

Structural transition and unusually strong antiferromagnetic superexchange coupling in perovskite KAgF_3 †‡

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High-purity samples of potassium trifluoroargentate(II), KAgF_3 , have been obtained via a novel synthetic pathway. This compound is found to exhibit an order–disorder phase transition around 230 K. Susceptibility measurements indicate that KAgF_3 exhibits strong antiferromagnetic (AFM) coupling reminiscent of that found in copper(II) oxides.

Silver(II) fluorides (compounds containing the spin- $\frac{1}{2}$ Ag^{2+} cation and F^- anion) are charge-transfer insulators that bear many similarities^{1,2} to copper(II) oxides – precursors of a rich family of high temperature superconductors (HTSCs). Recently it has been suggested that a new class HTSCs, based on silver(II) fluorides, might also be attainable.^{1,3} The 2D antiferromagnetic ordering seems to be a prerequisite for obtaining high superconducting temperatures upon chemical doping; however, experimental studies for the layered silver(II) fluoride, Cs_2AgF_4 , provided evidence for weak 2D ferromagnetic rather than strong antiferromagnetic ordering,⁴ which was attributed to orbital ordering originating from lattice distortions.^{4,5}

Divalent silver has a tendency towards disproportionation into Ag(I) and Ag(III) , as exemplified by AgO ($=\text{Ag}^{\text{I}}\text{Ag}^{\text{III}}\text{O}_2$). This links silver(II) compounds with such mixed-valence compounds as BaBiO_3 ($=\text{Ba}_2\text{Bi}^{\text{III}}\text{Bi}^{\text{V}}\text{O}_6$), which exhibits superconductivity upon doping,⁶ and the recently theorized superconductors based on CsTiX_3 compounds ($=\text{Cs}_2\text{Ti}^{\text{I}}\text{Ti}^{\text{III}}\text{X}_6$, $\text{X} = \text{F}, \text{Cl}$).⁷

In this context we have decided to investigate the structural and magnetic properties of potassium trifluoroargentate(II),

KAgF_3 , which, similar to BaBiO_3 , adopts a deformed perovskite structure.⁸ This communication describes the results of temperature resolved X-ray powder diffraction (XRPD) and magnetic susceptibility measurements of KAgF_3 . It was found that this compound undergoes an order–disorder structural phase transition around 230 K. Susceptibility data indicate that both phases of KAgF_3 exhibit strong 1D AFM interactions.

Silver(II) fluorides readily react with air and water. Therefore these compounds cannot be obtained via standard synthetic methods. KAgF_3 can be synthesized by a direct reaction of AgF_2 and KF , but the final product is contaminated with large amounts of paramagnetic impurities.⁹ A high-purity sample of KAgF_3 has been obtained by using a novel synthetic pathway, proceeding via thermal decomposition of KAgF_4 , an Ag(III) compound (Scheme 1). Performing this reaction under dynamic vacuum for six days led to the formation of brown KAgF_3 , contaminated with only traces of diamagnetic AgF (6.0 mol%), as shown by analysis of XRPD data (ESI†). A similar approach has been successfully employed in the synthesis of high-purity Na_2AgF_4 ¹⁰ and could also constitute a viable route for the synthesis of the yet unknown CsTiF_3 and CsTiCl_3 .

We have performed temperature resolved XRPD measurements of KAgF_3 at temperatures between 80 K and 330 K. The structure obtained by the Rietveld refinement of the 80 K diffractogram is in very good agreement with previously published room temperature data⁸ and our calculations based on the Density Functional Theory with the inclusion of on-site Coulomb repulsion (DFT + U, see ESI†). At 80 K KAgF_3 crystallizes with a perovskite-type structure (GdFeO_3 -type structure, $Pnma$ symmetry) in which edge sharing $[\text{AgF}_6]^{4-}$ octahedra are tilted about all three cell vectors (Fig. 1). These units are subject to axial elongation due to operation of the Jahn–Teller effect. The elongated octahedra are arranged in an antiferrodistortive pattern within the ac plane which leads to formation of $[\text{AgF}_{2+2/2}]^-$ chains which run along the b cell vector. These chains can be described as built from $[\text{AgF}_4]^{2-}$ plaquettes sharing two opposite vertices.

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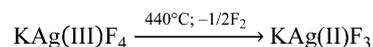
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† This work is dedicated to John B. Goodenough on the occasion of his 90th birthday.

‡ Electronic supplementary information (ESI) available: KAgF_4 synthesis, XRPD, and DFT + U calculations. See DOI: 10.1039/c3cc41521j



Scheme 1 Synthesis of KAgF_3 .

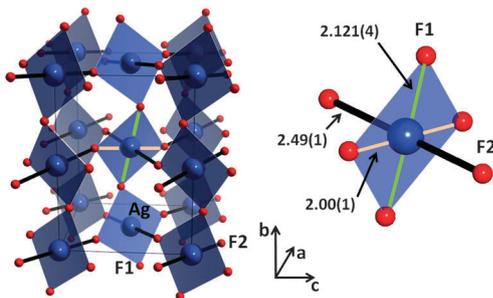


Fig. 1 View of the *Pnma* structure of KAgF_3 (K atoms are omitted for clarity) and the $[\text{AgF}_6]^{4-}$ octahedra. Bond lengths at 80 K are given in Å.

Upon heating KAgF_3 undergoes a phase transition between 225 K and 235 K, as can be seen by the temperature dependence of the cell vectors of the *Pnma* model of KAgF_3 (Fig. 2a). Although above 235 K the XRDP pattern can still be reasonably described by the *Pnma* model, the (111) and (212) reflexes disappear in this temperature region (ESI†). This indicates a transition to a structure with a b' cell vector twice as small as the b cell vector of *Pnma*. In fact a model of the *Pcma* symmetry (non-standard setting of the *Pbam* space group) with $b' \approx b/2$ (Fig. 2a) gives a better description of the XRDP pattern for $T > 235$ K, as evidenced by lower χ^2 values (ESI†).

The *Pcma* model, shown in Fig. 2b, can be derived from *Pnma* by introducing disorder in the tilting of $[\text{AgF}_4]^{2-}$ units about the a and c vectors. This results in half occupation of the 8i positions of F2 atoms and the 4h positions of F1/K atoms (Table 1). We note that the *Pcma* model does not yield a stable fit of the XRDP patterns below 225 K.

The obtained data clearly indicate that KAgF_3 adopts the disordered *Pcma* structure at room temperature, and not *Pnma* as reported earlier.⁸ It is noteworthy to point out that attempts to fit the XRDP patterns by a $P2_1/n$ model of KAgF_3 containing Ag(I) and Ag(III) sites (isostructural with the low temperature phase of BaBiO_3 ¹¹) did not yield a reliable geometry of these centres.

The essential features of the $[\text{AgF}_{2+2/2}]^-$ chains (*i.e.* the Ag–F bond lengths and ordering of the Jahn–Teller effect) are preserved upon the structural phase transition. Predictions based on the Goodenough–Kanamori–Anderson rules¹² indicate that superexchange interactions between neighbouring Ag^{2+} centres along these chains should be strong and antiferromagnetic. In contrast, inter-chain superexchange should be weakly ferromagnetic. Indeed, previous calculations performed for the *Pnma* structure show that it

Table 1 Structural details of the *Pnma* and *Pcma* polymorphs of KAgF_3 at 80 K and 298 K, respectively

	x	y	z	U_{iso}^a (Å ²)	occ.
<i>Pnma</i> ($T = 80$ K)					
Unit cell (Å): $a = 6.3815(9)$, $b = 8.254(1)$, $c = 6.0581(8)$					
Ag	0	0	0	0.0026(8)	1
K	0.0529(9)	0.25	0.486(2)	0.0026(8)	1
F1	0.483(4)	0.25	0.579(2)	0.003(3)	1
F2	0.317(2)	0.469(2)	0.236(2)	0.003(3)	1
<i>Pcma</i> ($T = 298$ K)					
Unit cell (Å): $a = 6.2685(6)$, $b = 4.1522(3)$, $c = 6.1828(5)$					
Ag	0	0	0	0.0080(6)	1
K	0.018(2)	0.5	0.528(1)	0.0080(6)	0.5
F1	0.931(2)	0.5	0.022(5)	0.016(3)	0.5
F2	0.311(1)	0.076(2)	0.235(2)	0.016(3)	0.5

^a Applied restraints: $U_{\text{iso}}(\text{Ag}) = U_{\text{iso}}(\text{K})$, $U_{\text{iso}}(\text{F1}) = U_{\text{iso}}(\text{F2})$.

can be described as a quasi-1D antiferromagnet with an intra-chain coupling constant (J)† equal to -125 meV¹³ – a value comparable to those exhibited by undoped copper(II) oxides, and surpassing those found for iron pnictides.

In order to experimentally verify the nature of magnetic interactions in KAgF_3 , temperature resolved measurements of the magnetic susceptibility of a powdered sample of this compound were conducted.‡ Previous studies reported conflicting values of the magnetic ordering temperature (68 K¹⁴ and 80 K¹⁵), as well as a nearly constant susceptibility at higher temperatures.^{14,15} In our measurements a much more complex dependence is found (Fig. 2c). The sudden increase in χ at 35 K and 66 K can be attributed to magnetic impurities present in the sample in concentrations not detectable in the XRDP experiment.¹⁶ It is also possible that the feature at 66 K is a result of spin-canted AFM ordering of KAgF_3 , as proposed earlier.¹⁴

Particularly interesting is the variation of the molar susceptibility of KAgF_3 at high temperatures. A nearly constant decrease in χ with decreasing temperature is observed in the 250–300 K region. This feature points to the presence of a short-range AFM order in KAgF_3 under these conditions. This is in accordance with above-mentioned DFT + U predictions which suggest that strong AFM interactions should persist at room temperature and well above (recall, 125 meV is equivalent of about 1400 K). In fact the magnetic susceptibility in this temperature region can be fitted with a model of a spin- $\frac{1}{2}$ uniform antiferromagnetic Heisenberg chain¹⁷ yielding a coupling constant of -97 meV (ESI†). This suggests that even in the structurally disordered *Pcma* phase KAgF_3 exhibits strong 1D AFM

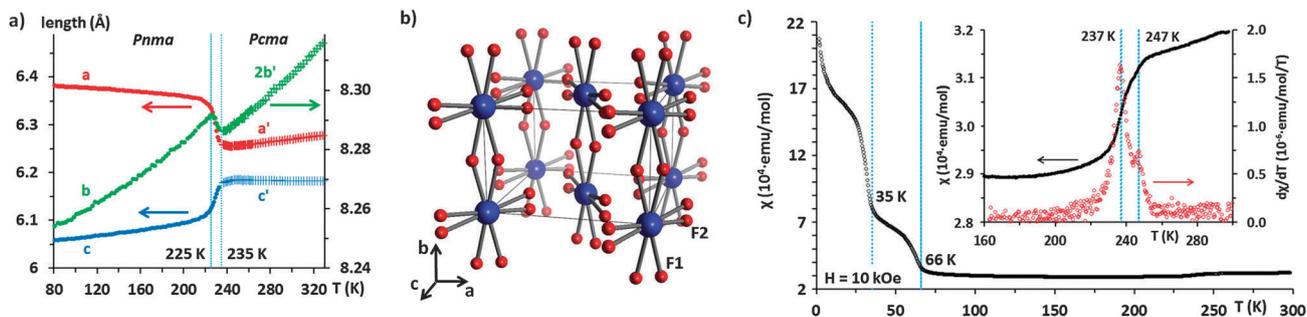


Fig. 2 Temperature dependence of the cell vectors of KAgF_3 (a), dots/crosses mark values obtained for the *Pnma*/*Pcma* model; view of the disordered *Pcma* structure (b), K atoms omitted for clarity; molar susceptibility (χ) of a powdered sample of KAgF_3 (c); the inset shows the high-temperature dependence of $\chi(T)$ and $d(\chi)/dT$ (black/red points, respectively).

interactions within the $[\text{AgF}_{2+2/2}]^-$ chains. This makes KAgF_3 similar to BaFe_2Se_3 – a 1D system in which strong AFM interactions also lead to decrease in χ with decreasing temperature.¹⁸

In the 230–250 K temperature range, corresponding to the $Pnma$ – $Pcma$ phase transition,¹⁹ a sudden change in χ is observed (inset of Fig. 2c). This feature can be explained in two ways: (i) KAgF_3 enters a metallic state below 250 K, or (ii) structural ordering in the $Pnma$ phase leads to enhancement of spin–spin interactions. The former scenario seems improbable as the $Pnma$ polymorph of KAgF_3 is predicted to be an orbital-ordered insulator with a band gap of 1.5 eV.¹³ We thus conclude that decrease in the magnetic susceptibility is a result of stronger AFM interactions originating from the ordering of tilts of $[\text{AgF}_6]^{4-}$ octahedra.

An analysis of the temperature derivative of χ in the 230–250 K region (inset of Fig. 2c) indicates that in fact two anomalies can be observed (at 237 K and 247 K). This situation resembles the one found in LaFeAsO where similar anomalies in the magnetic susceptibility can be attributed to structural and magnetic phase transitions, separated by just 18 K.²⁰ In the case of KAgF_3 one might speculate that the 237 K anomaly (characterized by a higher $d\chi/dT$ value) originates from the antiferromagnetic ordering, while the one at 247 K is a result of the $Pnma$ – $Pcma$ phase transition.¹⁹ However, more experiments are needed to verify this hypothesis.

In conclusion, adopting a new synthetic approach we were able to synthesize high-purity samples of $\text{KAg}(\text{II})\text{F}_3$. This method might be employed in the future for synthesis of other fluoride and chloride systems not attainable *via* standard procedures. We have reported for the first time the structural phase transition of KAgF_3 in which disorder appears in the tilting of $[\text{AgF}_6]^{4-}$ octahedra. Powder susceptibility measurements show large variations in magnetic susceptibility at this phase transition indicating that magnetism and structure are intimately coupled in KAgF_3 , similar to what is found in iron pnictides. The magnetic data presented here are the first experimental evidence of strong superexchange interactions in the spin- $\frac{1}{2}$ KAgF_3 system. Our analysis indicates that the coupling constant for the $Pcma$ phase is of an order of -100 meV. This indicates that considerably stronger interactions take place between Ag^{2+} centres along the $[\text{AgF}_{2+2/2}]^-$ infinite chain than between the $\text{Cu}(\text{II})$ centres for the related $\text{KCu}(\text{II})\text{F}_3$, which is a 1D antiferromagnet with a J value of -35 meV.²¹ Our finding suggests that fluoroargentates(II) indeed have the potential to become precursors of a new family of high-temperature superconductors which could benefit from enhancement of the critical superconducting temperature due to magnetic fluctuations, provided a 2D AFM precursor could be found. Although in our study we do not find proof for KAgF_3 entering the mixed-valent state ($\text{K}_2\text{Ag}^{(\text{I})}\text{Ag}^{(\text{III})}\text{F}_6$) such a transition might be attainable under different conditions (*e.g.* at high pressure).

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Notes and references

§ Temperature resolved XRDP measurement were conducted on a diffractometer equipped with a rotating Mo anode and a 2D MAR345 detector. Scans from a 0.3 mm quartz capillary filled with KAgF_3 were collected upon heating from 80 K to 330 K with 20 K h^{-1} rate (10 K h^{-1} in the range 220–265 K). The 2D images were integrated into 1D patterns with FIT2D²² and analysed in FullProf.²³ It was found that above 330 K a reaction between the quartz capillary and KAgF_3 commences. The temperature dependence of the magnetic susceptibility was measured using a superconducting quantum interference device magnetometer (MPMS SQUID VSM, Quantum Design). The measurement range spanned from 1.8 K to 300 K with a heating rate of 90 K h^{-1} . The obtained data was corrected for inner-shell diamagnetism of KAgF_3 and AgF electrons as well as contribution from the sample holder.

¶ Defined by the Hamiltonian $H_{ij} = -J_{ij} S_i \cdot S_j$.

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