
<th>( J_2/J_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( U = 7 ) eV</td>
<td>( U = 8 ) eV</td>
<td>( U = 9 ) eV</td>
<td>( U = 7 ) eV</td>
<td>( U = 8 ) eV</td>
<td>( U = 9 ) eV</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5.12</td>
<td>3.33</td>
<td>2.67</td>
<td>0.22</td>
<td>-0.04</td>
<td>0.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-44.74</td>
<td>-38.78</td>
<td>-33.11</td>
<td>-2.39</td>
<td>-2.37</td>
<td>-2.51</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-20.82</td>
<td>-18.10</td>
<td>-15.77</td>
<td>-30.56</td>
<td>-25.08</td>
<td>-20.36</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.26</td>
<td>1.67</td>
<td>1.39</td>
<td>0.14</td>
<td>0.35</td>
<td>0.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-23.65</td>
<td>-20.22</td>
<td>-17.22</td>
<td>-1.25</td>
<td>-1.17</td>
<td>-1.27</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.13</td>
<td>0.23</td>
<td>0.06</td>
<td>-14.71</td>
<td>-11.94</td>
<td>-9.56</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.28</td>
<td>0.83</td>
<td>0.67</td>
<td>0.05</td>
<td>-0.01</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.30</td>
<td>0.01</td>
<td>0.05</td>
<td>0.03</td>
<td>0.37</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-0.01</td>
<td>-0.01</td>
<td>0.00</td>
<td>11.79</td>
<td>10.18</td>
<td>7.55</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Structural effects on magnetic interactions

Changing strontium to barium has two effects on the structure that could explain the changes in magnetic interactions: it changes the Cu-O bond length and the Cu-O-Te/W bond angle in the \( ab \) plane, see Fig. 2 a). The equatorial Cu-O bonds in the \( ab \) plane are longer in the Ba-phases (2.01 vs 1.95 Å) but the Te/W-O bonds remain constant within experimental error. This lengthening of the Cu-O bond, on its own, would be expected to weaken the magnetic interactions in these materials. The other effect is related to the \( a^\alpha\alpha\alpha^\gamma \) octahedral tilting in these \( I4/m \) double perovskites. The CuO\(_6\) octahedrons tilt with \( c \) as the tilting axis, so that the Cu-O-Te/W angles in the \( ab \) plane are reduced from the ideal 180° (no octahedral tilting, \( I4/mmm \)). The larger size of the Ba\(^{2+}\) cation reduces this octahedral tilting, so that the Cu-O-Te/W angle in the \( ab \) plane is higher. This larger Cu-O-Te/W angle increases orbital overlap, and results in the observed significantly increased magnetic interactions in the Ba-phases in comparison to the Sr-phases.\(^3\) This effect is especially
strong in \( \text{Sr}_2\text{CuTeO}_6 \) and \( \text{Ba}_2\text{CuTeO}_6 \), where the Cu-O-Te bond angle increases from 158° to 175° when replacing strontium with barium, and as a consequence \( J_1 \) increases from -7.18 meV to -20.22 meV. The trends in bond lengths, angles and magnetic interactions are plotted in Fig. 2 panels b) and c). The trends in the Curie-Weiss constant and dominant magnetic interactions in Fig. 2 c) follow the trend in the Cu-O-Te/W angle in Fig. 2 b).

![Diagram](image)

**Fig. 2.** a) The structure of tetragonal \( \text{A}_2\text{CuB}^{V''}\text{O}_6 \) double perovskites with view down the c-axis. The Cu-O bond length and the Cu-O-Te/W angle are shown. b) The Cu-O bond length and Cu-O-Te/W angle in the compounds. c) The Curie-Weiss constant and dominant magnetic interactions \( (J_1 \text{ for } \text{Ba}_2\text{CuTeO}_6 \text{ and } \text{Sr}_2\text{CuTeO}_6, J_2 \text{ for } \text{Ba}_2\text{CuWO}_6 \text{ and } \text{Sr}_2\text{CuWO}_6) \). Figure adapted from ref. 6 with data from this work and refs. 4,6–8.

**Sample synthesis**

\( \text{Ba}_2\text{CuWO}_6 \) and triclinic \( \text{Ba}_2\text{CuTeO}_6 \) were prepared using a conventional solid state reaction method from stoichiometric amounts of \( \text{BaCO}_3, \text{CuO, WO}_3 \text{ and TeO}_2 \) (Alpha Aesar ≥99.995). The samples were calcined at 900 °C in air for 12 hours, reground, pelletized and fired twice at 1000 °C in air for 24 hours. Tetragonal double perovskite \( \text{Ba}_2\text{CuTeO}_6 \) was prepared from triclinic \( \text{Ba}_2\text{CuTeO}_6 \) under high-pressure high-temperature conditions. Sample powder enclosed in a gold capsule was pressed in a cubic-anvil Riken-Seiki high-pressure apparatus at 4 GPa and 900 °C for 30 min. The temperature was slowly cooled before gradually releasing the pressure. This procedure resulted in around 50 mg of sample powder.

**X-ray diffraction**

The phase purity of samples was investigated by x-ray diffraction. The diffraction data were collected on a Panalytical X’pert Pro MPD diffractometer using Cu \( K_{\alpha 1} \) radiation. The diffraction patterns were refined with the FULLPROF\(^3\) software suite. Rietveld refinement was carried out for both compounds, although the data quality for \( \text{Ba}_2\text{CuTeO}_6 \) was not as good due to the small amount of sample powder. The crystal structures were visualized with VESTA.\(^10\)

The measured x-ray diffraction patterns for \( \text{Ba}_2\text{CuTeO}_6 \) and \( \text{Ba}_2\text{CuWO}_6 \) are shown in Fig. 3. No impurity peaks are observed in \( \text{Ba}_2\text{CuTeO}_6 \) indicating that the material is phase pure. In the \( \text{Ba}_2\text{CuWO}_6 \) sample a minor (< 1%) \( \text{BaWO}_4 \) impurity is observed in addition to the main phase. The lattice parameters are in good agreement with literature.\(^6\)
Fig. 3. X-ray diffraction patterns of (a) Ba$_2$CuTeO$_6$ and (b) Ba$_2$CuWO$_6$. The minor BaWO$_4$ impurity in Ba$_2$CuWO$_6$ is marked with an asterisk. Bragg positions for the space group I4/m are shown.

**Magnetic measurements**

Magnetic properties were measured with a Quantum Design MPMS3 SQUID magnetometer. 120 mg of Ba$_2$CuWO$_6$ and 25 mg of Ba$_2$CuTeO$_6$ were enclosed in gelatin capsules and placed in plastic straws for measurements. DC magnetic susceptibility was measured in the temperature range 2-400 K under an applied field of 1 T in zero-field cool (ZFC) and field cool (FC) modes.

**References**