KAgF$_3$: quasi-one-dimensional magnetism in three-dimensional magnetic ion sublattice

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The electronic structure and magnetic properties of the Jahn-Teller-distorted perovskite KAgF$_3$ have been investigated using the full-potential linerized augmented plane-wave method. It is found that KAgF$_3$ exhibits significant quasi-one-dimensional antiferromagnetism with the ratio of exchange constant $|J_\perp|$ (perpendicular to the $z$ axis) and $J$ (along the $z$ axis) about 0.04, although the sublattice of magnetic ion is three-dimensional. The strong quasi-one-dimensional antiferromagnetism originates from the $C$-antiferro-distortive orbital ordering of the Ag$^{2+}$ 4$d^9$ ions. The orbital ordered antiferromagnetic insulating state in KAgF$_3$ is determined by on-site Coulomb repulsion to a large extent.

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I. INTRODUCTION

Low-dimensional magnets have unique electronic and magnetic properties. For example, the physical properties of quasi-two-dimensional (2D) high-temperature superconductor $^{1,2}$, spin-Peierls compound $^{3}$, Haldane chain $^{4}$ and spin-ladder $^{5}$ as well as spin-frustrated systems $^{6,7}$ have been extensively investigated. In most of the low-dimensional magnets, the magnetic cation sublattices consist of planes or chains which are kept reasonably far apart. Materials which exhibit three-dimensional (3D) magnetic ion sublattice and low-dimensional magnetic behavior have been of interest to both experimentalist and theorists $^{8-12}$. Up to date, the electronic orbital ordering (OO) is considered as an essential factor in determining the strong spacial exchange anisotropy in these materials.

KAgF$_3$ is a material which exhibit strong spacial exchange anisotropy within 3D magnetic Ag$^{2+}$ ion sublattice $^{13}$. It was first synthesized in 1971 by Odenthal et al $^{14}$ and received, as well as other silver fluorides, attention due to the pursuit of superconductivity $^{15-17}$ in transition-metal compounds other than the cuprates. Previous experimental studies $^{13,17}$ have provided the evidence of its antiferromagnetism with $T_N=64$ K as well as the insulating characteristic below this temperature. In contrast to the undoped cuprates that are quasi-2D antiferromagnetic (AFM) insulator, KAgF$_3$ was reported as a quasi-one-dimensional (1D) antiferromagnet using LSDA+U method $^{13}$. However, more efforts are still needed to well understand the origin of the quasi-1D antiferromagnetism.

In the present work, we investigate the electronic structure and the magnetic properties of KAgF$_3$ using density functional theory (DFT). The calculated $J_\perp / |J| = 0.04$ confirms that the compound is a quasi-1D antiferromagnet. Here, $J$ ($J_\perp$) refers to exchange constant along (perpendicular to) the $z$ axis. The quasi-1D antiferromagnetism can be understood by the C-antiferro-distortive OO which can be obtained in the presence of on-site Coulomb repulsion $U$. The picture of OO and AFM insulating state is thus very similar to that of an isoelectronic and isostructural compound, KCuF$_3$.

II. CALCULATION METHODS

Our electronic structure calculations are performed within the full-potential linearized augmented plane-wave framework $^{18}$. The generalized gradient approximation (GGA) of
Perdew-Burke-Ernzerhof form is adopted. To include the on site Coulomb interaction GGA+$U$ ($U=$on-site Coulomb repulsion strength) approach is used with $U_{\text{eff}}=U-J$ ($J$ is the exchange interaction) instead of $U$. Here in our work, on-site Coulomb repulsion $U$ is applied to Ag 4$d$ orbitals only. The Muffin-tin sphere radii are chosen to be 2.24, 2.09, and 1.85 bohr for K, Ag, and F atoms, respectively. Within the Muffin-tin sphere the electrons behave as they were in the free atom, and the wave functions are expanded using radial functions (solutions to the radial part of Schröinger equation) times spherical harmonics. Out of the Muffin-tin spheres wave functions are expanded using plane waves. The value of $R_{MT} K_{\text{max}}$ (the smallest muffin-tin radius multiplied by the maximum $k$ value in the expansion of plane waves in the basis set) is set to 7.0. We use 500 $k$ points (i.e., 192 $k$ points in the irreducible wedge of the Brillouin zone) for the integration over the Brillouin zone. Self-consistency was considered to be achieved when the total energy difference between succeeding iterations is less than $10^{-5}$ Ry/unit cell. The present setup ensures a sufficient accuracy of the calculations.

In our study, we carry out total energy calculations with three distinct spin states of (1) ferromagnetic (FM), (2) A-AFM (ferromagnetism in $xy$ plane, AFM stacking), and (3) G-AFM (antiferromagnetism in $xy$ plane, AFM stacking).

### III. RESULTS AND DISCUSSIONS

The calculations were performed for orthorhombic structure proposed by Mazej et al., space group $Pnma$ (No.62), with the lattice constants $a=6.2689$ Å, $b=8.3015$ Å, $c=6.1844$ Å (see Fig. 1). In our calculations we use for each AgF$_6$ octahedron such corresponding local $xyz$ coordinates that the $z$ axis is along the $b$ axis and the $x$ and $y$ axes are approximately along the inplane nearest neighbor Ag-Ag directions. In KAgF$_3$, the Ag ion sublattice forms a pseudocubic structure, in which Ag-Ag distance along $z$ direction is slightly shorter than that in the $xy$ plane. There are two types of F sites. One connects the Ag ions along the $z$-axis (named as F$_{ap}$) and the other connects the Ag ions in the $xy$ plane (named as F$_{pl}$). The AgF$_4$ planes are slightly puckered since the F$_{pl}$ ions have a 0.31 Å displacement from the plane formed by Ag ions. Each Ag and its six near F ions form a Jahn-Teller (JT) distorted AgF$_6$ octahedron. The distortion leads to the alternating long and short Ag-F bonds along the $x$ and $y$ axes. The four shorter Ag-F bonds are almost identical. The
cooperative JT distortion provides a signature of an orbital ordering (OO) at the Ag$^{2+}$ sites, which determines the electronic structure as well as the magnetic properties.

In order to clarify the electronic structure and the origin of the quasi-1D magnetism in KAgF$_3$, our calculations are designed in two stages. We start the study within GGA. To account for a possible lattice distortion, we carried out an optimization of the atomic positions, keeping the unit-cell parameters fixed and relaxing the atomic coordinates. The structural optimization shows that the Ag-F$_{ap}$ bond is elongated by 0.012 Å and the in-plane longer (shorter) Ag-F$_{pl}$ bond is shortened (elongated) by 0.085 Å (0.038 Å) as compared with the experimentally observed structure. As a result, the large in-plane distortion of about 0.3 Å found experimentally, decreases to 0.2 Å theoretically. Moreover, the GGA results for the optimized structure show that the FM, A-AFM and G-AFM spin states are not stable and converge to nonmagnetic (NM) metallic solution. Fig. 2 shows the total and the orbital-resolved density of states (DOS) for the NM KAgF$_3$. The distortive AgF$_6$ octahedron crystal field splits the Ag$^{2+}$ 4$d^9$ orbitals into fully occupied $t_{2g}$ ($xz$, $xy$, $yz$) and three fourth occupied $e_g$ ($z^2-y^2$, $3x^2-r^2$) orbitals. Both the anti-bonding Ag $d_{z^2-r^2}$ and $d_{3x^2-r^2}$ bands cross the Fermi level with large band widths of about 3 eV and have strong covalency with the F orbitals. The band center of the $d_{z^2-r^2}$ is higher in energy than that of $d_{3y^2-r^2}$ orbital. Thus, the JT distortion generates a crystal-field splitting which is not large enough to separate the two $e_g$ bands. Even the GGA calculations for the experimental structure still give a NM metallic solution for all the enforced spin states, in accordance with the previously published work. Unlike the electronic structure of GGA optimized structure with two type of $e_g$ bands crossing the Fermi level, the distortion alone separates the $e_g$ bands with only one of them cross the Fermi level (not shown). Therefore, the GGA calculations can not reproduce the insulating AFM nature of KAgF$_3$. This is in contrast to another fluoroargentate Cs$_2$AgF$_4$ in which JT distortion alone can lead to the orbital ordered insulating state.

As the second stage, we concern the correlation interaction by GGA+$U$ approach. In general, strong on-site Coulomb repulsion $U$ increases the localization of $d$ electrons and favors orbital ordering and/or magnetic order. However, the magnitude of the correlation for the Ag$^{2+}$ ion is not known. In order to determine its value, we performed a structural optimization as a function of $U$ (1-6 eV) and found the $U$ value with which the equilibrium structure matches the experimental one. This scheme to extract the Coulomb parameter is
feasible because the on-site Coulomb repulsion \( U \) determines the orbital polarization of the \( e_g \) states for a large extent, which, in turn, causes the structural JT lattice distortion. The optimized inequivalent Ag-F distances \( d_1, d_2 \) and \( d_3 \) are shown in Fig. 3. We find that the optimized structure for \( U=5.0 \) eV is the closest to the one obtained experimentally. And thus this \( U \) is adopted as the most reliable one. This value is smaller than the commonly used \( U=7-9 \) eV value for Cu\(^{2+}\) but still reasonable, because the 4\( d \) orbitals of an Ag\(^{2+}\) ion are less contracted than the 3\( d \) orbitals of a Cu\(^{2+}\) ion.

The GGA+\( U \) (5 eV) total energy calculations of various spin states shown in table I indicate that the ground spin state is the \( A \)-AFM insulating state. The obtained ground spin state is in accordance with the previous LSDA+U results.\(^{13} \) This indicates that the on-site Coulomb repulsion is important in determining the AFM insulating properties in KAgF\(_3\). We note that the difference in total energy between the \( A \)-AFM and \( G \)-AFM spin states is as small as 23 meV/4f.u., while the energy difference between the \( A \)-AFM and FM spin states is about 272 meV/4f.u. We should notice the fact that \( A \)-AFM and \( G \)-AFM spin states have opposite ordering in the \( xy \) plane but the same ordering along the \( z \) direction, whereas both the \( A \)-AFM and FM spin states have the same ordering in the \( xy \) plane but different ordering along the \( z \) axis. This reveals that AFM exchange interactions along the \( z \) direction are more favorable and robust than FM coupling in the \( xy \) plane, indicating a strong spacial exchange anisotropy in KAgF\(_3\).

To gain additional insight into the spacial exchange anisotropy, we evaluate the magnetic exchange constants along and perpendicular to the \( z \) axis numerically in terms of the Heisenberg spin Hamiltonian:

\[
H = J \sum_{i,j} \mathbf{S}_i \cdot \mathbf{S}_j + J_\perp \sum_{k,l} \mathbf{S}_k \cdot \mathbf{S}_l \tag{1}
\]

where the first (second) term refers to summing over all nearest neighbors along (perpendicular to) the \( z \) axis. By mapping the obtained total energies for each magnetic state to the next nearest Heisenberg model, the exchange interactions \( J \) and \( J_\perp \) are

\[
J = \frac{1}{8S^2}(E_{FM} - E_{A-AFM}) \tag{2}
\]

\[
J_\perp = \frac{1}{16S^2}(E_{A-AFM} - E_{G-AFM}) \tag{3}
\]

With the spin \( S=1/2 \) of a 4\( d^9 \) Ag\(^{2+}\) ion, we get \( J=136 \) meV and \( J_\perp=-5.8 \) meV, indicating strong AFM coupling along the \( z \) axis and a much weaker FM coupling in the \( xy \) plane.
\(|J_\perp|/J=0.04\) reflects strong quasi-1D magnetism in KAgF\(_3\). Thus, it has been concluded that KAgF\(_3\) is another material exhibiting quasi-1D magnetic behavior within 3D magnetic ions sublattice, which is in accordance with the results of Mazej et al.\(^{13}\) The relatively large \(J\) and \(J_\perp\) values are consistent with the findings that the DFT electronic structure calculations generally overestimate the magnitude of spin exchange interactions.\(^{24}\)

The quasi-1D magnetic behavior can be understood from the ground state electronic structure and OO of KAgF\(_3\). The total and the orbital-resolved DOS for the \(A\)-AFM spin state experimental structure are shown in Fig. 4. The Coulomb repulsion \(U\) pushes the occupied and unoccupied 4\(d\) levels downward and upward respectively and opens up an insulating gap. It is obvious that the one hole states mainly occupy the higher level \(d_{z^2-y^2}\) bands and the orbital polarization of \(e_g\) states is enhanced. Actually, due to the strong Ag-F covalency\(^{16}\) the one hole spreads over the six fluorine atoms of the AgF\(_6\) octahedron. This is also reflected by the magnitude of local spin magnetic moments within each muffin-tin sphere, \(\pm 0.62 \ \mu_B/\text{Ag, } 0\mu_B/\text{F}_{ap}\) and \(\pm 0.09\mu_B/\text{F}_{pl}\) (see table I). The hole states have alternating \(d_{z^2-y^2}\) and \(d_{z^2-x^2}\) symmetry for Ag\(^{2+}\) ions in the xy plane (see the last panel in Fig. 5) because of the cooperative JT distortion. The in-plane \(d_{z^2-x^2}/d_{z^2-y^2}\) OO repeats along the \(z\)-axis and \(C\)-antiferro-distortive OO is formed, which is clearly shown in Fig. 5. The overlap of Ag-F-Ag along the \(z\)-axis (see the upper and middle panel in Fig. 5) is larger than that in the xy plane (the lower panel in Fig. 5) leading to the dominate magnetic interaction along \(z\)-axis. The \(C\)-antiferro-distortive OO would immediately give \(A\)-AFM spin state, according to Goodenough-Kanamori-Anderson rules. Also, our GGA+\(U\) calculation results confirm this mechanism since it shows that the \(A\)-AFM state is indeed more stable than the \(G\)-AFM and FM states (see Table I). Therefore, the results of our calculations have clearly illustrated that KAgF\(_3\) is an orbitally ordered quasi-1D AFM insulator, in close analogy to KCuF\(_3\).

**IV. CONCLUSIONS**

By GGA and GGA+\(U\) electronic structure calculations, we have found the quasi-one-dimensional (1D) antiferromagnetism of KAgF\(_3\) with \(|J_\perp|/J|=0.04\), which may stimulate further experimental studies. Here, \(J\) (\(J_\perp\)) refers to exchange constant along (perpendicular to) the \(z\) axis. The quasi-1D antiferromagnetism can be understood by the \(C\)-antiferro-
distortive orbital ordering. The orbital ordered insulating state can only be obtained when the on-site Coulomb repulsion of Ag 4d electrons is in consideration. With $U=5$ eV for Ag 4d electrons the optimized structure is in the best agreement with experiment. The picture of orbital ordering and AFM insulating state is thus very similar to that of an isoelectronic and isostructural compound, KCuF$_3$.

V. ACKNOWLEDGMENTS

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FIG. 1: (color online) Crystal structure of KAgF$_3$. The blue, gray and yellow spheres represent K, Ag and F atoms, respectively.

FIG. 2: (color online). The total and partial DOS of GGA optimized structure for nonmagnetic state obtained in GGA. The Fermi level is set at zero energy.

FIG. 3: (color online). Deviation of relaxed inequivalent Ag-F distances $d_1$, $d_2$ and $d_3$ from the experiment as a function of the Coulomb repulsion $U$. The data of $U=0$ denotes the GGA optimized results.

FIG. 4: (color online). The total and partial DOS of KAgF$_3$ for A-AFM spin state from GGA+$U$ with $U=5$ eV. The up and down panels in each DOS plot denote the spin-up and spin-down states respectively.

FIG. 5: (color online). The contour plot of spin density in $xz$ (upper panel), $yz$ (middle panel) and $xy$ (lower panel) planes of KAgF$_3$ for A-AFM state from GGA+$U$ (5 eV). The solid (dot) lines depict the spin-up (spin-down) states.

TABLE I: Electronic structure of KAgF$_3$ in FM, A-AFM and G-AFM spin states obtained by GGA+$U$ with $U=5$ eV. The total energy difference ($\Delta E$, meV/4f.u.), the energy gap ($E_g$, eV), the local spin moment ($SM$, $\mu_B$) of each Ag, apical F ($F_{ap}$), and planar F ($F_{pl}$) atoms are shown.

|      | $\Delta E$ | $E_g$ | Ag-$SM$ | $F_{ap}$-$SM$ | $F_{pl}$-$SM$ |
|------|------------|-------|---------|---------------|---------------|
| FM   | 272        | 0.5   | 0.67    | 0.12          | 0.1           |
| A-AFM| 0          | 1.5   | $\pm 0.62$ | 0             | $\pm 0.09$    |
| G-AFM| 23         | 1.4   | $\pm 0.6$  | 0             | $\pm 0.09$    |
Fig. 1 Zhang.eps
Fig. 2: Zhang.png

The figure shows the density of states (DOS) for different orbitals of KAgF₃, Ag e₉, Ag t₂g, F 2p, F⁻ 2p, and F⁻ pl 2p. The energy is plotted on the x-axis, ranging from -6 to 4 eV, and the DOS is plotted on the y-axis, ranging from 0 to 20 states/eV. The orbitals are labeled and their corresponding energy levels are indicated.

- KAgF₃
- 3x²−r²
- Ag e₉
- z²−y²
- Ag t₂g
- F 2p
- F⁻ 2p
- F⁻ pl 2p
Fig. 3 Zhang.eps
Fig. 4 Zhang.ep
Fig. 5 Zhang.eps