Microscopic model for the novel frustrated Cu(II)-spin tetrahedron-based Cu$_4$Te$_5$O$_{12}$X$_4$ (X=Cl, Br) systems

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We present a microscopic study of the electronic and magnetic properties of the newly synthesized Cu(II)-spin tetrahedron-based Cu$_4$Te$_5$O$_{12}$Cl$_4$ compound based on Density Functional calculations and on ab initio-derived effective models. In view of these results, we discuss the origin of the observed differences in behavior between this system and the structurally similar and much studied Cu$_2$Te$_2$O$_5$Cl$_2$. Since the Br analog of the title compound has not been synthesized yet, we derive the crystal structure of Cu$_4$Te$_5$O$_{12}$Br$_4$ by geometry optimization in an ab initio molecular dynamics calculation and investigate the effect of substituting Cl by Br as well as the possible magnetic behavior of this system and compare with the recently studied sister compound, Cu$_2$Te$_2$O$_5$Br$_2$.

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Introduction.- Frustrated magnetism has gained a lot of attention in recent years due to the wealth of new exotic behavior that arises out of this condition such as spin ice and spin liquid phases. In the search for new materials exhibiting frustrated magnetism, a few years ago Johnsson et al. synthesized for the first time a family of oxohalogenides Cu$_2$Te$_2$O$_5$X$_2$, X=Br, Cl whose structure was based on weakly coupled tetrahedra of Cu(II) with geometrically frustrated antiferromagnetic (AF) interactions. These materials have been intensively studied both experimentally and theoretically. The show magnetic ordering with incommensurate wave vectors at temperatures $T_N = 18$ K (Cl) and 11 K (Br) and the observation of a longitudinal magnon in Cu$_2$Te$_2$O$_5$Br$_2$ was interpreted as evidence for the proximity of this system to a quantum phase transition between antiferromagnet and spin liquid behavior.

The various intratetrahedral and intertetrahedral couplings and the relative strengths of exchange pathways in these compounds have been obtained in detail by using the electronic structure technique of muffin-tin orbital (MTO) based ab-initio downfolding. The results predicted by this study have been confirmed by subsequent neutron diffraction experiments proving the powerfulness of this ab initio Density Functional Theory (DFT) based technique in predicting the underlying microscopic model of a complex material.

By changing the subtle ratio between the various interaction paths in these materials, for instance by applying pressure or by introducing chemical modifications, one can attempt to drive these systems into quantum criticality. Following these ideas, a new oxohalogenide Cu$_4$Te$_5$O$_{12}$Cl$_4$ has been very recently synthesized by Takagi et al. which orders antiferromagnetically at $T_N = 13.6$ K. This system is structurally similar to the previously discussed Cu$_2$Te$_2$O$_5$Cl$_2$ compound but presents some markedly different features. As pointed out by Takagi et al., the primary structural difference between the new Cu$_4$Te$_5$O$_{12}$Cl$_4$ (which we refer to as Cu-45124(Cl) following Ref. 16) and Cu$_2$Te$_2$O$_5$Cl$_2$ (Cu-2252(Cl)) is the presence of a TeO$_4$ complex in the middle of the Cu-tetrahedral network in the ab plane (see Fig. 1). This fact led the authors of Ref. 16 to expect an increase in the separation between the Cu$_4$ tetrahedra and hence an increase in the relative importance of the intratetrahedral coupling with respect to the intertetrahedral coupling.

In the following, we study this proposition within the framework of the NMTO-downfolding technique. In addition, motivated by the more anomalous properties of Cu$_2$Te$_2$O$_5$Br$_2$ compared to Cu$_2$Te$_2$O$_5$Cl$_2$ as reported in the literature, we explore the implications of substituting Cl by Br in the new oxohalogenide Cu$_4$-5124(Cl). Since the Cu-45124(Cl) system has not been synthesized yet, we propose the crystal structure of Cu$_4$Te$_5$O$_{12}$Br$_4$ by performing a geometry relaxation in the framework of ab-initio molecular dynamics and we analyze its electronic structure by the NMTO-downfolding technique.

Structure.- Both Cu-45124(Cl) and Cu-2252(Cl) compounds crystallize in a tetragonal structure. The basic structural unit in both systems is the [CuO$_2$Cl] distorted square (marked in thin lines in Fig. 1) with Cu (marked in magenta in Fig. 1) at the center. Groups of four such squares share corners, giving rise to [Cu$_4$O$_6$Cl$_4$] units with Cu ions in tetrahedral coordination forming a magnetic cluster of four Cu ions. Cu-45124(Cl) has two inequivalent Te atoms, Te(1) and Te(2) (marked in green and cyan in Fig. 1 top panel), while Cu-2252(Cl) has only one type of Te atoms (marked in cyan in Fig. 1 bottom panel). The Te(2) atoms in Cu-45124(Cl) sit on an equivalent position to the Te atoms in Cu-2252(Cl). Viewing the structures along the [001] direction (see Fig. 2), they show a stacking of Cu$_4$ tetrahedra separated by layers of Te(2)-O(3) (Cu-45124(Cl)) or Te-O(2) (Cu-2252(Cl)) units. In the case of Cu-45124(Cl), additional Te(1)-O(1)
FIG. 1: (Color online) Crystal structure of Cu-45124(Cl) (top panel) and Cu-2252(Cl) (bottom panel) projected on the \( ab \) plane. In order to emphasize the similarity between the Cu-2252(Cl) and Cu-45124(Cl) structures, we use four unit cells of Cu-45124(Cl) but show only the section that makes this structure analogous to a section of four Cu-2252(Cl) unit cells showing four connected Cu tetrahedra. Magenta and yellow atoms stand for Cu and Cl. Two inequivalent Te atoms, Te(1) and Te(2) in Cu-45124(Cl) are shown in green and cyan colors (top panel), while the only one inequivalent Te atom present in Cu-2252(Cl) is shown in cyan (bottom panel). The brown, white and black balls denote O(1), O(2) and O(3) respectively for Cu-45124(Cl) (top panel) and O(3), O(1) and O(2) for Cu-2252(Cl). Note that every four Cu atoms appearing in a square arrangement, due to the projection, actually form tetrahedra. We also show the various interaction paths in black arrows (see the text for discussion).

units appear in the same layer as Cu. The relative orientation of the Cu\(_4\) tetrahedra along the [001] direction is also different between the two compounds. In the case of Cu-2252(Cl) the Cu\(_4\) tetrahedra show the same orientation, while for Cu-45124(Cl) they alternate between successive rows. The latter feature leads to two different space group symmetries, \( P4 \) for Cu-2252(Cl) and \( P4/n \) for Cu-45124(Cl) with elongation of the unit cell in the \( ab \) plane with lattice parameter \( a = 11.35 \) Å for Cu-45124(Cl) compared to \( a = 7.84 \) Å for Cu-2252(Cl). The unit cell dimensions along the \( c \) axis remain comparable with \( c = 6.32 \) Å for Cu-2252(Cl) and \( c = 6.33 \) Å for Cu-45124(Cl). The change in space group defines Cu-45124(Cl) as centrosymmetric compared to the noncentrosymmetric Cu-2252(Cl).

A crucial difference between the two compounds apart from the change in bond lengths, is the relative orientation of the Cu-Cl bonds (Cl atoms are marked in yellow in Fig. 1) among different Cu\(_4\) tetrahedra. As has been discussed in Ref. 6, the Cl atoms play an important role in mediating the Cu-Cu interaction in the Cu-2252 systems. While for Cu-2252(Cl) the Cu-Cl bonds belonging to different Cu\(_4\) tetrahedra point towards each other (marked with red arrows in Fig. 1 bottom panel), in the case of Cu-45124(Cl), due to the relative shift of the tetrahedra, they are oriented parallel to each other (see the red arrows in Fig. 1 top panel). This aspect is found to have
An important consequence in the context of hopping interaction pathways as will be discussed later.

Bandstructure.- Fig. 3 shows the non spin-polarized band dispersion of Cu-45124(Cl) obtained with the linear muffin-tin orbital (LMTO) basis within the framework of local density approximation (LDA). The bands are plotted along the various symmetry directions of the tetragonal Brillouin zone. The orbital characters indicated in the figure are obtained by choosing the local coordinate system with the $y$ axis pointing along the Cu-O(3) bond and the $x$ axis pointing along the Cu-Cl bond. The square planar symmetry of the ligands surrounding the Cu$^{2+}$ ion sets the Cu-3$d_{x^2-y^2}$ energy level as the highest energy level. Consistent with the Cu$^{2+}$ valency, eight bands (there are 8 Cu atoms in the unit cell) dominated by Cu-$d_{x^2-y^2}$ character and split off from the rest of the bands, span an energy range from $\approx -0.3$ eV to 0.2 eV with the zero of energy set at the LDA Fermi level. The energy bands dominated by other $d$ characters like $d_{xy}$, $d_{xz}$, $d_{yz}$ and $d_{3z^2-1}$ span the energy range between $\approx -3$ and $-2$ eV overlapping with the O-$p$ manifold. The Cl-$p$ dominated bands appear right above and partly overlapping the O-$p$ dominated bands spanning an energy range of $\approx 1$ eV. These Cl-$p$ dominated bands are separated by a gap of $\approx 0.5$ eV from the Cu-$d_{x^2-y^2}$ dominated bands. There is only a negligible contribution of Te(1) and Te(2) to the bands crossing the Fermi energy. We note that in the low-energy scale, the LDA calculation leads to eight almost half-filled bands. Introduction of correlation effects within an LDA+U treatment is expected to drive the system insulating. In what follows though we will focus on the ab initio determination of effective one electron hopping interactions which are well described within LDA and GGA.

In Fig. 4 we show a comparative study of the various partial LDA density of states (DOS) for Cu-45124(Cl) and Cu-2252(Cl).

While the basic features of the DOS remain the same between the two compounds, indicating that the overall nature of the interactions will be similar for both systems, there are a few quantitative differences. The Cu-$d$ bandwidth at $E_F$ is narrower in Cu-45124(Cl) than in Cu-2252(Cl). The relative proportion of the Cl-$p$ and O-$p$ contribution to the bands at $E_F$ is also smaller in the case of Cu-45124(Cl). The O-$p$ and Cl-$p$ dominated bands, instead of being separated, overlap to a larger extent in the case of Cu-45124(Cl). Understanding and quantifying these differences requires the analysis of the bandstructure in terms of a microscopic model.

Downfolding and effective model.- A powerful technique to construct a low-energy, tight-binding (TB) Hamiltonian starting from a complex LDA bandstructure is achieved via the NMTO-downfolding technique. It does so by constructing energy dependent, effective orbitals by integrating out irrelevant degrees of freedom - a method called downfolding. The accuracy of such a procedure can be tuned by the choice of $N$, the number of energy points used in the NMTO calculation. For an isolated set of bands, as is the case in the present study, these effective orbitals define the Wannier functions corresponding to the Hamiltonian in the downfolded representation. The real space representation of the downfolded Hamiltonian in the Wannier function basis gives the information of the effective hopping matrix elements.

For the present study, we construct the massively downfolded Hamiltonian by keeping only the Cu-$d_{x^2-y^2}$ degrees of freedom active and integrating out all the rest.
FIG. 4: (Color online) Comparison of the density of states between the Cu-45124(Cl) (top panel) and Cu-2252(Cl) (bottom panel) compounds.

The computed, downfolded bands are shown in the top panel of Fig. 5 with dotted lines. With the choice of two energy points, $E_0$ and $E_1$, the downfolded bands are indistinguishable from the Cu-$d_{x^2-y^2}$ dominated bands of the full LDA calculation shown in solid lines in the top panel of Fig. 5.

The corresponding Wannier function is plotted in Fig. 6. Two different views of the same orbital are shown. The central part has the $3d_{x^2-y^2}$ symmetry with the choice of the local coordinate system as stated above, while the tails are shaped according to Cl-$p_x$ and O-$p_x/p_y$ symmetry demonstrating the hybridization effects. The strong $pd\sigma$ antibonds are evident in the plot with Cu hybridization being stronger with Cl than with O, a fact also evident in the density of states plot, shown in Fig. 4.

The real space representation of the downfolded Hamiltonian in the Wannier function basis, $H_{TB} = -\sum_{ij} t_{ij} (c_i^\dagger c_j + h.c.)$ provides the information of the effective hopping interaction $t_{ij}$, between the Cu$^{2+}$ ions at sites $i$ and $j$. The various dominant hopping interactions are tabulated in Table I. The notation for the hoppings are shown in Figs. 1 and 2. While the hoppings $t_1$, $t_2$, $t_x$, $t_o$ and $t_r$ are in-plane hoppings in the plane defined by the Cu tetrahedra, $t_x$ and $t_r$ are out-of-plane hoppings. For the sake of consistency, we adopt for Cu-45124(Cl) the same hopping notation introduced earlier for Cu-2252(Cl) in Ref. 6.

For comparison, in Table I we reproduce the results for the Cu-2252(Cl) compound from Ref. 6. The bond lengths corresponding to each hopping element have been also tabulated. For the dominant, intratetrahedral nearest neighbor interaction, $t_1$, we observe that while the bond length is decreased by only 2.5% for Cu-45124(Cl) compared to Cu-2252(Cl), $t_1$ is reduced by as much as 22% due to a smaller superexchange path angle in Cu-45124(Cl) ($\angle Cu-O(2)-Cu = 105.7^\circ$ for Cu-45124(Cl) and $\angle Cu-O(1)-Cu = 109.8^\circ$ for Cu-2252(Cl)). The intratetrahedral hopping $t_2$ which was weak for Cu-2252(Cl) - a fact also supported by neutron diffraction - remains weak for Cu-45124(Cl). The in-plane intertetrahedral hopping $t_x$, remains in magnitude similar to its analog in Cu-2252(Cl) while other in-plane intertetrahedral hop-
The values for Cu-2252(Cl) have been reproduced from Ref. 6. The crucial role of long-ranged interactions is demonstrated in the Wannier function plot (see Fig. 7), where a comparison between Cu-45124(Cl) and Cu-2252(Cl) regarding the intertetrahedral hopping $t_{ij}$ is presented. This difference is caused by the elongation of the bond lengths due to the presence of the Te(1)O$_4$ group in Cu-45124(Cl), as suggested in Ref. 16. We reveal the origin of this marked difference in the following in terms of a detailed analysis of the involved hopping paths.

The tight-binding (TB) bands, constructed out of the hopping parameters tabulated in Table I, are shown on the bottom panel of Fig. 6 in comparison to downfolded bands. The TB bands compare satisfactorily with the downfolded bands. Omission of long-ranged interactions such as $t_c$ and $t_r$ deteriorates the agreement of the TB bands with the downfolded bands, proving the essential need for inclusion of long-ranged interactions in the correct description of this compound.

**Interaction pathways.** It was pointed out in Ref. 6 that Cl-$p$ degrees of freedom play a crucial role in the renormalization process of the effective Cu-Cu hopping. Keeping this fact in mind, we carried out downfolding calculations where the Cl-$p$ degrees of freedom have been kept active in addition to Cu-$d_{x^2-y^2}$, so as to define a basis consisting of Cu-$d_{x^2-y^2}$ and Cl-$p$. The Cu-Cu hopping interactions extracted out of such calculation are tabulated in Table 2. For comparison, we show the results for Cu-2252(Cl) reproduced from Ref. 6. The crucial role of hopping paths involving Cl-$p$ is evident by comparing the hopping interactions between the massively downfolded Cu-$d_{x^2-y^2}$ only calculation and the Cu-$d_{x^2-y^2}$ + Cl-$p$ calculation. The former includes the renormalization due to Cl-$p$’s while the latter does not. While the pattern of renormalization remains essentially the same for the intratetrahedral hopping $t_d$ and the intertetrahedral out-of-plane hopping $t_{ri}$, it is quite different for intertetrahedral hoppings like $t_x$, $t_y$, $t_d$, $t_r$, and $t_z$ which involve pathways via Cl atoms belonging to two different Cu$_4$ tetrahedra. The most significant change happens for the in-plane intertetrahedral diagonal hopping, $t_d$. The bare hopping strength of $t_d$ in absence of the renormalization effect of Cl-$p$ is more or less the same between the two compounds (8 meV for Cu-2252(Cl) and 9 meV for Cu-45124(Cl)). However, while a large renormalization is observed for Cu-2252(Cl) when integrating out the Cl-$p$ degrees of freedom, such renormalization is practically absent in Cu-45124(Cl). This difference is caused due to the different alignment of the Cu-Cl bonds belonging to neighboring Cu$_4$ tetrahedra which are parallel to each other in Cu-45124(Cl) while in Cu-2252(Cl) they point to each other. This makes the intertetrahedral Cl-$p$ - Cl-$p$ bonding in Cu-45124(Cl) of $pp\sigma$ type as opposed to the Cu-2252(Cl) case, where the Cl-$p$ - Cl-$p$ bonding was of $pp\pi$ type. This is nicely demonstrated in the Wannier function plot (see Fig. 7), where...


The effective Cu-\(d_{x^2-y^2}\) like Wannier orbitals are placed at the Cu sites at in-plane diagonal positions. The overlap between the two orbitals provides a rough estimate of the strength of the hopping matrix elements. In the case of Cu-2252(Cl), the Cl-\(p\) tails from two Cu sites belonging to two different Cu tetrahedra overlap to a large extent due to direct alignment providing a Cl-\(p\)-Cl-\(p\) \(pp\sigma\) bonding which mediates the Cu-Cu bonding between different Cu tetrahedra. For Cu-45124(Cl), in contrast, the overlap of the Cl-\(p\) tails from different Cu sites belonging to two different Cu tetrahedra is practically negligible due to misalignment of the Cl orbitals.

The nature of the discussed interaction paths plays a crucial role in the magnetic properties of this material. Starting from the hopping parameters, \(t\)'s, the exchange integrals, \(J\)'s, for antiferromagnetic superexchange paths may be estimated by making use of the expression \(J \approx 4t^2/U\). While this is a valid approach for cases like the \(t_1\) and \(t_2\) interaction paths, in general for more complicated paths this expression is not anymore precise and one has to use more involved estimations of the exchange coupling constants. Nevertheless, already the knowledge of the hopping parameters gives us the clue about the important interaction paths. The drastic reduction of the in-plane \(t_d\) and to a lesser extent of \(t_o\) and the longer-ranged \(t_z\), in Cu-45124(Cl) compared to Cu-2252(Cl), indicate an overall weakening of the inter-tetrahedral coupling in the new compound with respect to Cu-2252(Cl) and therefore if the system orders at low temperatures, the ordering should occur at a lower \(T_N\) than in Cu-2252(Cl), as observed experimentally. The spin ordering patterns will be also strongly influenced by the change of interaction paths, especially by the near absence of the \(t_d\) and reduction of the \(t_o\) path (we refer to the discussion in Ref. 12) which places the system in the limit of weakly coupled tetrahedra. Also the reduction by 22\% of the \(t_1\) value implies a smaller intratetrahedron exchange coupling \(J_1\) than in Cu-2252(Cl). By considering \(J \approx 4t^2/U\), with \(U=4eV\) we obtain as exchange coupling constants \(J_1 \approx 5.8meV = 67K\) and \(J_2 \approx 0.02meV = 0.2K\) in comparison with the values \(J_1 = 2.84meV = 32.9K\) and \(J_2 = 1.58meV = 18.4K\) obtained by fitting the susceptibility of a model of independent tetrahedra to the experimental data. The ratio of \(J_2/J_1\) is largely overestimated in the fitting, presumably because of the neglect of the inter-tetrahedral interactions.

In an attempt to predict the properties of the not yet synthesized Cu₄Te₂O₅Br₂ (Cu-45124(Br)) and motivated by the discussed proximity to a quantum critical behavior of the much studied Cu₄Te₂O₅Br₂ (Cu-2252(Br)), we have investigated the electronic and magnetic properties of the \textit{ab initio} relaxed structure Cu-45124(Br) obtained from first principles calculations. In order to obtain a theoretical prediction of the Cu-

| Set-1: Massively downfolded Cu-\(d_{x^2-y^2}\), Set-2: minimal set consisting of Cl-\(p\) and Cu-\(d_{x^2-y^2}\) degrees of freedom (Cu+Cl downfolding). The numbers for Cu-2252(Cl) have been reproduced from Ref. 6 |
| Cu-45124(Cl) | Cu-2252(Cl) |
| Cu | Cu+Cl | Cu | Cu+Cl |
|---|---|---|---|
| \(t_1\) | 76 | 82 | 98 | 181 |
| \(t_2\) | 4 | -117 | 0 | -132 |
| \(t_3\) | 12 | -42 | -10 | -14 |
| \(t_4\) | 8 | -39 | -29 | 8 |
| \(t_5\) | 7 | 9 | -80 | 8 |
| \(t_6\) | 18 | -11 | -48 | -72 |
| \(t_7\) | 24 | 27 | 12 | 33 |
| \(t_{-48}\) | -15 | -45 | -19 |

FIG. 7: (Color online) Overlap between Cu-\(d_{x^2-y^2}\) downfolded MTOs, placed at two Cu sites situated at in-plane intertetrahedral, diagonal positions. Opposite signed lobes of the orbitals are colored as blue or magenta and red or orange.
TABLE III: Fractional coordinates obtained by AIMD of the relaxed Cu-45124(Br).

|      | x    | y    | z     |
|------|------|------|-------|
| Te(1)| 0.25 | 0.25 | 0.37660383 |
| Te(2)| 0.67370804 | 0.01872727 | 0.87086473 |
| Cu  | 0.75587933 | 0.40510264 | 0.34817424 |
| Br  | 0.89355065 | 0.56680922 | 0.32307512 |
| O(1) | 0.29531785 | 0.40609792 | 0.32373845 |
| O(2) | 0.28384154 | 0.87238649 | 0.36101169 |
| O(3) | 0.291597 | 0.58080843 | 0.93893775 |

TABLE IV: Cu-Cu hopping parameters corresponding to the massively downfolded Cu-d_{x^2−y^2} Hamiltonian. The bond lengths are in Å and the hopping interaction strengths in meV corresponding to hoppings shown in Figs. 1 and 2. The numbers for Cu-2252(Br) has been reproduced from Ref. 6.

|      | Cu-45124(Br) | Cu-2252(Br) |
|------|--------------|--------------|
|      | Bond length | Interaction | Bond length | Interaction |
| t_{x} | 3.147 | 75 | 3.195 | 80 |
| t_{y} | 3.522 | 0 | 3.543 | 4 |
| t_{z} | 5.535 | 23 | 4.385 | −16 |
| t_{d} | 6.248 | 20 | 6.289 | −30 |
| t_{l} | 7.829 | 3 | 8.439 | −73 |
| t_{u} | 8.251 | −29 | 9.130 | −35 |
| t_{v} | 5.064 | 19 | 5.059 | 11 |
| t_{w} | 6.332 | −39 | 6.378 | −48 |

TABLE V: Cu-Cu hopping parameters in meV corresponding to two sets of calculations. Set-1: Massively downfolded Cu-d_{x^2−y^2}, Set-2: minimal set consisting of Br-p and Cu-d_{x^2−y^2} degrees of freedom (Cu+Br downfolding). The numbers for Cu-2252(Br) have been reproduced from Ref. 6.

|      | Cu-45124(Br) | Cu-2252(Br) |
|------|--------------|--------------|
|      | Cu | Cu+Br | Cu | Cu+Br |
| t_{x} | 75 | 106 | 80 | 155 |
| t_{y} | 0 | −60 | 4 | −156 |
| t_{z} | 23 | −16 | −16 | −10 |
| t_{d} | 20 | −16 | −30 | 5 |
| t_{l} | 3 | 11 | −73 | 8 |
| t_{u} | −29 | −16 | −35 | −62 |
| t_{v} | 19 | 68 | 11 | 34 |
| t_{w} | −39 | −53 | −48 | −26 |

45124(Br) crystal structure, we substituted Cl by Br in the original Cu-45124(Cl) structure and we relaxed the volume and internal coordinates performing Car-Parrinello \textit{ab initio} molecular dynamics (AIMD) calculations \textsuperscript{29} with a projector augmented wave (PAW) basis set \textsuperscript{30}. This procedure has proven to be very suitable for predicting reliable new crystal structures \textsuperscript{21}. For Cu-45124(Br) we assume the same tetragonal space group P4/n (No. 85) as for Cu-45124(Cl). Of the seven atoms in the primitive cell, only Te(1) is in Wyckoff position 2c, while all others (Te(2), Cu, Br, O(1), O(2), O(3)) are in position 8g. We thus have 19 degrees of freedom, but as the AIMD relaxation is done in the conventional cell, we need 131 constraints for the 50 atoms in order to preserve the symmetry. We verify convergence of our structure relaxation not only with the help of the forces but we check that each of the 19 independent coordinates has converged. This is especially important in this structure as we find that the relaxation happens in two steps: First, the Br atoms introduced into the Cl positions rearrange, increasing their bond distance to the Cu atoms which are the nearest neighbors. This Cu-Br repulsion makes an adjustment of the O(1) positions next to Br and the O(2) and O(3) positions next to Cu necessary. But as soon as the Br atom has found a relatively favorable position, some changes to Cu and O(1)-O(3) coordinates are actually reversed. Thus, the structure immediately following the first fast rearrangement would have produced quite different interactions strengths than the final relaxed structure given in Table III. As would be expected from the different radii of Br and Cl atoms, we find the largest adjustments in the Br atom positions which change by 0.16 Å during the relaxation. The other changes are 0.05 Å for Te(1), 0.04 Å for Te(2), 0.04 Å for Cu, 0.10 Å for O(1), 0.04 Å for O(2) and 0.07 Å for O(3).

While the volume of the new structure shows a negligible change with respect to the volume of Cu-45124(Cl), appreciable changes in bond lengths and angles are observed. The Cu-O(2) distance which alternates between 1.94 Å and 2.01 Å in Cu-45124(Cl), becomes 1.91 Å and 2.01 Å in Cu-45124(Br). The Cu-O(3) distance is slightly smaller at 1.90 Å (from 1.91 Å in Cu-45124(Cl)) \textsuperscript{22}. The Cu-O(2)-Cu angle changes from 105.7° in Cu-45124(Cl) to 107.2° in Cu-45124(Br), while the O-Cu-O angle stays nearly constant at 87.0° (87.1° in Cu-45124(Cl)). The Cu-Cl distance is 2.24 Å, the Cu-Br distance 2.42 Å. Finally, the Cl-O(1) distances alternate between 3.27 Å and 3.40 Å while the Br-O(1) distances are 3.22 Å and 3.55 Å. In Table III we present the relaxed coordinates of Cu-45124(Br).

We performed AMTO-downfolding for this system and in Tables IV and V we present the bond distance and hopping values together with those of (Cu-2252(Br)). Both a Cu-d_{x^2−y^2} and a Cu-d_{x^2−y^2}+Br-p downfolding were performed.

Cu-45124(Br) shows the same trend as Cu-45124(Cl) regarding the intertetrahedral hopping \textit{t}_d, namely the near absence of Cu-Cu interaction along this path. The rest of in-plane intertetrahedral hopping paths in Cu-45124(Br) are a bit larger than in Cu-45124(Cl) but, except for \textit{t}_x, they are smaller than in Cu-2252(Br). From the knowledge of the previous systems, a phase transition to an ordered state is also to be expected for this system at low temperatures.

An important issue to be mentioned at this point is the...
value of the intratetrahedron ratio \( t_2/t_1 \) in all the compounds discussed here. Large values of this ratio can be related to an enhancement of intratetrahedron frustration, what has been already discussed for Cu-2252(Br). Cu-2252(Br) is found to have a small but nonzero \( t_2 \) in comparison to its value for Cu-2252(Cl), where the \( t_2 \) hopping path is basically zero, mainly due to the Cl renormalization. The new set of systems, i.e. the synthesized Cu-45124(Cl) and the \textit{ab initio} computer designed Cu-45124(Br) seem to behave in the opposite way. While Cu-45124(Cl) has a small but nonzero \( t_2 \), Cu-45124(Br) relaxes into a structure where the \( t_2 \) path is completely renormalized to zero by the hybridization with the Br ions (see Table VI in the square planar configuration. Though we found an interesting transient structure for Cu-45124(Br) with a moderate intratetrahedron \( t_2/t_1 \), this doesn’t seem to be the energetically favored structure within the AIMD approach.

Finally, we would like to note that the value of the \textit{ab initio} calculated hopping parameters is very susceptible to small changes of distances and angles between the atoms. Our AIMD calculations were performed, as mentioned previously, within the GGA approximation. Consideration of other exchange correlation potentials may change slightly the relaxed structure, which could be important especially for the intratetrahedron hopping paths, where changes of 0.02 to 0.03 Å in the distance between Cu and O(2) and of 2.9° in the Cu-O(2)-Cu angle are decisive for the variation of the hopping parameters.

**Summary.**- To conclude, we have made a comparative study between the spin tetrahedron system Cu\(_2\)Te\(_2\)O\(_5\)Cl\(_2\) and a newly synthesized compound Cu\(_4\)Te\(_5\)O\(_{12}\)Cl\(_4\) belonging to the same family, in terms of the microscopic analysis of the electronic structure. Our study shows that although the basic nature of the interactions remains the same, there is a drastic reduction of the in-plane intertetrahedral diagonal interaction in comparison to the case of Cu\(_2\)Te\(_2\)O\(_5\)Cl\(_2\) where this diagonal interaction was estimated to be nearly as strong as the Cu\(_4\) intratetrahedral nearest neighbor interaction \( t_1 \). We show that the origin of this reduction is due to subtle changes in the crystal structure of Cu\(_4\)Te\(_5\)O\(_{12}\)Cl\(_4\) which causes Cu-Cl bonds belonging to different Cu\(_4\) tetrahedra to align in parallel in the new compound rather than pointing towards each other as was the case in Cu\(_2\)Te\(_2\)O\(_5\)Cl\(_2\). This reduction of the in-plane diagonal hopping in turn increases the importance of the out-of-plane hopping to the extent that some intertetrahedral hoppings along [001] (\( t_c \)) are even about three times stronger than those within the plane.

In absence of the, yet to be synthesized, Cu\(_4\)Te\(_5\)O\(_{12}\)Br\(_4\) and motivated by the more anomalous properties observed in the Br analog to Cu\(_2\)Te\(_2\)O\(_5\)Cl\(_2\), we have theoretically derived the hypothetical crystal structure of Cu\(_4\)Te\(_5\)O\(_{12}\)Br\(_4\) by performing a geometry relaxation in the framework of \textit{ab initio} molecular dynamics. We have analyzed the electronic properties of this new system within the AMTO downfolding procedure. We observe that, while the overall electronic and magnetic behavior seems to be similar to its Cl sister compound, this computer designed Br system shows (except for \( t_d \)) a stronger in-plane intertetrahedron interaction than the Cl system -an effect that was also observed in the comparison between Cu\(_2\)Te\(_2\)O\(_5\)Br\(_2\) and Cu\(_2\)Te\(_2\)O\(_5\)Cl\(_2\). We, however, don’t observe any noticeable effect on the intratetrahedron frustration in the final relaxed Cu\(_4\)Te\(_5\)O\(_{12}\)Br\(_4\) structure.

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