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Received 1 May 2013
Published 27 June 2013
Online at stacks.iop.org/JPhysCM/25/295502

Abstract

Hybrid organic–inorganic compounds are an intriguing class of materials that have been experimentally studied over the past few years because of a potential broad range of applications. The electronic and magnetic properties of three organic–inorganic hybrid compounds with compositions \((\text{NH}_4)_2\text{CuCl}_4\), \((\text{CH}_3\text{NH}_3)_2\text{CuCl}_4\) and \((\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4\) are investigated for the first time with density functional theory plus on-site Coulomb interaction. A strong Coulomb interaction on the copper causes a relatively weak exchange coupling within the layers of the octahedral network, in good agreement with experiment. The character of the exchange interaction (responsible for magnetic behavior) is analyzed. The calculations reveal that \((\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4\) has the strongest Jahn–Teller (JT) distortion in comparison with the two other compounds. The easy axis of magnetization is investigated, showing a weak anisotropic interaction between inter-layer \(\text{Cu}^{2+}\) ions in the \((\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4\) structure. Orbital ordering is concluded from our partial density of states calculations: a cooperation of the JT distortion with an antiferro-distortive pattern.

(Some figures may appear in colour only in the online journal)

1. Introduction

Hybrid organic–inorganic compounds, synthesized by self-assembly from the solution, provide a considerable opportunity for scientific studies and technological applications [1–5]. This broad range of materials allows the combination of properties of organic and inorganic moieties within a single structure. The inorganic network can be considered as a collection of atoms that are held together by covalent and ionic interactions. The organic blocks, which generally interact through weaker interactions like hydrogen and van der Waals bonding, provide a degree of freedom to optimize magnetic and structural properties. Hybrid organic–inorganic compounds based on the perovskite structures are an interesting class of materials [4]. The basic building block of the organic–inorganic perovskite family is the ABX\(_3\) perovskite structure. The structure consists of a 3D network of corner-sharing BX\(_6\) octahedra in which the B atom is a metal cation, X is an anion, and A is selected as a cation in order to neutralize the total charge, and it can even be a molecule. In addition to the 3D perovskites, layered perovskite structures can be formed by slicing ABX\(_3\) into slabs parallel to the [001] direction, with a thickness of one BX\(_6\) octahedron. In this thought experiment the A and X atoms within the slice planes will be cut into halves. This situation can be improved by refilling the affected atoms, resulting in a structure of general formula A\(_2\)BX\(_4\).
term ‘layered perovskite’ has been chosen for this type of structure because one of the most characteristic features of perovskites is the strong JT effect [4, 8]. Among the layered perovskite compounds the low-dimensional octahedra, although in two dimensions only [6, 7]. The structure comprises layers of corner-sharing BX₆ octahedra with the monovalent A cations occupying the cavities. The geometrical constraints parallel to the layers are similar to those of 3D perovskites, i.e. the positions of the A cations are not yet well known, we focus our attention on magnetic and electronic properties of three members of these materials for n = 0, 1, 2 . . . have been studied experimentally in recent years [4, 5, 8–15] because of the promising magnetic and electronic properties. The (C₆H₂ₙ₊₁NH₃)₂BCl₄ in which n = 0, 1, 2 . . . have been given. The compound that shows the strongest JT distortion is the compound (NH₄)₂CuCl₄. The yellow compound (NH₄)₂CuCl₄ crystallizes in the orthorhombic cell with space group Cmca and lattice parameters a = 15.46 Å, b = 7.20 Å and c = 7.20 Å at room temperature [34]. (In order to be consistent with the two other compounds, we describe the structure of (NH₄)₂CuCl₄ with a = 7.20 Å, b = 7.20 Å and c = 15.46 Å as lattice parameters.) The structure is the first member of the (C₆H₂ₙ₊₁NH₃)₂CuCl₄ compounds with square planar CuCl₄²⁻ ions. The octahedral coordination of Cu²⁺ is
completed by sharing two chlorine atoms from adjacent \( \text{CuCl}_4^{2-} \) ions along one axis, as shown in figure 1. The Cu–Cl...Cu bond angle is linear (180°); no tilting with respect to the \( c \) axis or \( ab \) plane occurs (figures 2 and 3). The \((\text{NH}_4)^+\) groups occupy the holes between the chlorine atoms in the adjacent sheets. They form N–H···Cl bonds to any of the eight halogens, with four terminal and four bridging halogens. In order to find the ground state, we perform four calculations, nonmagnetic (N) and three different magnetic structures: ferromagnetic (FM), antiferromagnetic type 1 (ferromagnetic layers coupled antiferromagnetically, AFM\(_1\)) and antiferromagnetic type 2 (antiferromagnetic layers coupled antiferromagnetically, AFM\(_2\)) configurations. We used the x-ray diffraction data as the starting point for the optimization of the atomic positions. The initial positions of hydrogen atoms have been constructed, assuming a tetrahedral coordination for \((\text{NH}_4)^+\). The calculations reveal that the compound has a stable layer-type ferromagnetic structure, with a very weak antiferromagnetic interaction between the layers (AFM\(_1\)). A view of the optimized structure is shown in figure 1. The space group that results from our calculation, considering hydrogen atoms as well, has a lower symmetry. We determine \( \text{Pbc}a \) as an appropriate space group for the optimized structure (table 1). The optimized \( \text{Cu}^{2+} \) lies approximately at the center of a distorted octahedron with two short (s) (2.28 Å), two long (l) equatorial (2.84 Å) and two medium (m) apical Cu–Cl (2.34 Å) bonds. The long equatorial Cu–Cl bond indicates a puckering of the CuCl\(_4^{2-}\) sheets in the \( ab \) plane as a result of the hydrogen bonding interaction between the \( \text{NH}_4^+ \) groups and chloride ions. A schematic view of the perpendicular orientation of the neighboring long equatorial Cu–Cl bonds is shown in figure 4. A quantitative measure of the magnitude of the JT distortion is given by the octahedral distortion parameter \( \Delta d \) [35] defined as

\[
\Delta d = \langle 1/6 \rangle \sum_{i=0}^{5} \left( (d_n - d)/d \right)^2,
\]

in which \( d \) is the mean Cu–Cl bond distance and \( d_n \) are individual Cu–Cl bond distances. By mapping Cu–Cl distances onto equation (1), we have \( \Delta d = 8.93 \times 10^{-3} \). The optimized octahedral network is tilted along the \( z \) axis...
Figure 4. The schematic view of the alternation perpendicularly of the elongated Cu–Cl bonds in the ab plane. The Cl\textsuperscript{s} and Cl\textsuperscript{b} represent the interactions of p\textsubscript{x} and p\textsubscript{y} orbitals with the Cu atoms along x' and y' axes, respectively. The s and l stand for the short and long bonds, respectively. The unit cell is sketched for clarity.

Table 1. The position of atoms for the ground state of \((\text{NH}_4)\text{CuCl}_4\) structure in the Pbca space group (no 61).

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff letter</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>4a</td>
<td>0.002</td>
<td>0.003</td>
<td>0.001</td>
</tr>
<tr>
<td>Cl\textsuperscript{s} \parallel ab plane</td>
<td>8c</td>
<td>0.208</td>
<td>0.232</td>
<td>0.019</td>
</tr>
<tr>
<td>Cl\textsuperscript{b} \perp ab plane</td>
<td>8c</td>
<td>0.034</td>
<td>0.020</td>
<td>0.150</td>
</tr>
<tr>
<td>N</td>
<td>8c</td>
<td>0.021</td>
<td>0.006</td>
<td>0.357</td>
</tr>
<tr>
<td>H\textsubscript{1}</td>
<td>8c</td>
<td>0.015</td>
<td>0.358</td>
<td>0.124</td>
</tr>
<tr>
<td>H\textsubscript{2}</td>
<td>8c</td>
<td>0.057</td>
<td>0.414</td>
<td>0.104</td>
</tr>
<tr>
<td>H\textsubscript{3}</td>
<td>8c</td>
<td>0.018</td>
<td>0.490</td>
<td>0.207</td>
</tr>
<tr>
<td>H\textsubscript{4}</td>
<td>8c</td>
<td>0.159</td>
<td>0.487</td>
<td>0.136</td>
</tr>
</tbody>
</table>

The order of magnitude and sign of the exchange interaction can be estimated by the Heisenberg model [38].

\[ H = - \sum_{ij} J_{ij} S_i \cdot S_j \quad (2) \]

The summation is taken over the neighboring spins; \(J_{ij}\) denotes the exchange constant between spins and \(S\) is the operator magnetic moment on each copper. The character of

Figure 5. Total density of states for FM, AFM\textsubscript{1} and AFM\textsubscript{2} configurations of \((\text{NH}_4)\text{CuCl}_4\) structure with \(U = 0\) eV.

Figure 6. PDOS of Cu d, Cl\textsuperscript{1}p, Cl\textsuperscript{2}p and N\textsubscript{p+s} (p + s orbitals of N) for FM, AFM\textsubscript{1} and AFM\textsubscript{2} configurations of \((\text{NH}_4)\text{CuCl}_4\) structure with \(U = 0\) eV.
the exchange interaction in our compounds (predominantly a weak in-plane interaction) is superexchange, as a result of short range interactions. In order to check the dominance of the superexchange interaction, we expand our cell in the $ab$ plane. We double the tetragonal unit cell by rotation of $a$ and $b$ (with $c$ within the layers of octahedra ($ab$) plane) for AFM$_1$ alignment of $(NH_4)_2CuCl_4$ structure with $U = 0$ eV.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>$U = 0$ eV</th>
<th>$U = 7$ eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J/k_B$</td>
<td>17</td>
<td>80.0</td>
</tr>
</tbody>
</table>

4. The electronic properties of $(CH_3NH_3)_2CuCl_4$

The monoclinic structure of $(CH_3NH_3)_2CuCl_4$ (space group $P2_1/a$ and lattice parameters $a = 7.155$ Å, $b = 7.424$ Å, $c = 9.814$ Å and $β = 109.18°$ at $T = 100$ K) shows the JT distorted octahedron [16, 39, 40]. The compound is a second example of square planar $CuCl_2^-$ ions from $(CuH_2e+NH_3)_2CuCl_4$ perovskite structures, as is shown in figure 10. The methylammonium moieties are located between the layers and connected by hydrogen bonds to the $Cl^-$ ions, leading to one bridging and two terminal chlorine ligands. In order to find the ground state, we construct a monoclinic unit cell with the same $a$ and $b$ parameters and $c$ twice the primitive lattice parameter. We consider five calculations, nonmagnetic (N) and four different magnetic structures: ferromagnetic (FM) and antiferromagnetic type 1 (AFM$_1$), antiferromagnetic type 2 (AFM$_2$) and antiferromagnetic type 3 (AFM$_3$) configurations, based on the number of the nearest-neighbors and the sign of the superexchange interaction (figure 11). The compound favors an isolated two-dimensional ferromagnetic alignment (negligible energy difference between FM and AFM$_1$ structures). The $Cu^{2+}$ has distorted octahedral coordinates, with two short ($s$) (2.29 Å), two medium ($m$) (2.33 Å) and two long ($l$) (2.91 Å) $Cu$–$Cl$ bonds. The elongated $Cu$–$Cl$ bonds are orientated perpendicularly to each other (figure 12). By using equation (1), we have the magnitude of the JT distortion, $Δd = 1.12 \times 10^{-2}$. The structure is tilted along the $z$ axis ($θ_z = 9.11°$) and the $ab$ plane ($θ_{ab} = 163.51°$). The
The DOS, PDOS and alternating interaction of Cl p states (p orbitals in the ab plane) with eg states of Cu within the layers of octahedra (ab plane) with $U = 7$ eV, for AFM$_1$ alignment of (NH$_4$)$_2$CuCl$_4$ structure (note the different energy scale compared to DOS and PDOS plots with $U = 0$ eV).

Figure 10. The structure of (CH$_3$NH$_3$)$_2$CuCl$_4$; the octahedra are sandwiched between methylammonium groups.

Figure 11. The schematic depiction of FM, AFM$_1$, AFM$_2$ and AFM$_3$ configurations. The arrows on each Cu represent spin direction.

Figure 12. A schematic view of the antiferro-orbital ordering in the ab plane. The Cl$^a$ and Cl$^b$ represent the interaction of p$_x$ and p$_y$ with the Cu atoms along x$'$ and y$'$ axes, respectively. The s and l stand for the short and long bonds, respectively. The unit cell is sketched for clarity.

The tilting of the octahedral network in the ab plane and along the c axis is depicted in figure 13. The C–N groups are almost perpendicular to the ab plane with angles of $\theta_a = 79.64^\circ$ and $\theta_b = 67.92^\circ$ with respect to the a and b axes, respectively. The size of the intra-layer exchange coupling constant, by using equation (2) and considering the relative energy of the ferromagnetic and antiferromagnetic alignment, is given in table 3. The difference in magnetic anisotropy shows that the localized magnetic moments on each Cu atom lie in the ab plane ($E_{1_a} - E_{1_b} = 1.0$ meV/Cu site). The density of states (DOS) and projected density of states (PDOS) for
Figure 13. A tilted perspective of \((\text{CH}_3\text{NH}_3)_2\text{CuCl}_4\) in the \(ab\) plane and along the \(c\) axis. The unit cell is sketched for clarity.

Figure 14. The DOS and PDOS for ferromagnetic (FM) configuration of \((\text{CH}_3\text{NH}_3)_2\text{CuCl}_4\) with \(U = 0\) eV.

Figure 15. The DOS and PDOS for ferromagnetic (FM) configuration of \((\text{CH}_3\text{NH}_3)_2\text{CuCl}_4\) with \(U = 7\) eV (note the different energy scale compared to figure 14).

Figure 16. The DOS and PDOS (for Cu d and Cl p orbitals) with \(U = 7\) eV are shown in figure 15. The calculated parameter, \(J\), from GGA + \(U\) calculation shows a good agreement with experimental measurement [8].

Table 3. The estimated \(J/\kappa_B\) and the experimental measurement (exp.) [8] (in K) for the \((\text{CH}_3\text{NH}_3)_2\text{CuCl}_4\) compound from GGA and GGA + \(U\) calculations with \(U = 7\) eV.

<table>
<thead>
<tr>
<th></th>
<th>(\text{Exp.})</th>
<th>(U = 0) eV</th>
<th>(U = 7) eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>(J/\kappa_B)</td>
<td>19.2</td>
<td>82.2</td>
<td>21</td>
</tr>
</tbody>
</table>

The DOS and PDOS (for Cu d and Cl p orbitals) with \(U = 7\) eV are shown in figure 15. The calculated parameter, \(J\), from GGA + \(U\) calculation shows a good agreement with experimental measurement [8].

5. The electronic properties of \((\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4\)

The compound \((\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4\) [15, 18, 19] is the third member of the \((\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{CuCl}_4\) series with the square planar \(\text{CuCl}_4^{2-}\). The lattice constants of \((\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4\) are \(a = 7.47\ \text{Å}, b = 7.17\ \text{Å}\) and \(c = 21.24\ \text{Å}\) at \(T = 100\ \text{K}\) with the \(\text{Pbca}\) space group [41]. The face-centered orthorhombic unit cell is shown in figure 16. We construct four calculations, nonmagnetic (N) and three different magnetic orderings: including ferromagnetic (FM), antiferromagnetic type 1 (ferromagnetic layers coupled antiferromagnetically...
Figure 16. The structure of $(C_2H_5NH)_2CuCl_4$; the CuCl$_6$ sheets are sandwiched between two layers of ethylammonium.

Table 4. The estimated $J/k_B$ and the experimental measurement $(\text{exp.})$ [8] (in K) for the $(C_2H_5NH)_2CuCl_4$ compound from GGA and GGA + $U$ calculations with $U = 7$ eV.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>$U = 0 \text{ eV}$</th>
<th>$U = 7 \text{ eV}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J/k_B$</td>
<td>18.6</td>
<td>83</td>
</tr>
</tbody>
</table>

AFM$_1$ and antiferromagnetic type 2 (antiferromagnetic layers coupled antiferromagnetically AFM$_2$) in order to find the ground state. The compound favors a layered-ferromagnetic structure with a very weak antiferromagnetic coupling between the layers. The Cu$^{2+}$ ions are located approximately in the center of a distorted octahedron with two short ($s$) (2.29 Å), two medium ($m$) (2.32 Å) and two long ($l$) (2.93 Å) Cu–Cl bonds. The alternate elongated Cu–Cl bonds are perpendicular to each other (figure 17). The magnitude of the JT distortion, by using equation (1), is $\Delta d = 1.21 \times 10^{-2}$. The octahedral network is tilted with respect to the $ab$ plane and the $z$ axis with angles of $\theta_{ab} = 163.75^\circ$ and $\theta_z = 8.95^\circ$, respectively. The neighboring octahedra along the $ab$ plane and the $z$ axis have the same tilting direction. The size of intra-layer exchange coupling constant, by mapping the relative energy of FM and AFM$_1$ alignment onto the Heisenberg model (equation (2)), is given in table 4. The calculated energy difference ($E_{\perp ab} - E_{\parallel ab} = 0.90$ meV/Cu site) implies that the magnetic moments on copper atoms lie in the $ab$ plane with a very small deviation in comparison with two former structures. The density of states (DOS) and projected density of states (PDOS) of the structure for the ground state is shown in figure 18 (consistently with figure 17). The band gap is mostly dominated by Cu $d$ orbitals, and the alternating arrangement of $d_{2z^2}$ and $d_{x^2-y^2}$ orbitals is confirmed from the PDOS in figure 18, as a result of cooperative JT distortion with antferro-orbital ordering of CuCl$_6$ octahedra. The intra-layer exchange parameter from DFT + $U$ with $U = 7$ eV is given in table 4, in good agreement with experiment. For $U = 7$ eV we have $\theta_{ab} = 163.45^\circ$, $\theta_z = 9.12^\circ$ and $\Delta d = 1.70 \times 10^{-2}$. Also the DOS and PDOS (for Cu $d$ and Cl $p$ orbitals) are shown in figure 19.
Figure 19. The DOS and PDOS for antiferromagnetic type 1 \((\text{AFM}_1) (\text{C}_2\text{H}_3\text{NH}_3)_2\text{CuCl}_4\) with \(U = 7\) eV (note the different energy scale compared with figure 18).

6. Conclusion

We have given a detailed analysis of the electronic properties of the three organic–inorganic hybrids with formulas \((\text{NH}_4)_2\text{CuCl}_4\), \((\text{CH}_3\text{NH}_3)_2\text{CuCl}_4\) and \((\text{C}_2\text{H}_3\text{NH}_3)_2\text{CuCl}_4\). A weak contribution of the next-nearest-neighbor interaction (one order of magnitude smaller than the nearest-neighbor interaction) results in the dominance of the superexchange interaction within the layers. With GGA + \(U\) \((U = 7\) eV) good agreement with the experimental intra-layer exchange coupling constant is obtained. The Jahn–Teller effect is stronger for the compound with the longest organic cation, \((\text{C}_2\text{H}_3\text{NH}_3)_2\text{CuCl}_4\), in DFT and DFT + \(U\) calculations. In fact, we found a linear relation between the magnitude of the Jahn–Teller distortion and the length of the organic cation. The anisotropic interaction between \(\text{Cu}^{2+}\) ions in \((\text{C}_2\text{H}_3\text{NH}_3)_2\text{CuCl}_4\) is stronger than in the two other compounds, in spite of the increasing length of one \((z)\) direction as a result of the increasing organic cation sizes. The relatively appreciable anisotropy for \((\text{C}_2\text{H}_3\text{NH}_3)_2\text{CuCl}_4\) may be a result of the appreciable effect of magnetic dipolar interactions (of the order of \(10^{-4}\) in K) as well as superexchange interactions between the layers. The existence of orbital ordering is shown from our partial density of states (PDOS) calculations as a result of the alternating interaction of the two possible combinations of \(d_{x^2-z^2}\) and \(d_{z^2-x^2}\) orbitals with \(\text{Cl}\) \(p_x\) and \(\text{Cl}\) \(p_y\) orbitals. We show that the contributions of the inorganic components, by considering the antiferro-distortive pattern of the octahedral network and the manner of orbital ordering, are similar in these three compounds. The organic contributions, however, vary significantly for different organic components. It is interesting to mention that the octahedral tilting has been modified with respect to the temperature as well as the organic constituent: the absence of the tilting for the \((\text{C}_2\text{H}_3\text{NH}_3)_2\text{CuCl}_4\), \(\theta_{ab} = 170.96^\circ\) for the \((\text{CH}_3\text{NH}_3)_2\text{CuCl}_4\), and \(\theta_{ab} = 169.63^\circ\) for the \((\text{C}_2\text{H}_3\text{NH}_3)_2\text{CuCl}_4\) at room temperature are the evidence for this effect.

Acknowledgments

This work was carried out with the support of the Stichting voor Fundamenteel Onderzoek der Materie (FOM). FOM is financially supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO).

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