Rare case of magnetic Ag$^{3+}$ ion: double perovskite Cs$_2$KAgF$_6$

Ting Jia$^1$, Xiaoli Zhang$^1$, Ting Liu$^1$, Fengren Fan$^2$, Zhi Zeng$^{1,3*}$, X. G. Li$^4$, D. I. Khomskii$^5$, and Hua Wu$^{2\dagger}$

$^1$Key Laboratory of Materials Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei 230031, China
$^2$Laboratory for Computational Physical Sciences (MOE), State Key Laboratory of Surface Physics, and Department of Physics, Fudan University, Shanghai 200433, China
$^3$Department of Physics, University of Science and Technology of China, Hefei, 230026, China
$^4$Hefei National Laboratory for Physical Sciences at Microscale, Department of Physics, University of Science and Technology of China, Hefei 230026, China and
$^5$Department of Physics, University of Cologne, Cologne 50937, Germany

(Dated: June 5, 2014)

Normally 4$d$ or 5$d$ transition metals are in a low-spin state. Here using first-principles calculations, we report on a rare case of a high-spin S=1 magnetic state for the Ag$^{3+}$ ion in the double perovskite Cs$_2$KAgF$_6$. We also explored a possibility of a conventional low-spin S=0 ground state and find an associated tetragonal distortion to be 0.29 Å. However, the lattice elastic energy cost and the Hund exchange loss exceed the $e_g$ crystal-field energy gain, thus making the low-spin tetragonal structure less favorable than the high-spin cubic structure. We conclude that the compact perovskite structure of Cs$_2$KAgF$_6$ is an important factor in stabilizing the unusual high-spin ground state of Ag$^{3+}$.

I. INTRODUCTION

Transition metal compounds possess diverse properties, largely due to their electronic correlation effects and the interplay of charge, spin, and orbital degrees of freedom. For many of them, spin state is an important issue. It can be a high-spin (HS), low-spin (LS), or even an intermediate-spin (IS) state. The corresponding electronic configurations, e.g., for a Fe$^{3+}$ ion in an octahedral crystal field, are $t_{2g}^6e_g^2$, $t_{2g}^5$, and $t_{2g}^4e_g$. The spin state is intimately related to materials properties such as magnetic transitions, metal-insulator transition, and transport behavior. In the past decades, a lot of research has been carried out on the spin state of 3$d$ transition-metal compounds [1–8]. A consensus has been reached that the spin state issue arises mainly from a competition between the Hund’s rule coupling and crystal-field splitting. The former favors a HS state, and the later a LS state. Compared to the well studied spin state issue of 3$d$ transition metals, little research has been done on the spin state of 4$d$/5$d$ transition-metal compounds [9,10], which is probably due to a fact that in most cases, 4$d$/5$d$ transition metals are in a LS state. As 4$d$/5$d$ orbitals are spatially more extended than 3$d$ ones, their stronger interaction with the anionic ligands and a larger crystal-field splitting but a moderate or weak Hund exchange normally stabilize the LS state [9,10].

In this work, we have studied the double perovskite Cs$_2$KAgF$_6$ using first-principles calculations, focusing on its exotic spin state. Fig. 1 shows its cubic structure, in which K$^+$ and Ag$^{3+}$ ions form an ordered arrangement on the B-sites of the perovskite ABF$_3$ [11][12], and the Ag-F bond distance is 2.13 Å (see also the structural parameters in Table I). Although a Ag$^{3+}$ ion ($4d^8$) could in principle be either in a LS state ($S=0, t_{2g}^6(3z^2-r^2)^2(x^2-y^2)^0$) or in a HS state ($S=1, t_{2g}^6(3z^2-r^2)^1(x^2-y^2)^1$), in reality almost in all known cases the Ag$^{3+}$ ion is in the LS state and is thus nonmagnetic [13]. Actually, very few Ag$^{3+}$ and Cu$^{2+}$ (both with $d^9$ electronic configuration) crystalline compounds are known. These compounds mostly have a tetragonal or lower symmetry structure to maintain the LS S=0 ground state [14]. Similar to the well-known Jahn-Teller (JT) ions like Cu$^{2+}$ and Ag$^{3+}$, the Cu$^{2+}$ and Ag$^{3+}$ ions could have an even stronger tendency to JT-driven distortions (local elongation of ligand octahedra). Such distortions are usually so strong that the corresponding energy gain exceeds the intraatomic Hund’s exchange energy, thus stabilizing the LS state. Indeed, the energy of the state with the tetragonal distortion $u$ can be written as

$$E = -gmu + Bu^2/2,$$  \hspace{1cm} (1)

where $g$ is the JT coupling constant determining the splitting of the originally degenerate $e_g$ levels with the distortion, and $n$ is the number of electrons or holes on the $e_g$ levels (in our case $n=2$, in contrast to $n=1$ (one hole) in the more familiar ion Cu$^{2+}$ ($d^9$)). The second term on the right of the above equation corresponds to lattice elastic energy. Minimizing this equation with respect to the distortion $u$, we get the equilib-

FIG. 1: (color online) Double perovskite structure of Cs$_2$KAgF$_6$. 

*Corresponding author. zzeng@theory.issp.ac.cn
†Corresponding author. wuh@fudan.edu.cn
TABLE I: The lattice parameters of Cs$_2$KAgF$_6$ in the experimental cubic structure[13], and in the optimized tetragonal and ac-tetragonal phases.

| phases          | cubic          | tetragonal     | ac-tetragonal |
|-----------------|----------------|----------------|---------------|
| space group     | Fm$ar{3}$m | I4/mmm         | I4/mmm        |
| a (Å)           | 9.175          | 6.488          | 6.195         |
| b (Å)           | 9.175          | 6.488          | 6.195         |
| c (Å)           | 9.175          | 9.175          | 10.062        |
| x,y,z (Cs)      | (0.75, 0.25, 0.25) | (0.0, 0.5, 0.25) | (0.0, 0.5, 0.25) |
| x,y,z (K)       | (0.5, 0, 0)    | (0, 0, 0)      | (0, 0, 0)     |
| x,y,z (Ag)      | (0, 0, 0)      | (0, 0, 0.5)    | (0, 0, 0.5)   |
| x,y,z (F)       | (0, 0, 0.232)  | (0.213, 0.213, 0.5) | (0.224, 0.224, 0.5) |
|                 | (0, 0, 0.745)  | (0, 0, 0.745)  | (0, 0, 0.724) |

The cutoff energy of 16 Ryd was used for plane wave expansion. The calculations were fully converged using 300 k points in the first Brillouin zone.

TABLE II: The relative total energies $\Delta E$ (meV/fu), band gap $E_g$ (eV) and $\epsilon_g$ orbital occupation (up/down) of Cs$_2$KAgF$_6$ in different states calculated by LSDA+$U$. The $3d_{\uparrow}$ orbitals are fully occupied in all cases and omitted here. The cubic HS state is the ground state.

| State           | $\Delta E$ | $E_g$ | $z^2 - r^2$ | $x^2 - y^2$ |
|-----------------|------------|-------|-------------|-------------|
| cubic HS        | 0          | 1.12  | 0.95/0.48   | 0.95/0.48   |
| tetragonal LS   | 366        | 0.11  | 0.94/0.94   | 0.49/0.49   |
| tetragonal HS   | 441        | 0.03  | 0.94/0.94   | 0.97/0.45   |
| ac-tetragonal LS| 336        | 0.23  | 0.94/0.94   | 0.49/0.49   |

We have used the experimental cubic structure of Cs$_2$KAgF$_6$ and the optimized tetragonal structures, see Table

II. COMPUTATIONAL DETAILS

We used the experimental cubic structure of Cs$_2$KAgF$_6$ and the optimized tetragonal structures, see Table

III. RESULTS AND DISCUSSION

To see first the nature of Ag-F interaction, a spin-polarized LSDA calculation is performed for the cubic structure of Cs$_2$KAgF$_6$ in a ferromagnetic state. We also calculated an an-
tiferromagnetic state and find that the exchange between two
nearest-neighboring Ag ions is weakly antiferromagnetic, be-
ing only about 1 meV. The electronic structures of the fer-
omagnetic and antiferromagnetic states are practically the
same. Considering a magnetic frustration associated with the
FCC sublattice of the Ag ions, a paramagnetic state, or a spin
glassy one below very low temperature (few K) can be ex-
pected for Cs$_2$KAgF$_6$. Our LSDA calculations show that it
is an insulator with a band gap of 0.5 eV given by the $e_g$
exchange splitting, see Fig. 2. Besides the common $t_{2g}$-
e$g$ crystal-field splitting, there is a large bonding-antibonding
splitting due to the strong Ag-4d-F 2p covalency, being about
5 and 3 eV for the $e_g$ and $t_{2g}$ orbital, respectively. As a re-
result, the $e_g$ bonding state is even lower than the $t_{2g}$ one.[26].
The $t_{2g}$ bands are fully occupied and the $e_g$ bands are 3/4 oc-
cupied, with the fully occupied up-spin $t_{2g}$ and $e_g$ channels.
This demonstrates the existence of a HS state and a $d^9\,L_6$
configuration for the formal Ag$^{3+}$ ($d^6$) ion. The one hole spreads
over the six F atoms in the AgF$_6$ unit, which accounts for a
reduced spin moment of 0.90 $\mu_B$ on the Ag site and a finite
spin moment of 0.16 $\mu_B$ on each F. Summing up all of these
moments and a small fraction in the interstitial region gives a
total integer spin moment of 2 $\mu_B$/fu, confirming the formal
HS $S=1$ state for the Ag$^{3+}$ ion. As these magnetic AgF$_6$ units
are separated in this double perovskite by the corner-shared
KF$_6$ units, they form narrow bands (sharp DOS curves) and
are weakly antiferromagnetically coupled.

Late 4d transition-metal oxides or fluorides often have a
moderate electron correlation. As Cs$_2$KAgF$_6$ is a narrow band
system, it is natural to study its electron correlation effect. In
the following, we carried out LSDA+$U$ calculations to study
the electron structure of Cs$_2$KAgF$_6$ and its spin state. By a
comparison of Figs. 3 and 2, we see that with inclusion of
the Hubbard’s interaction $U$ the Ag 4d states undergo some
changes, and the biggest effect is that the band gap is in-
creased from 0.5 eV by LSDA to 1.1 eV by LSDA+$U$. The
HS $S=1$ state remains, and the strong Ag-F covalency is re-
flected again by the occupied bonding state of the otherwise
empty down-spin $e_g$ orbital. It is the covalent electron occu-
pation of 0.48e $\times$ 2 (see Table II) that accounts for the actual
configuration $d^9\,L_6$ of the formal Ag$^{3+}$ ion which is a negative
charge transfer cation.[14].

The above HS magnetic state of the formal Ag$^{3+}$ ion seems
to be a straightforward result, but it is actually quite unusual as
4d transition metals are normally in a LS state and the Ag$^{3+}$
is indeed in the LS state for almost all known cases[13]. We
are thus motivated to check whether there exists another stable
structural phase for Cs$_2$KAgF$_6$ in which the normal LS state
could become a ground state. For this purpose, we have also
studied a tetragonal structure and carried out a structural op-
timization. A tetragonal distortion would yield an $e_g$ crystal-
field splitting, and if the splitting is big enough, the LS state
could become the ground state.

To explore the possibility of the LS ground state, we lower
the lattice symmetry to allow a local tetragonal distortion of
the AgF$_6$ octahedra. We first use the above cubic lattice
constants but optimize the internal atomic positions under a
tetragonal symmetry, by minimizing the atomic forces[27] till
each one being smaller than 25 meV/Å. After a full electronic
and atomic relaxation associated with the initialized LS setup
$d^9\,L_6(3z^2 - r^2)(x^2 - y^2)^0$ for the formal Ag$^{3+}$ ion, the LS so-
lution is indeed achieved. It is a local minimum of the energy
and has an elongated apical Ag-F bondlength of 2.25 Å and a
shrinking planar Ag-F bondlength of 1.96 Å (see Table I for the
tetragonal phase). Thus, the LS solution is stabilized by the
tetragonal distortion (0.29 Å, 2.25/1.96 = 1.15). Moreover, in
this tetragonally distorted structure, the corresponding HS
solution turns out to be less stable than the LS state by 441–
366 = 75 meV/fu, see Table II. However, the tetragonal LS
phase is 366 meV/fu higher in energy than the above cubic HS

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig2.png}
\caption{(color online) The density of states of Ag-4d and F-2p orbitals for the cubic phase of Cs$_2$KAgF$_6$ by LSDA.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig3.png}
\caption{(color online) The density of states of Ag-4d and F-2p orbitals for the cubic phase of Cs$_2$KAgF$_6$ by LSDA+$U$.}
\end{figure}
one. We further calculated a regular tetragonal structure with $c_0/a_0$ [i.e., $c/\sqrt{2}a_0$] $= 1.15$, see Table I for the ac-tetragonal structure which preserves the volume of the experimental cubic cell and the above tetragonal distortion. This ac-tetragonal LS phase turns out to be still higher in energy than the cubic HS phase by 336 meV/fu.

Now we carry out a volume optimization for both the cubic HS state and the ac-tetragonal LS state. The results are shown in Fig. 4. The equilibrium volume of the cubic HS state is about 11% smaller than the experimental one (i.e., within 4% underestimation of the lattice constant, within a few percent error bar of density-functional calculations). The equilibrium volume of the ac-tetragonal LS state is also 5% smaller than the experimental one. Note that the energy difference between the two equilibrium states, the cubic HS and the ac-tetragonal LS states, increases up to 750 meV/fu. This indicates that the cubic HS ground state is robust against the structural optimization. The metastable LS state is stabilized by the tetragonal distortion, which could be realized in a biaxial pressure experiment. The present bistable HS and LS solutions can also be understood by a pseudo Jahn-Teller mechanism for the $e_g^2$ system $^{28}$.

Before analyzing the reason why the cubic HS phase is the ground state, we now have a close look at the tetragonal phase either in the LS or HS state. In the tetragonal LS state, the degeneracies of both $e_g$ and $t_{2g}$ states are lifted, see Fig. 5. The threefold degenerate $t_{2g}$ states split into doubly degenerate ($d_{x^2-y^2}$,$d_{xy}$) states and singlet $d_{xy}$ state. Similarly, the twofold degenerate $e_g$ states split into nondegenerate $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ states. It is also an insulator with a small band gap of 0.1 eV, which lies between the occupied $p$ orbitals antibonding band of the $d_{3z^2-r^2}$ orbital and the unoccupied $p$ orbitals antibonding band of the $d_{x^2-y^2}$ orbital. The equal occupation of the spin-up and spin-down orbitals results in a nonmagnetic state without any exchange splitting, in accordance with the LS $S=0$ character. Note that the strong hybridization between Ag 4$d$ and planar-F/apyral-F 2$p$ orbitals is similar to that in cubic phase (see Table II), by which the Ag 4$d$ orbitals split into a series of narrow bonding and antibonding orbitals. Such electronic structure, with narrow-band and large bonding-antibonding splitting, is governed by the behavior of the isolated AgF$_6$ clusters. Generally speaking, the bonding-antibonding splitting of both $e_g$ orbitals is larger than that of $t_{2g}$ orbitals due to larger overlap between $e_g$ and $p$ orbitals. Furthermore, the bonding-antibonding splitting of $d_{x^2-y^2}$ orbital in the tetragonal phase is larger than that of $d_{3z^2-r^2}$ due to the shrinking planar Ag-F bond length. The $t_{2g}$ and $d_{3z^2-r^2}$ bands are fully occupied and the $d_{x^2-y^2}$ band is half occupied. Hence, the 4$d$ occupation of 9$e$ is one more electron than the nominal value for Ag$^{3+}$. This suggests the strong covalent nature of the Ag-F bonds, in contrast to the naive ionic picture.

For the spin-polarized HS state of the tetragonal phase (Fig. 6), the band splitting and Ag-F hybridization are similar to those in the LS state, but the occupation of $e_g$ orbitals has a remarkable change. While the up-spin $d_{2z^2-r^2}$ and $d_{3z^2-r^2}$ states are fully occupied, their down-spin counterparts are half occupied. The unequal occupation of the up-spin (5$e$) and down-spin (4$e$) states results in a considerable exchange splitting, reflecting a HS state character. Although the double degeneracy of $e_g$ orbitals is lifted by the tetragonal distortion, the electron configuration of $(d_{2z^2-r^2})^{10.5}$ and $(d_{3z^2-r^2})^{10.5}$ for down-spin is the same as that in cubic phase with $e_g$ degeneracy, indicating again the significant Ag-F covalency. A tiny band gap lies between the occupied $p$ orbitals antibonding band of the $d_{x^2-y^2}$ orbital and the unoccupied $p$ orbitals antibonding band of the $d_{3z^2-r^2}$ orbital.

Here we clarify the reason why the cubic HS phase is the lowest energy state, using the above total-energy results (see Table II). The 441 meV/fu increase of energy from the cubic HS phase to the tetragonal HS phase is attributed to the lattice
FIG. 6: (color online) The density of states of Ag-4d and planar/apical F-2p orbitals for the tetragonal HS phase of Cs$_2$KAgF$_6$ by LSDA+U.

elastic energy cost ($E_{el}$) associated with the tetragonal distortion, as the electronic configuration remains unchanged in both HS states and no crystal-field energy is involved. The energy difference of 75 meV/fu between the tetragonal HS and tetragonal LS (both in the same lattice) is due to the competition between the Hund exchange ($J_H$) and the crystal-field level splitting ($E_{CF}$) of the $e_g$ electrons, with $E_{CF}$ and $J_H$ being both about 1 eV and $E_{CF}$ slightly larger than $J_H$. Whether the cubic HS phase or the tetragonal LS one is the ground state depends on three competing contributions: $\Delta E = E$(tetragonal LS) – $E$(cubic HS) = $E_{el} + J_H - E_{CF}$. Taking $J_H - E_{CF} = -75$ meV/fu from above, the tetragonal LS phase could become the ground state ($\Delta E < 0$) only when the $E_{el}$ is lower than 75 meV/fu. However, here $E_{el}$ is up to 441 meV/fu. Therefore, the cubic HS phase is the ground state, and the large elastic energy cost in this compact double perovskite structure prevents the tetragonal distortion from yielding a large $E_{CF}$ to stabilize the LS state.

As seen in Figs. 5 and 6, in the tetragonal phase, the $e_g$ crystal-field splitting and the exchange splitting are quite close in size. This explains the small band gap present in both the LS and HS solutions. This also accords with the small energy difference of 75 meV/fu between the tetragonal HS and LS phases. As discussed above, three competing contributions get involved in determination of the ground spin-state solution: $\Delta E = E$(tetragonal LS) – $E$(cubic HS) = $E_{el} + J_H - E_{CF}$. Among them, the lattice elastic energy cost $E_{el}$ and the $e_g$ crystal-field splitting $E_{CF}$ are most influenced by the structural details, but the Hund exchange $J_H$ is almost a constant, being about 1 eV. Therefore, only a large $E_{CF}$ but a small $E_{el}$ would favor a tetragonal LS ground state. We thus conceive that such a situation could be met in an open structure, which can maintain a large Jahn-Teller distortion (and thus a large $E_{CF}$) but with a low $E_{el}$ cost. For example, in the well-known La$_2$CuO$_4$, there is a huge distortion (0.5 Å) of the Cu-O bonds, being 1.90 Å × 4 in plane and 2.40 Å × 2 out of plane[29]. This is due to a lattice strain effect in this layered material[30] and to the Cu-O bondlength adjustment for the $x^2-y^2$ type hole-orbital order driven by an anisotropic crystal field[31][32]. Upon a hole doping, the holes spread over the in-plane ligand oxygens and they hybridize with the central Cu$^{3+}$ $S=1/2$ to form a Zhang-Rice singlet[33] (the $d^9\uparrow\uparrow$ configuration with $S=0$ or a nominal LS Cu$^{3+}$ with two holes on $d_{x^2-y^2}$ orbital). It is the large $e_g$ crystal-field splitting but a small elastic energy cost which lead to the formation of the LS state upon hole doping. We can expect to have a similar situation in the layered 214 structure with Ag instead of Cu. However, in the compact perovskite structure of Cs$_2$KAgF$_6$, the tetragonal distortion cannot become as large as in the layered La$_2$CuO$_4$. As a result, here the LS state is disfavored, but the magnetic HS state of the Ag$^{3+}$ ion is the ground state.

IV. CONCLUSIONS

To summarize, using first-principles calculations, we find that the cubic double perovskite Cs$_2$KAgF$_6$ has a strong Ag-F covalency, and that the formal Ag$^{3+}$ ion has an unusual high-spin (HS) $S=1$ ground state. This is in sharp contrast to a common view that Ag$^{3+}$ always prefers a tetragonal or lower-symmetry coordination and a low-spin (LS) $S=0$ state. In calculations, we could also get the "normal" LS state, associated with a tetragonal distortion of 0.29 Å. However, the tetragonal LS state turns out to be energetically less favorable than the cubic HS state. We propose that these competing contributions tip the balance between the HS and LS states, which is formulated by the expression $\Delta E = E_{LS} - E_{HS} = E_{el} + J_H - E_{CF}$. As the compact perovskite structure of Cs$_2$KAgF$_6$ allows only a moderate tetragonal distortion (but with a large elastic energy cost $E_{el}$), a corresponding moderate crystal-field energy gain $E_{CF}$ in the tetragonal LS state cannot compensate for the $E_{el}$ and Hund’s exchange loss $J_H$ of the LS state. As a result, the cubic HS phase is the ground state. We thus conclude that Cs$_2$KAgF$_6$ is a rare case of the magnetic Ag$^{3+}$ ion, and suggest that the Ag$^{3+}$ LS nonmagnetic state can readily be formed in open structure materials such as layered systems.

V. ACKNOWLEDGMENTS

This work was supported by the NSF of China (Grant No. 11204309, U1230202), Anhui Province (Grant No. 1308085QA04), the special Funds for Major State Basic Research Project of China (973) under Grant No. 2012CB933702, Hefei Center for Physical Science and Technology under Grant No. 2012FXZY004, and the Director Grants of Hefei Institutes of Physical Science, Chinese Academy of Science (CAS). The calculations were performed in Center for Computational Science of CASHIPS and on the ScGrid of Supercomputing Center, Computer Network Information Center of CAS. H. Wu is supported by the NSF of
China (Grant No. 11274070), Pujiang Program of Shanghai (Grant No. 12PJ1401000), and ShuGuang Program of Shanghai (Grant No. 12SG06). D. Kh. is supported by the German Project FOR 1346 and by Cologne University via German Excellence Initiative.

[1] Yayu Wang, N. S. Rogado, R. J. Cava, and N. P. Ong, Nature (London) 423, 425 (2003).
[2] H. Hsu, P. Blaha, M. Cococcioni, and R. M. Wentzcovitch, Phys. Rev. Lett. 106, 118501 (2011).
[3] P. M. Raccah and J. B. Goodenough, Phys. Rev. 155, 932 (1967); J. Appl. Phys. 39, 1209 (1968); M. A. Senaris-Rodriguez and J. B. Goodenough, J. Solid State Chem. 116, 224 (1995).
[4] G. R. Zhang, E. Gorelov, E. Koch, and E. Pavarini, Phys. Rev. B 86, 184413 (2012).
[5] V. Krajcek, P. Novak, J. Kunes, D. Novoselov, Dm. M. Korotin, and V. I. Anisimov, Phys. Rev. B 86, 195104 (2012).
[6] T. Jia, H. Wu, G. R. Zhang, X. L. Zhang, Y. Guo, Z. Zeng, and H.-Q. Lin, Phys. Rev. B 83, 174433 (2011).
[7] J. P. Rueff, C. C. Kao, V. V. Struzhkin, J. Badro, J. Shu, R. J. Hemley, and H. K. Mao, Phys. Rev. Lett. 82, 3284 (1999).
[8] C. F. Chang, Z. Hu, T. Burnus, N. Hollmann, M. Benomar, T. Lorenz, A. Tanaka, H.-J. Lin, H. H. Hsieh, C. T. Chen, and L. H. Tjeng, Phys. Rev. Lett. 102, 116401 (2009).
[9] H. Wu, Z. Hu, T. Burnus, J. D. Denlinger, P. G. Khalifah, D. G. Mandrus, L.-Y. Jang, H. H. Hsieh, A. Tanaka, K. S. Liang, J. W. Allen, R. J. Cava, D. I. Khomskii, and L. H. Tjeng, Phys. Rev. Lett. 96, 256402 (2006).
[10] M. Itoh, M. Shikano, and T. Shimura, Phys. Rev. B 51, 16432 (1995).
[11] R. Hoppe and R. Homann, Naturwissenschaften 53, 501 (1966).
[12] W. Grochala and R. Hoffmann, Angew. Chem. Int. Ed. 40, 2742 (2001).
[13] H. Muller-Buschbaum, Z. Anorg. Allg. Chem. 630, 2125 (2004).
[14] These high-valent materials could well correspond to a negative charge transfer gap system [J. Zaanen, G. A. Sawatzky, and J. W. Allen, Phys. Rev. Lett. 55, 418 (1985)]. Therefore, their actual configuration is not so much Cu$^{3+}$ or Ag$^{3+}$, but rather Cu$^{2+}$ or Ag$^{2+}$, where $\mathbf{L}$ is a ligand hole. Usually this ligand hole forms a singlet state with the $S=1/2$ state of the central Cu$^{2+}$ or Ag$^{2+}$ ion (Zhang-Rice singlet in hole doped cuprates).

Then the quantum number of such state is the same as the LS $S=0$ state of Cu$^{3+}$ or Ag$^{3+}$.
[15] P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, and J. Luitz, Wien2k package, [http://www.wien2k.at]
[16] J. P. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992).
[17] V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B 44, 943 (1991).
[18] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys and A. P. Sutton, Phys. Rev. B 57, 1505 (1998).
[19] G. K. H. Madsen and P. Novak, Europhys. Lett. 69, 777 (2005).
[20] V. I. Anisimov, I. V. Solovyev, M. A. Korotin, M. T. Czyzyk and G. A. Sawatzky, Phys. Rev. B 48, 16929 (1993).
[21] R. Laskowski, P. Blaha, and K. Schwarz, Phys. Rev. B 67, 075102 (2003).
[22] D. Kasinathan, K. Koepernik, U. Nitzsche, and H. Rosner, Phys. Rev. Lett. 99, 247210 (2007).
[23] H. Wu and D. I. Khomskii, Phys. Rev. B 76, 155115 (2007).
[24] J. P. Perdew, M. Ernzerhof and E. Burke, J. Chem. Phys. 105, 9982 (1996); M. Ernzerhof, and G. E. Scuseria, J. Chem. Phys. 110, 5029 (1999).
[25] C. Adamo and V. Baronea, J. Chem. Phys. C 118, 7554 (2014).
[26] F. Tran, J. Kunes, P. Novak, P. Blaha, L. D. Marks, and K. Schwarz, Comp. Phys. Commun. 179, 784 (2008).
[27] P. Garcia-Fernandez and I. B. Bersuker, Phys. Rev. Lett. 106, 246406 (2011).
[28] J. M. Longo and P. M. Raccah, J. Solid State Chem. 6, 526 (1973).
[29] H. Wu and T. Burnus, Phys. Rev. B 80, 081105(R) (2009).
[30] H. Wu, C. F. Chang, O. Schumann, Z. Hu, J. C. Cezar, T. Burnus, N. Hollmann, N. B. Brookes, A. Tanaka, M. Braden, L. H. Tjeng, and D. I. Khomskii, Phys. Rev. B 84, 155126 (2011).
[31] P. Garcia-Fernandez, M. Moreno, and J. A. Aramburu, J. Phys. Chem. C 118, 7534 (2014).
[32] F. C. Zhang and T. M. Rice, Phys. Rev. B 37, 3759 (1988).