Halogen-mediated exchange in the coupled-tetrahedra quantum spin systems
\( \text{Cu}_2\text{Te}_2\text{O}_5\text{X}_2 \) \((\text{X}=\text{Br}, \text{Cl})\)

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The recently discovered \([1]\) spin-tetrahedral compounds \(\text{Cu}_2\text{Te}_2\text{O}_5\text{X}_2 \) \((\text{X}=\text{Cl}, \text{Br})\) open the possibility to study the interplay between localized many-body tetrahedral cluster excitations and inter-tetrahedral magnetic couplings leading to a quantum-phase transition with various possible ordered states \([2]\). Transitions to ordered states have been observed experimentally \([3]\) in these compounds with \(T_N^{\text{Br}} = 11.4\) K and \(T_N^{\text{Cl}} = 18.2\) K. These phase-transitions exhibit unusual magnetic-field dependences which have been linked to the closeness to a quantum-critical point \([3,4]\). Unconventional Raman-scattering has been found in the magnetic channel \([2,3]\) and the occurrence of low-lying singlet excitations has been proposed \([1]\) and observed by Raman together with a longitudinal magnon \([4]\).

The nature of the ordered states in \(\text{Cu}_2\text{Te}_2\text{O}_5\text{X}_2 \) has not yet been definitely settled. There is some evidence for a Néel state from thermodynamic and susceptibility experiments and \(\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2\) has been proposed to be closer to a non-magnetic singlet state than \(\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2\) \([4]\). Thus, it is important to examine the microscopic behavior of both \(\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2\) and \(\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2\) by \textit{ab initio} methods and investigate whether the electronic properties reveal some non-trivial differences between the two systems. The magnetic exchange coupling parameters in these systems estimated from susceptibility measurements \([1]\) are small, of the order 40 – 50 K, implying a small bandwith for the electronically active Cu-3d orbitals close to the Fermi-edge.

Here we present a comprehensive first-principles density functional theory (DFT) study of the electronic properties of these systems within the local spin density (LSDA) and the generalized gradient approximation (GGA) \([5]\).

**Crystal structure.** Both \(\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2\) and \(\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2\) systems crystallize in the non-centrosymmetric tetragonal \(P\bar{4}\) space group with two formula units per unit cell. \(\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2\) with lattice parameters \(a=7.84\) Å, \(c=6.38\) Å has a larger unit cell than \(\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2\) with \(a=7.62\) Å, \(c=6.32\) Å.

In Fig. 1 we show the crystal structure for \(\text{Cu}_2\text{Te}_2\text{O}_5\text{X}_2\). The four equivalent \(\text{Cu}^{2+}\)-ions in the unit cell of these systems form distorted tetrahedra which are located on a tetragonal lattice. The structure contains three inequivalent oxygen positions: The intra-tetrahedral \(\text{O}1\), and the inter-tetrahedral \(\text{O}2\) and \(\text{O}3\). Of special interest are the four equivalent halogen-ions, \(\text{X}\), per unit-cell which form together with the \(\text{O}1\) and \(\text{O}2\) the \(\text{X}-\text{O}1-\text{O}1-\text{O}2\) distorted square with the \(\text{Cu}^{2+}\)-ions in their respective centers, see inset of Fig. 1. The inter-tetrahedron distances are slightly smaller in \(\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2\) than in \(\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2\) due to the size difference of the respective halogen-ions. The Cu-Cu intra-tetrahedron distances are, on the other hand, slightly larger in the Cl-compound.

**Band-structure.** In Fig. 2 we present the non-spin-polarized band-structure of \(\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2\) and \(\text{Cu}_2\text{Te}_2\text{O}_5\text{Cl}_2\) near the Fermi-level along various symmetry directions in the Brillouin zone. Calculations have been performed within the framework of the full potential linearized augmented plane wave (LAPW) method based on the WIEN97 \([6]\) code, the full potential minimum basis local orbital code \(\text{FPLO}\) \([7]\) and the linearized muffin tin orbital (LMTO) method based on the Stuttgart TBLMTO-47 code \([8]\). The band structures obtained by the three methods are in overall agreement with each other.

The four narrow bands of width \(\sim 0.7\) eV are well separated from the occupied low-lying valence band by a gap of \(\sim 0.25\) eV and the high-lying unoccupied Te-p bands by a gap of \(\sim 2\) eV. The bands near the Fermi-level do not contain essentially any Te-orbitals. They are of dominant Cu-3d character (predominantly 3d\(x^2-y^2\) in the local frame of reference) as shown in the partial density of states (DOS) in Fig. 3 with substantial admixture with Br(Cl) \(p\), \(\text{O}1\) and \(\text{O}2\) \(p\) states as shown in Fig. 4.

We can investigate these results further by analyzing the electron-density. In Fig. 5 we present the electron density for \(\text{Cu}_2\text{Te}_2\text{O}_5\text{Br}_2\) for one tetrahedral-unit. The
lobes of the Cu-3d orbitals are oriented towards the nearest neighbor Br, O1, O1 and O2 ions, which form the distorted square surrounding of the Cu ion. The covalent bonding in between the Cu-3d orbital and the respective halogen-p and oxygen-p orbitals leads to the admixture of halogen and oxygen character at the Fermi-level, as seen in the respective DOS (Fig. 4).

Comparing the band-structure of both compounds near the Fermi level (see Fig. 2) we note that the bands of both systems are quite similar and only differ in some details that will translate in quantitative differences in the behavior of the effective model. The band dispersion, due to inter-tetrahedral matrix elements, is substantial (within the narrow bandwidth) along all three crystallographic directions indicating that the inter-tetrahedral couplings are non-negligible in all three directions.

The DFT-calculation yield, within the LDA or GGA-approximation, to four half-filled (metallic) bands. We performed a spin polarized calculation which leads to an antiferromagnetic groundstate in agreement with the experiment, although the resulting band gap is too small. An additional local Coulomb-repulsion – not taken fully into account in the LSDA or GGA-approximation – will basically further shift these bands, enlarging the gap and resulting in the picture of lower- and upper-Hubbard bands in agreement with experiment. In the following, however, we did not do the simulation of the missing Coulomb interaction in an LDA+U type calculation, which is in general useful but we do not expect from it new insights about the important couplings.

Attempts to directly compute the exchange integrals by comparing the LSDA total energy differences for different spin arrangements to that of a Heisenberg-like model faced two basic short-comings: (i) The resulting magnetic moments at the copper sites were quite different for different spin arrangements. This leads to a strong bias of the inter-atomic exchange energies due to different intra-atomic contributions to the total energy. (ii) The important interactions in these compounds have a rather long-ranged nature as mentioned below. This would demand the calculation of large unit cells beyond the present computational capabilities. Therefore, we focus this letter to accessing the corresponding transfer integrals thereby pointing out the important interaction path-ways in these systems.

**Effective Model.** In order to quantify the results obtained from the *ab-initio* calculation in terms of hopping matrix elements, $t_{ij}$, we have employed LMTO-based downfolding [9] and tight-binding analysis on the band structure of these systems. The downfolding method consists in deriving a few-orbital effective hamiltonian from the full LDA or GGA Hamiltonian by folding down the inactive orbitals in the tails of the active orbitals kept in the basis chosen to describe the low-energy physics of the system. This procedure naturally takes into account the proper renormalization effect of integrated-out inactive orbitals in the effective interactions defined in the basis of the active orbitals. Using the real-space description of the downfolded Hamiltonian one gets

$$H_R = -\sum_{ij} t_{ij} \left( c_i^\dagger c_j + c_i c_j^\dagger \right)$$

where $t_{ij}$ provides the effective hopping matrix elements between the active orbitals. In Table I we present the results for the most significant hopping matrix elements shown schematically in Fig. 6 obtained from downfolding the full LMTO Hamiltonian to effective Cu-only Hamiltonian by integrating out everything except the $d_{x^2-y^2}$ orbital for each Cu atom in the unit cell to reproduce accurately the four narrow bands close to the Fermi energy. The first and second column of Table I show the hopping parameters for Cu$_2$Te$_2$O$_5$Br$_2$ and Cu$_2$Te$_2$O$_5$Cl$_2$ respectively.

The predominant matrix elements consist of a set of nine different hopping parameters, some of them quite long-ranged and which couldn’t be neglected in order to get a good description of the energy bands. Apart from the intra-tetrahedra $t_1$ and $t_2$ parameters, the inter-tetrahedra $t_x$, $t_z$, $t_a$, $t_{tv}$, $t_d$ and $t_r$ are important (see Fig. 6). For instance, $t_z$ is needed in order to get dispersion along the path $\Gamma - M$ and $t_a$ and $t_{tv}$ are essential in order to get the correct behavior along the path $X - A$. The need of including such longer-ranged hoppings like $t_r$ is set by the renormalization process of the downfolding procedure [10]. We note, that long-ranged hopping matrix elements have proven to be essential for the description of some related copper systems [11].

In order to investigate more in detail the nature of the Cu-Cu interaction path-ways and in particular the role of the halogen ion, we have also performed, a TB-downfolding analysis of the bandstructure of both systems by keeping the halogen X-p orbitals active in addition to four Cu-d orbitals in the basis set (Cu+X downfolding, see Table I). The results will be discussed in the following.

**Table I. TB-Downfolding parameters for the effective Cu-Cu hoppings in meV units obtained by keeping active (i) the Cu-3d orbitals (first and second columns, Cu-downfolding) and (ii) both the Cu-3d with the halogen-3p/4p orbitals (third and fourth columns, Cu+X downfolding).**

|       | CuBr   | CuCl   | Cu+Br | Cu+Cl |
|-------|--------|--------|-------|-------|
| $t_1$ | 80     | 98     | 155   | 181   |
| $t_2$ | 4      | 0      | -156  | -132  |
| $t_4$ | -16    | -10    | -10   | -14   |
| $t_5$ | 11     | 12     | 34    | 33    |
| $t_6$ | -30    | -29    | 5     | 8     |
| $t_7$ | -48    | -45    | -26   | -19   |
| $t_8$ | -24    | -23    | 9     | 8     |
| $t_9$ | -73    | -80    | 8     | 8     |
| $t_{10}$ | -35    | -48    | -62   | -72   |

**Intra-tetrahedral couplings.** The nearest neighbor...
(n.n.) intra-tetrahedral Cu-Cu transfer matrix element $t_1$ is mediated by O1-ions located in between two Cu-ions and responsible for the Cu-O1-Cu superexchange generating the spin-spin coupling $J_1$. This superexchange-path is evidenced in Fig. 5. The angle Cu-O1-Cu is 107°/109° for $X = Br/Cl$. Assuming a similar crystal field, the larger superexchange-angle for $X=Cl$ results -following the Goodenough-Kanamori-Anderson rules [12]- in $t_1(X = Cl) > t_1(X = Br)$, in agreement with the downfolding results, see Table I.

The intra-tetrahedral hopping matrix element $t_2$ corresponds to the effective next nearest neighbor (n.n.n.) Cu-Cu overlap. A comparison of the Cu- and the Cu+X downfolding result shows a substantial drop of $t_2$ for both systems when the halogen-orbitals are integrated out. This drop indicates that paths of the type Cu-X-X-Cu are important for the effective $t_2$ matrix element and that they compensate to a certain extend the contribution of the direct Cu-Cu path (see Fig. 5) and of other possible paths through oxygen ions. We note, that $t_2$ is vanishingly small in the Cl-compound.

**Inter-tetrahedral coupling.**- The coupling $t_x$ via the O3 along the $x$- and $y$-direction in between two Cu4-tetrahedra (see Fig. 6 and Table I), is small, partly because the O3-weight is small at the Fermi-level. There is, however, a substantial inter-tetrahedral coupling $t_a$ and diagonal $t_d$ within the $xy$-plane mediated by the halogen-$p$ orbitals, (see Fig. 6 and Fig. 7). The role of the halogen ions for the inter-tetrahedral couplings can be quantified by analysing the Cu-downfolding and the Cu+X-downfolding results presented in Table I. Comparing the two corresponding values (CuX and Cu+X) we observe that $t_a$ and $t_d$ are nearly exclusively due to halogen-containing exchange paths.

The reason for this unusual large inter-tetrahedron coupling in Cu2Te2O2ClX2 is the large extension of the Cl-3p and Br-4p wave functions which do not occur in cuprates containing only O-2p orbitals (i.e. CuO4 units). In contrast to certain other cuprate compounds containing halogen-ions like Sr2CuO2Cl2 [13], the situation for the Cu2Te2O2ClX2-compounds is unique. Here, the halogen is part of the covalent Cu-O-Cl(Br) network, whereas in the former mentioned compound family the halogens play only the role of an anionic charge reservoir [13].

A closer analysis of the electron density presented in Fig. 7 leads to two observations, which are in agreement with Cu+X downfolding results: (i) The Cl-3p orbital at the Fermi-level is more strongly distorted towards the Cu-3d orbital compared to the Br-4p orbital, indicating stronger copper-halogen coupling for $X = Cl$ than for $X = Br$ (see arrows in Fig. 7) (ii) The Br-4p orbital is reoriented somewhat towards the n.n. Br-4p orbital indicating a stronger covalent Br-Br overlap.

In addition to the inter-tetrahedral hopping processes along $x$ and $y$ there are substantial contributions to the inter-tetrahedral coupling terms $t_{cc}$, $t_{cv}$ and $t_{vd}$ along the $z$-direction, compare Fig. 6 and Table I.

**Discussion.**- It has been recently argued [4] that Cu2Te2O2Br2 and Cu2Te2O2Cl2 differ only quantitatively but not qualitatively in their magnetic properties, with Cu2Te2O5Br2 being somewhat closer to a quantum-critical phase transition. Here we present evidence from ab-initio calculations that the electronic properties of these two compounds are indeed close and that the inter-tetrahedral coupling is considerable. We note that a substantial coupling between Cu-tetrahedra is necessary in order to establish magnetic long-range order [4].

We have also presented a detailed analysis in terms of two different downfolding models (Cu and Cu+X) which reveal the important result that the halogen-ions are essential for the inter-tetrahedral exchange couplings. We find that four halogen orbitals, coupled by considerable $(X-p)$-$(X-p)$ covalent bonding give rise to X4-rings which mediate long-ranged inter-tetrahedral couplings. These X4-rings are covalently coupled to the respective Cu4-tetrahedrons.

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**FIG. 1.** Crystal structure of Cu$_2$Te$_2$O$_5$X$_2$. The small green balls in the center of the bonds represent Cu, the medium sized yellow and large blue balls O and the halogen X, respectively. The atom not connected to a bond is O3. For simplicity the Te atom was dropped. The inset presents an idealized Cu$_4$-tetrahedron with the four corner-sharing O1-O1-O2-X idealized squares and the Cu$^{2+}$-ion in the center.

**FIG. 2.** Comparison of the band structure near the Fermi level between Cu$_2$Te$_2$O$_5$Br$_2$ (full squares) and Cu$_2$Te$_2$O$_5$Cl$_2$ (empty circles), with $\Gamma = (0, 0, 0)$, $X = (\pi, 0, 0)$, $M = (\pi, \pi, 0)$, $Z = (0, 0, \pi)$, $R = (0, \pi, \pi)$ and $A = (\pi, \pi, \pi)$.

**FIG. 3.** Density of states for the partial Cu-3$d$ orbitals.

**FIG. 4.** Density of states for the (total) halogen-$p$ and the O1-$p$ and the O2-$p$ orbitals, for Cu$_2$Te$_2$O$_5$Br$_2$ (left) and Cu$_2$Te$_2$O$_5$Cl$_2$ (right).
FIG. 5. Electron density for Cu$_2$Te$_2$O$_5$Br$_2$ at the 0.2 (e/Å$^3$) isovalue for one tetrahedron. The dashed and dashed-dotted lines indicate the four Br-O1-O1-O2 distorted squares with Cu placed in the respective centers, they share O1-corners. The solid line indicates the Cu-O1-Cu exchange paths ($t_1$ in Fig. 6).

FIG. 6. Illustration of the hopping matrix elements $t_{\alpha}$ ($\alpha = 1, 2, x, z, a, c, d$) in between the Cu$^{2+}$ ions which are located in the center of the O$_3$X distorted square (X=Br,Cl), indicated by the shaded regions (not to scale, in reality the distorted squares share O1-corners). The filled circles denote the direction of the halogen-sites. The parameters $t_x$ and $t_y$ correspond to the hopping elements between Cu$^{2+}$ ions at A and B and at M and N respectively and equivalent positions.

FIG. 7. Electron density for Cu$_2$Te$_2$O$_5$Br$_2$ (left) and Cu$_2$Te$_2$O$_5$Cl$_2$ (right) at the 0.05 (e/Å$^3$) isovalue. for a projection on the $xy$-plane in between four Cu-tetrahedra (compare with Fig. 6, left). The four $p$ orbitals at the center are Br-3$p$ (left) and Cl-4$p$ (right). The respective arrows indicate the distortion of the X-$p$ orbitals.