Theoretical prediction of Jahn-Teller distortions and orbital ordering in Cs$_2$CuCl$_2$Br$_2$

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With the use of density function calculations we show that the actual crystal structure of Cs$_2$CuCl$_2$Br$_2$ should contain elongated in the $ab$-plane CuCl$_4$Br$_2$ octahedra, in contrast to the experimentally observed compression in the $c$ direction. We also predict that the spins on Cu$^{2+}$ ions should be ferromagnetically ordered in the $ab$ plane, while the exchange interaction along the $c$ direction is small and its sign is uncertain.

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I. INTRODUCTION

The system Cs$_2$Cu(ClBr)$_4$ attracts a lot of attention mainly because of its unconventional magnetic properties. Cs$_2$CuBr$_4$ is the only triangular-lattice antiferromagnet which exhibits an unusual quantum magnetization plateau, while Cs$_2$CuCl$_4$ shows field-induced Bose-Einstein condensation of magnons. Thus the investigation of intermediate compositions of Cs$_2$CuCl$_4$-Br$_x$ may not only shed some light on the magnetic properties of both compounds, but may also result in the discovery of new phenomena.

The mixed Cs$_2$CuCl$_4$-Br$_x$ crystal series was successfully grown at 50°C with orthorhombic crystal structure. However, at room temperature in the synthesis process the stabilization of a new tetragonal phase for 1 < $x$ < 2 was observed.

The crystal structure of tetragonal specimens consists of the CuCl$_2$ layers stacking in the $c$ direction and divided by the Cs and Br atoms, see Fig. 1. It is important to mention that Cu ions in one of the layers is placed on the top/bottom of the void between CuCl$_4$ plaquettes of another layer. According to Ref. 3, the Cl and Br ions form octahedra surrounding Cu with two short, apical, Cu-Br and four long, planar, Cu-Cl bonds. Such kinds of the compressed octahedra are quite untypical for the Jahn-Teller Cu$^{2+}$ ions with $d^9$ electronic configuration for the dense crystal structures, and the authors of Ref. 3 mentioned that the real type of distortions may be hidden by the multidomain structures.

There are a lot of insulating materials where ligand octahedra surrounding Jahn-Teller active metal ion turn out to be elongated: KCrF$_4$, Cs$_2$AgF$_4$, K$_2$CuF$_4$, and others, while there are only a few systems with the opposite distortion. Generally speaking, there can be different mechanisms which stabilize elongated octahedra. One of the reasons can be the gain in the magnetic energy due to more efficient hoppings between half-filled $x^2$−$y^2$-like and oxygen $p$ orbitals in the case of the $d^9$ configuration. Another one is related to the features of the elastic interactions. It can be shown that the total energy of elongated octahedra is lower than compressed if in the expression for the elastic energy the terms of higher order than quadratic are taken into account.

In the present paper, using ab initio band structure calculations, we found that the crystal structure of Cs$_2$CuCl$_2$Br$_2$ ($x = 2$), which corresponds to the lowest total energy, indeed corresponds to the elongated CuCl$_4$Br$_2$ octahedra. This is in contrast to the observed experimental structure, but supports the general tendency in the Jahn-Teller distortions to stabilize elongated, not compressed octahedra. The more detailed structural study should be carried out to confirm (or disprove) the predicted lattice and orbital ordering.

II. CALCULATION DETAILS

The pseudopotential PWscf code was chosen for the calculations. We used ultrasoft pseudopotentials with the Perdew-Burke-Ernzerhof (PBE) version of the exchange-correlation potential. The nonlinear core correction was included in the Cu, Cs, and Cl pseudopotentials, while semicore states were not considered in the present calculations.

In order to take into account strong Coulomb repulsion on the Cu sites the GGA + U approximation was utilized. On-site Coulomb repulsion parameter $U$ was chosen to be 7.0 eV, while intra-atomic Hund’s rule exchange $J_H = 0.9$ eV.

The charge density and kinetic energy cut-offs equal 40 and 200 Ry, respectively. 144 $k$ points ($6 \times 6 \times 4$) in a full part of the Brillouin zone for the unit cell, consisting of 4 formula units (f.u.), were used in the self-consistency course. The integration over the Brillouin zone was performed with the use of the Gaussian smearing of 10 meV. The structural optimization was performed while each component of the force was more than 2 mRy/a.u. No symmetry operations were used in the course of self-consistency.

The crystal structure was taken for Cs$_2$CuCl$_2$Br$_3$. We used the supercell $\sqrt{2} \times \sqrt{2} \times 2$ cell to allow the simplest types of the orbital ordering.

III. CALCULATION RESULTS

The total energy is known to depend on the type of magnetic ordering, and this magnetic ordering may have an influence on the lattice distortions through the stabilization of the particular orbital ordering. That is why it is important to study possible lattice distortions together with the analysis of the magnetic interactions.

The total energies of the following magnetic configuration were calculated: nonmagnetic (NM), ferromagnetic (FM), AFM-A type (when all ions in the $ab$ plane are ferromagnetically ordered, while the interaction between planes is antiferromagnetic), and AFM-C type (nearest Cu in the $ab$ plane are AFM ordered, the next nearest neighbors in the $c$ direction are ferromagnetically coupled).

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The lowest in energy in the tetragonal crystal structure of Ref. 3 turns out to be the FM configuration (see Table I). The analysis of the occupation matrix shows that the single hole in the 3$d$ shell of Cu$^{2+}$ is localized on the $3z^2 - r^2$ orbital in the FM configuration. Such an orbital filling is obviously a result of the local compression of CuCl$_4$Br$_2$ octahedra in the structure of Ref. 3.

The ground state is metallic for any of the investigated magnetic configurations. This is in contrast to the fact that the undoped materials Cs$_2$CuCl$_4$ and Cs$_2$CuBr$_4$ are Mott insulators (the results of the GGA + U calculations can be found in Ref. 22), and the samples of the intermediate compound Cs$_2$CuCl$_2$Br$_1.6$ do not have a metallic shine.\(^3\)

The compression of the octahedra in Cs$_2$CuCl$_2$Br$_2$ in the $c$ direction prevents the $x^2 - 2z^2/y^2 - z^2$ orbital order observed in KCuF$_3$ and K$_2$CuF$_4$,\(^9,23\) where Cu ions also have one hole in the $e_g$ subshell. In order to allow the same type of orbital pattern and compare total energies of different solutions we tetragonally distorted CuCl$_4$Br$_2$ in the $ab$ plane and relaxed crystal structure with the constraint to keep the same cell volume. In addition, we also performed the lattice optimization for the initial nondistorted in the $ab$-plane structure since the experimental structure does not necessarily corresponds to the ground state crystal structure in the chosen approximation (GGA + U). In effect we obtained two crystal structures corresponding to the same magnetic order (relaxed initial experimental and relaxed distorted in the $ab$-plane structures). The results are summarized in Table II, where the second, forth, and fifth lines refer to the structure optimized starting from the lattice presented in Ref. 3 (four equal Cu-Cl distances) and the first and the third lines correspond to the results for the structure with the octahedra elongated in the $ab$ plane.

The lowest total energy corresponds to FM and AFM-A type configurations with strongly distorted $ab$-plane CuCl$_4$ plaquettes, as shown in Fig. 1. The energy difference between these two solutions is tiny and may depend on the details of the calculations, but both lie much lower (~558 meV) in energy than the ground state magnetic configuration (FM) for the tetragonal not optimized crystal structure. Moreover, it is clearly seen from Table II that only half of this difference can be compensated by the ionic relaxation which does not change a local symmetry of Cu$^{2+}$ ions (i.e., that there are four equal Cu-Cl bonds in the $ab$ plane).

The second half of the total energy decrease is related to the distortions in the $ab$ plane such that they do not change the average Cu-Cl bond length, but create a checkerboard order of the long and short Cu-Cl bonds. The distortions in the $ab$ plane are accompanied by a moderate elongation of the CuCl$_2$Br$_2$ octahedra in the $c$ direction, Cu-Br bond length increases on ~0.1 Å, which is compensated by the Cs-Br bond squeezing. Thus, instead of compression in the $c$ direction octahedra, the ionic relaxation rather stabilizes the elongation in alternating directions in the $ab$-plane CuCl$_4$Br$_2$ octahedra.

Such types of distortions result in the $x^2 - z^2/y^2 - z^2$ orbital order, like in KCuF$_3$, see Fig. 3. This orbital pattern leads to a strong ferromagnetic superexchange in the $ab$ plane, which stabilizes FM or AFM-A magnetic configurations, which agrees with our total energy calculations.

It is also worth mentioning that the distortion in the $ab$ plane stabilizes insulating ground state: The band gap is ~0.5 eV both for FM and AFM-A. In contrast, all the calculations for the initial, experimental structure, as well as the relaxed undistorted $ab$-plane structure result in metallic ground states. So to get an insulator it is important to have the distorted crystal structure, but not a specific magnetic order.

In order to check how present results depend on the choice of the Hubbard $U$ parameter we repeat the GGA + U calculations including the lattice relaxation for $U = 5$ eV and $J_{H} = 0.9$ eV. The lowest in energy again was the AFM-A solution ($E_{\text{AFM-A}} = -0.8$ meV), the FM configuration is slightly higher ($E_{\text{FM}} = 0$ meV), while the AFM-C and FM with four equal Cu-Cl bonds have total energies of 280.7 and 283.3 meV, respectively. Thus, one may see that the present results hardly depend on the value of the Hubbard $U$ parameter. The role of the $U$ correction in this situation is not simply to produce Hubbard lower and upper bands, but to allow a certain orbital order through the orbitally dependent LDA + U/GGA + U potential.\(^{15}\)

| Configuration | Total energy, meV |
|---------------|------------------|
| FM            | 0                |
| AFM-A         | 3.7              |
| AFM-C         | 2.9              |
| NM            | 8.8              |

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Finally, we present the total and partial density of states (DOS) plots for the distorted \textit{ab} plane relaxed crystal structure, for example, for FM configuration (Fig. 2). Due to a large on-site Coulomb repulsion the Cu 3\textit{d} band goes away from the Fermi level and is placed mainly in the energy range from $-5.5$ to $-3$ eV. The Br \textit{p} and Cl \textit{p} states are concentrated from $-3$ to $1$ eV. It is important to note, that in contrast to a naive expectation, the largest contribution to the bottom of the conduction band (as well as to the top of the valence band) comes from Cl \textit{p} and Br \textit{p} states: $\sim 3.6$ states/(eV f.u.), while Cu \textit{d} provides only $1.9$ states/(eV f.u.) (the rest belongs to other states of Cu, Cl, and Br ions). This means that the hole is actually localized not on the Cu $x^2 - y^2$-like orbital, but rather on the Wannier orbital, which is centered on the Cu site, has $x^2 - y^2$ symmetry, but also has significant contributions (tails) on the surrounding Cl and Br ions. This is similar to the situation in Cs$_2$Au$_2$Cl$_6$,\textsuperscript{24} but here the spatial orientation of the Wannier orbital is different. The strong admixture of Cl \textit{p} and Br \textit{p} states to the conduction band may be the reason for the small band gap value $\sim 0.5$ eV in the present GGA + U calculations since these states act as a ballast. We expect that the LDA + U\textsubscript{WF} approximation, where $U$ is applied not only on the \textit{d} part, but on a whole Wannier function will result in a larger band gap.

Summarizing, on the basis of the \textit{ab initio} calculations we have shown that the layered material Cs$_2$CuCl$_2$Br$_2$, containing Jahn-Teller ion Cu$^{2+}$, which was considered earlier as a rare example of the Jahn-Teller system with localized electrons and $e_g$ degeneracy with locally compressed ligand octahedra, must in fact have elongated octahedra with the long axes alternating in the basal plane. Thus, yet one more Jahn-Teller material turns out to be not an exception, but rather follows the general rule that the octahedra around such ions are elongated. This form of the Jahn-Teller distortions and orbital ordering should lead to strong ferromagnetic exchange in the \textit{ab} plane, the interlayer exchange being very weak. The predicted crystal and magnetic structure should be observable by the detailed structural and magnetic studies.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2.png}
\caption{(Color online) The total and partial DOS for FM configuration in the relaxed crystal structure with alternating long and short Cu-Cl bonds in the \textit{ab} plane. Positive (negative) values correspond to spin majority (minority) states. The Fermi level is set to zero.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3.png}
\caption{(Color online) The sketch of the proposed orthorhombic distortions corresponding to the lowest total energy in Table II, when all CuCl$_2$Br$_2$ octahedra are elongated in alternating directions in the \textit{ab} plane (long Cu-Cl bonds are shown in red) and the orbital order, which is expected for such kinds of distortions (hole orbitals of Cu$^{2+}$ are shown).}
\end{figure}
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