Magnetic interactions in the *S* = 1/2 square-lattice antiferromagnets Ba_2CuTeO_6 and Ba_2CuWO_6

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Electronic Supporting Information

Density functional theory calculations

Density functional theory was used to calculate the magnetic exchange constants in Ba_2CuTeO_6 and Ba_2CuWO_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 × 2 × 1 (1 × 1 × 2) supercells were needed to calculate the exchange constants (Fig. 1.).[3,4] A *k* point grid of 4 × 4 × 6 (8 × 8 × 3) was used. A plane-wave cutoff of $|G + k|_{max} = 8/R_{MT}$ a.u.$^{-1}$ was used, where R_{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.

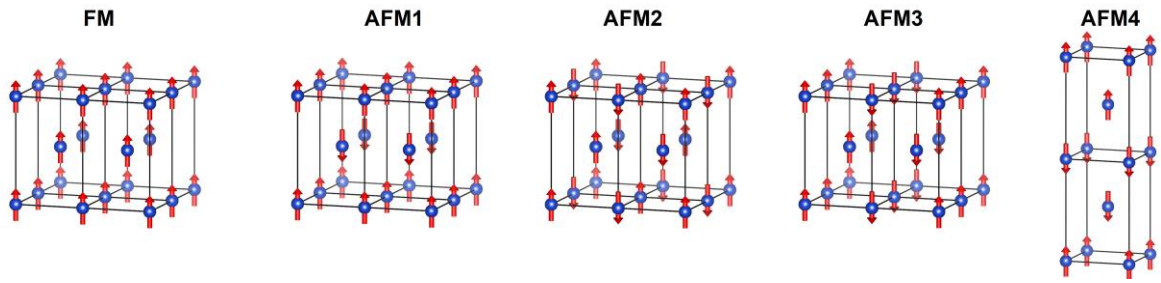

Fig. 1. The five different spin configurations used in the density functional theory calculations. Only the magnetic Cu^{2+} cations and their spins are shown. The energies are calculated in 2 × 2 × 1 (and one 1 × 1 × 2) supercells.

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-J_4 can then be obtained from:[3]

$$J_3 = (E_{AFM1} - E_{FM})/16S^2$$

$$J_1 = (E_{AFM2} - E_{FM} - 8J_3S^2)/8S^2$$

$$J_2 = (E_{AFM3} - E_{FM} - 4J_1S^2 - 8J_3S^2)/8S^2$$

$$J_4 = (E_{AFM4} - E_{FM} - 8J_3S^2)/4S^2$$

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

Table 1. Relative total energies of the different spin configurations of Ba_2CuTeO_6 and Ba_2CuWO_6 calculated by density functional theory. Energy of the ferromagnetic configuration is set as zero.

	Ba_2CuTeO_6			**Ba_2CuWO_6**		
	U = 7 eV	U = 8 eV	U = 9 eV	U = 7 eV	U = 8 eV	U = 9 eV
E_{FM} (meV/2f.u.)	0	0	0	0	0	0
E_{AFM1} (meV/2f.u.)	5.12	3.33	2.67	0.22	-0.04	0.04
E_{AFM2} (meV/2f.u.)	-44.74	-38.78	-33.11	-2.39	-2.37	-2.51
E_{AFM3} (meV/2f.u.)	-20.82	-18.10	-15.77	-30.56	-25.08	-20.36
E_{AFM4} (meV/2f.u.)	2.26	1.67	1.39	0.14	0.35	0.04
J_1 (meV)	-23.65	-20.22	-17.22	-1.25	-1.17	-1.27
J_2 (meV)	0.13	0.23	0.06	-14.71	-11.94	-9.56
J_3 (meV)	1.28	0.83	0.67	0.05	-0.01	0.01
J_4 (meV)	-0.30	0.01	0.05	0.03	0.37	0.02
J_2/J_1	-0.01	-0.01	0.00	11.79	10.18	7.55

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 $a^0a^0c^-$ octahedral tilting in these *I*4/*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, *I*4/*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.[6] This effect is especially

strong in Sr_2CuTeO_6 and Ba_2CuTeO_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).

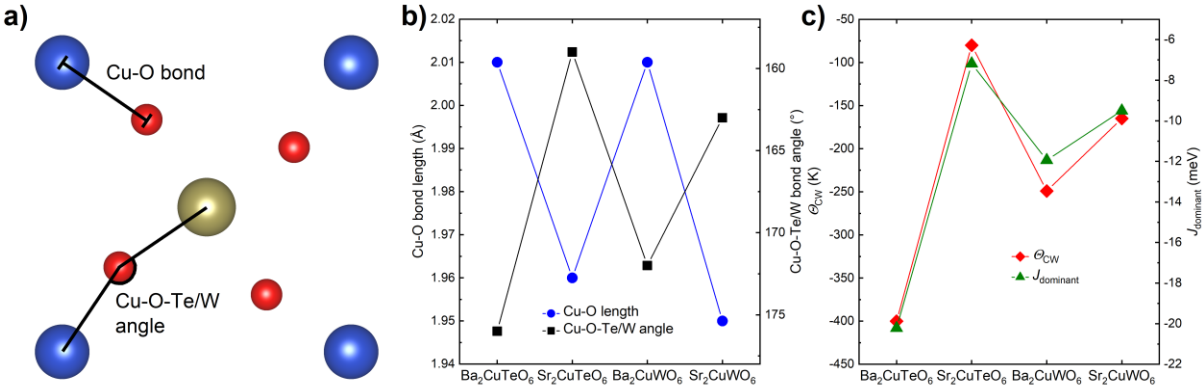

Fig. 2. a) The structure of tetragonal $A_2CuB''O_6$ double perovskites with view down the *c*-axis. The Cu-O bond length and the Cu-O-Te/W angle are shown. b) The Cu-O bond length and Cu-O-Te/W angle in the compounds. c) The Curie-Weiss constant and dominant magnetic interactions (J_1 for Ba_2CuTeO_6 and Sr_2CuTeO_6, J_2 for Ba_2CuWO_6 and Sr_2CuWO_6). Figure adapted from ref. 6 with data from this work and refs. 4,6–8.

Sample synthesis

Ba_2CuWO_6 and triclinic Ba_2CuTeO_6 were prepared using a conventional solid state reaction method from stoichiometric amounts of $BaCO_3$, CuO, WO_3 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 Ba_2CuTeO_6 was prepared from triclinic Ba_2CuTeO_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[9] software suite. Rietveld refinement was carried out for both compounds, although the data quality for Ba_2CuTeO_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 Ba_2CuTeO_6 and Ba_2CuWO_6 are shown in Fig. 3. No impurity peaks are observed in Ba_2CuTeO_6 indicating that the material is phase pure. In the Ba_2CuWO_6 sample a minor (< 1%) $BaWO_4$ impurity is observed in addition to the main phase. The lattice parameters are in good agreement with literature.[6]

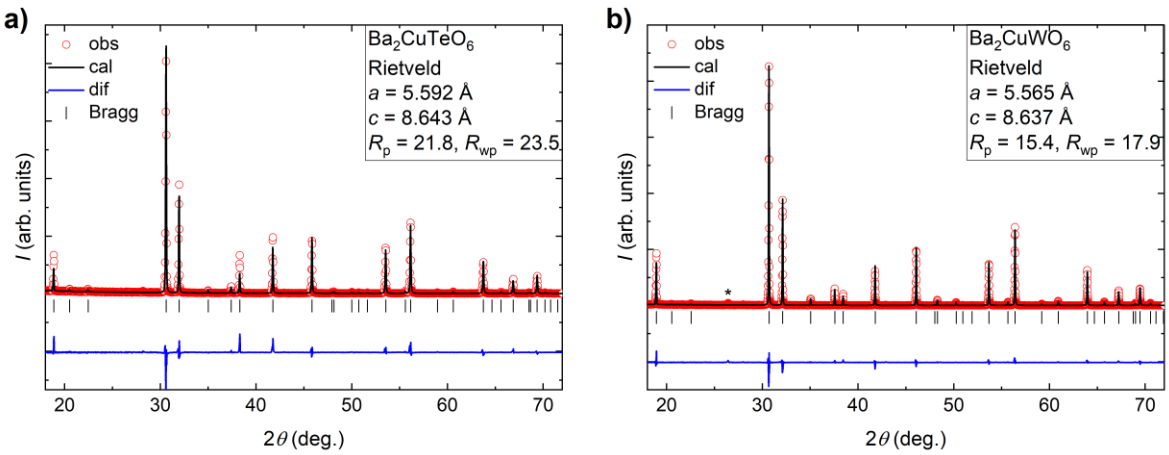

Fig. 3. X-ray diffraction patterns of (a) Ba_2CuTeO_6 and (b) Ba_2CuWO_6. The minor $BaWO_4$ impurity in Ba_2CuWO_6 is marked with an asterisk. Bragg positions for the space group *I*4/*m* are shown.

Magnetic measurements

Magnetic properties were measured with a Quantum Design MPMS3 SQUID magnetometer. 120 mg of Ba_2CuWO_6 and 25 mg of Ba_2CuTeO_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.

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