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Supplementary Information

Structural Transition and Unusually Strong Antiferromagnetic Superexchange Coupling in Perovskite $KAgF_3$

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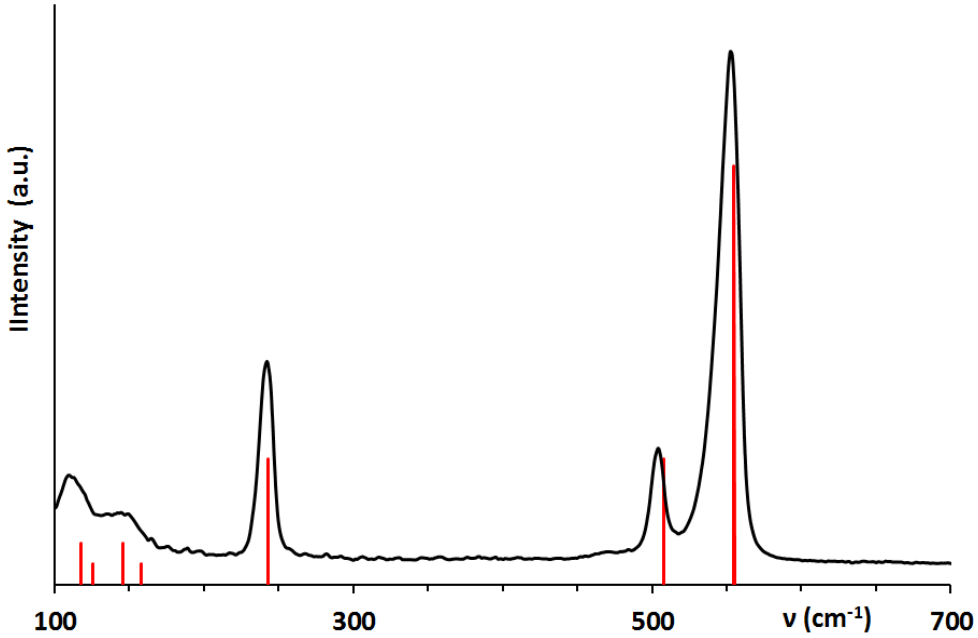
1. Details of $KAgF_4$ synthesis

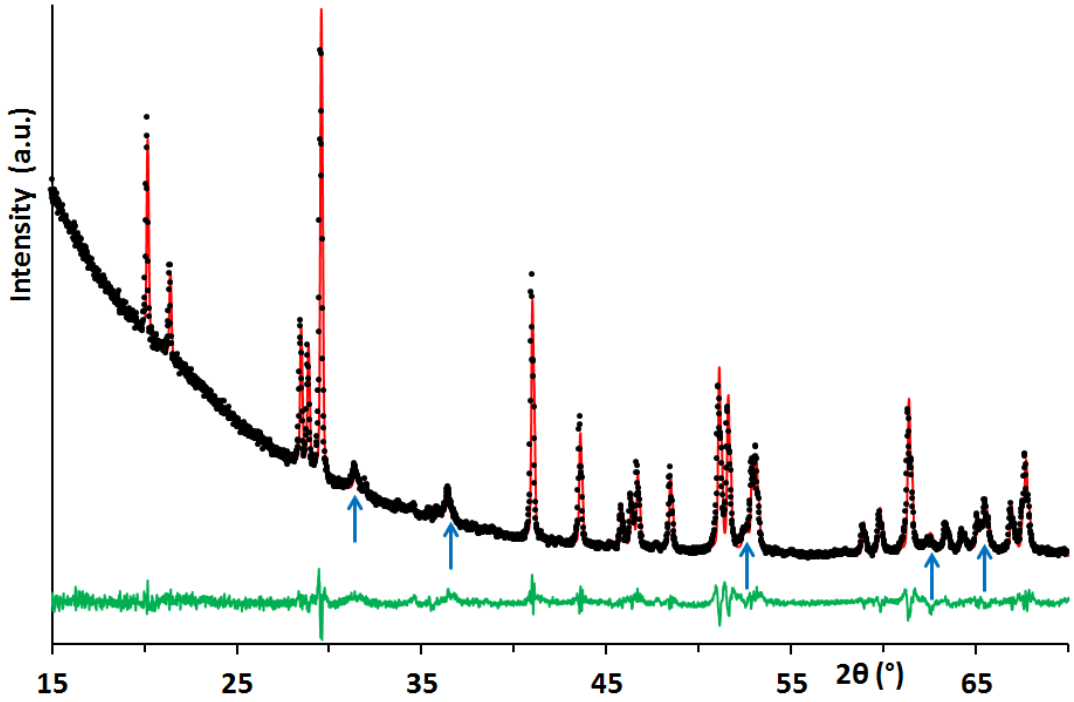


$KAgF_4$ has been synthesized by fluorinating an equimolar mixture of KF and AgF_2 with 2000 Torr of F_2. The reagents were placed in a nickel reactor connected to a nickel-Teflon® vacuum line. The reaction was conducted for four days at 300°C.

Raman scattering of the obtained product (black line) has been recorded using a high-resolution spectrometer (LabRAM, Horiba Jobin-Yvon) at the 632.81 nm excitation line of He-Ne laser. The resulting spectra is in good accordance with previous data for $KAgF_4$[1] (red bars).

[1] K. Lutar, S. Milicev, B. Žemva, B. G. Müller, G. Bachmann, R. Hoppe, *Eur. J. Solid State Inorg. Chem.* 1991, **28**, 1335.

2. Room temperature x-ray powder diffraction pattern of $KAgF_3$

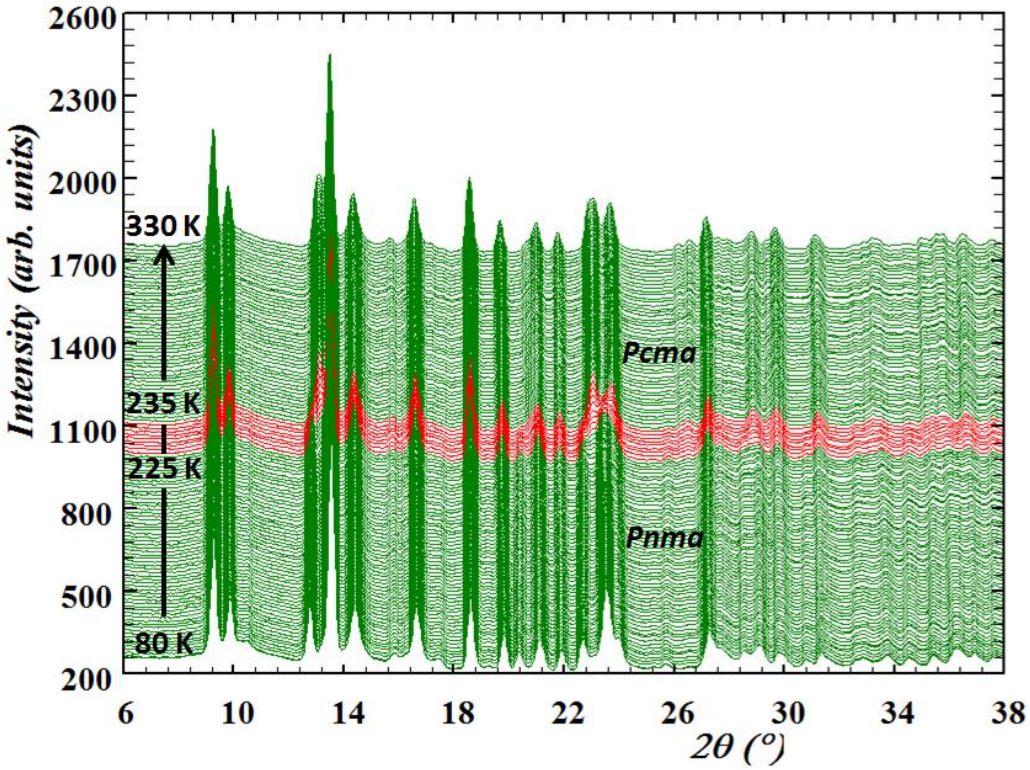


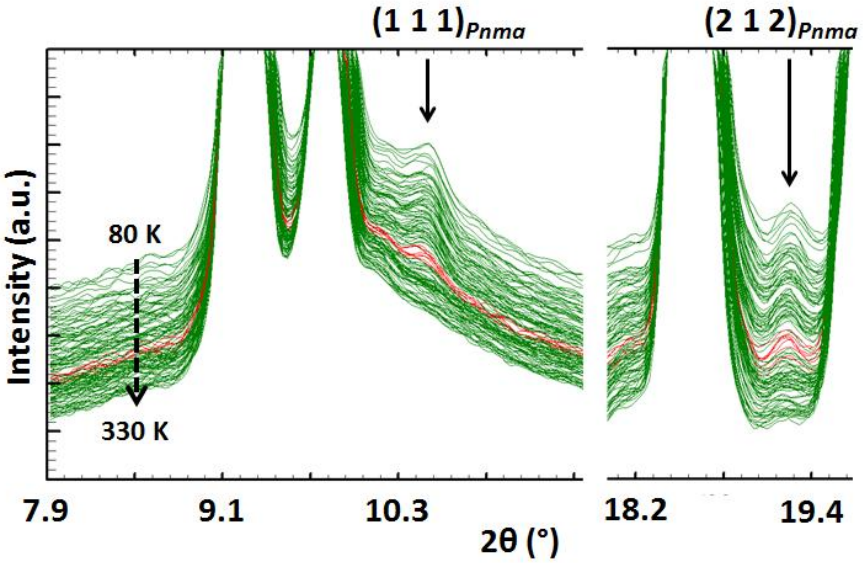
The room temperature x-ray powder diffraction pattern (black dots) has been collected from a 0.3 mm capillary with the use of Bruker D8 Discover diffractometer. A 18 mm parallel beam from the Cu-*K*α X-ray tube (λ = 1.5406 Å) was used to record diffractograms with a Vantec detector. The measurements were carried out in the range of 2θ from 10° to 70° with a 0.018° step (the counting time per step was 2245 seconds).

Rietveld refinement (red lines; difference plot – green lines) has been carried in the JANA2006 software.[2] The model included $KAgF_3$ and AgF (rock salt structure, observed reflexes marked by blue arrows). The absorption correction for a cylindrical sample ($\mu \cdot r$) has been set at 6.0 ($\mu \cdot r$ for 100 % efficient packing equals 9.15). The final reliability parameters of the model were: χ^2 = 1,86, R_p = 2,60 %, R_{wp} = 4,00 % with the mass percent of AgF equal to 3.8 % (*i.e.* 6,0 % mole percent).

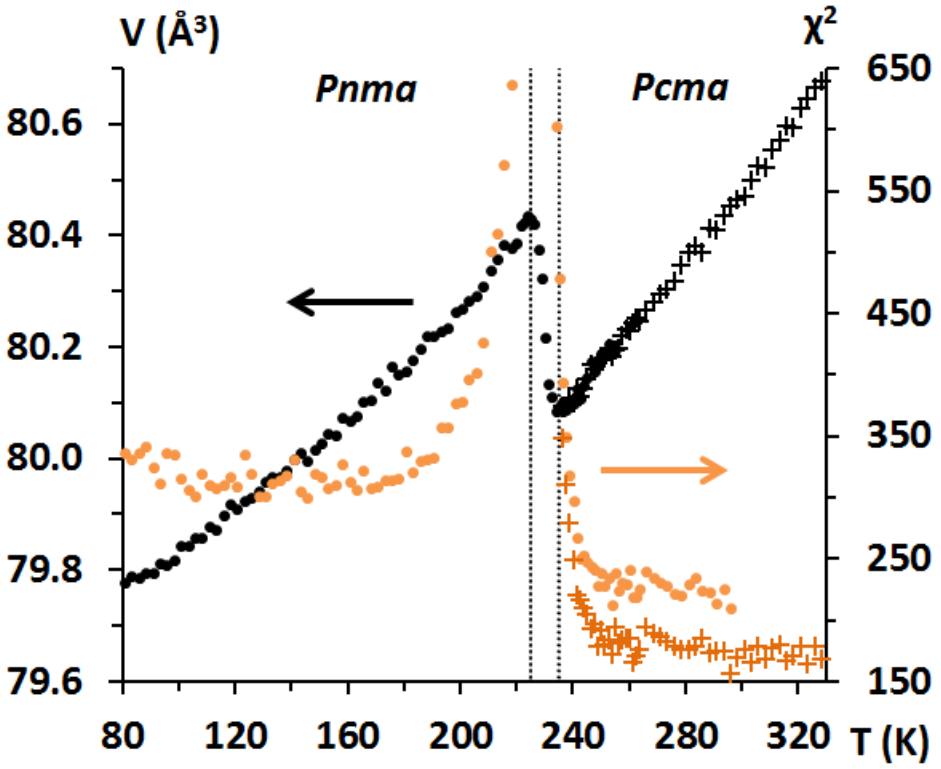
[2] V. Petricek, M. Dusek, L. Palatinus, *Jana2006. The Crystallographic Computing System*, Institue Of Physics, Praga, **2006**.

3. Details of temperature resolved XRDP pattern of $KAgF_3$





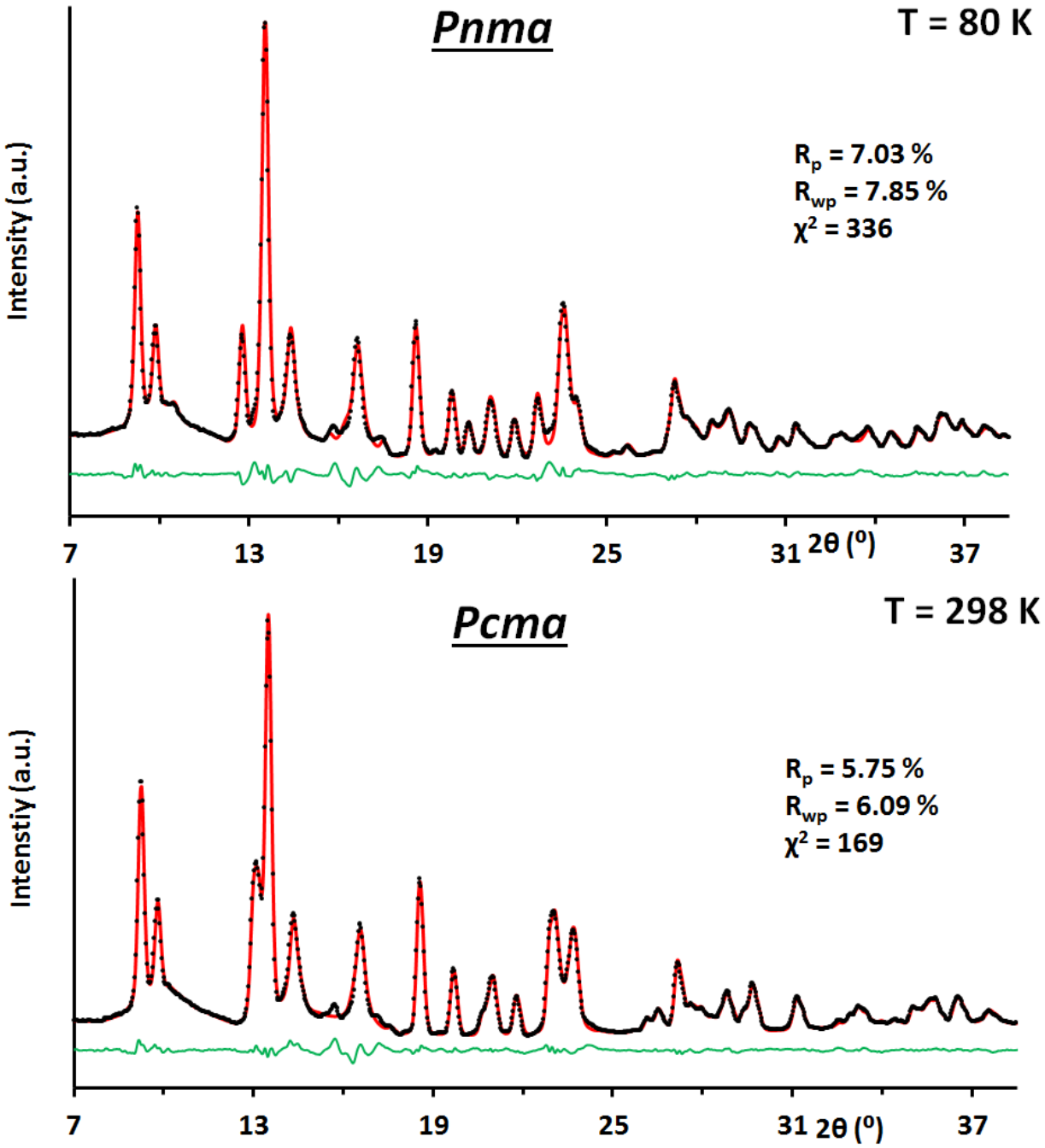
4. Temperature dependence of the volume and goodness of fit (χ^2) for *Pnma* and *Pcma* models of $KAgF_3$



Dots/crosses mark values obtained for the *Pnma*/*Pcma* model. Dotted vertical lines mark the range of the phase transition (225 K – 235 K). Note that the high values of χ^2 are the result of extremely high counting statistic of a 2D detector .[3]

[3] See: Y.-S. Lee, Y. Filinchuk, H.-S. Lee, J.-Y. Suh, J. W. Kim, J.-S. Yu, and Y. W. Cho, *J. Phys. Chem. C*, 2011, **115**, 10298.

5. Results of Rietveld refinement of patterns at two selected temperatures



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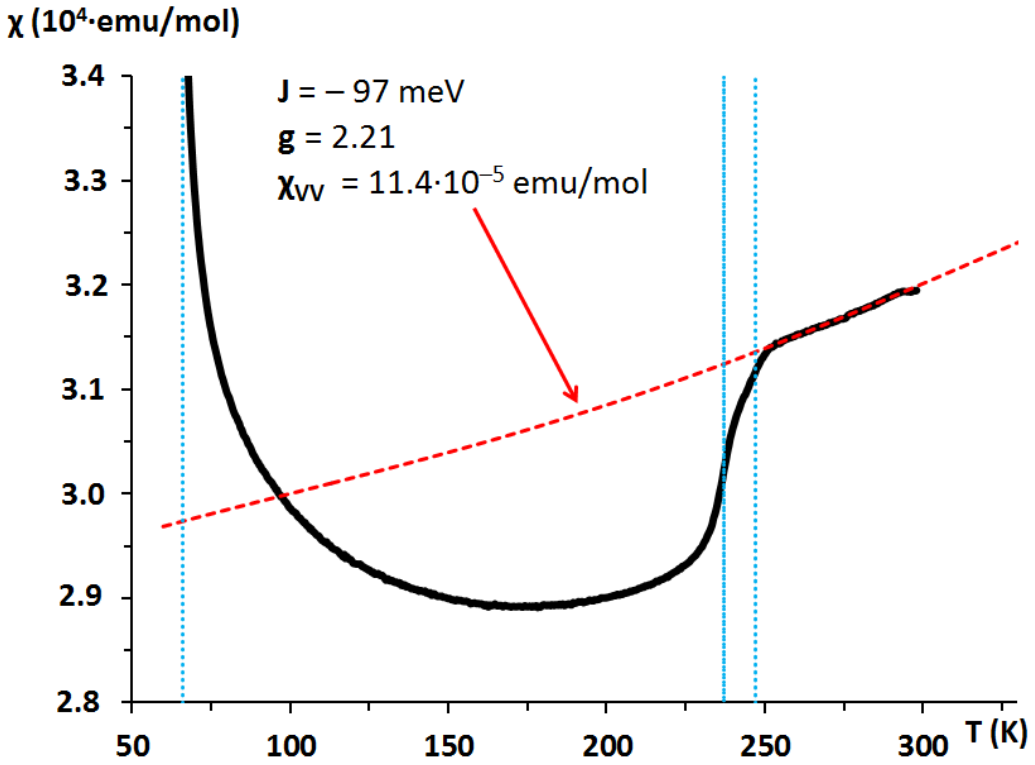
6. Fit of the magnetic susceptibility to the model of a spin-1/2 uniform antiferromagnetic Heisenberg chain



An attempt to fit the experimental values of χ with the model of a spin-1/2 uniform antiferromagnetic Heisenberg chain[4] was made. A constant positive term corresponding to the Van Vleck paramagnetic susceptibility (χ_{VV}) was also included in the fit. The value of the g-factor was not refined - its value (2.21) was taken from previous electron spin resonance measurements.[5] The model obtained after least-square refinement (red dashed line) fits the experimental data very well. The refined values of χ_{VV} and J are equal to $11.4\cdot10^{-5}$ emu/mol and –97.0 meV, respectively. The Van Vleck term is comparable to that reported for other fluoroargentates(II) ($2.3\cdot10^{-5}$ emu/mol for Cs_2AgF_4[6], $0.9\cdot10^{-5}$ emu/mol for Na_2CuF_4[7]). The slightly larger value of χ_{VV} obtained for $KAgF_3$ might originate from not including in the fit the contribution from the paramagnetic impurity.

[4] D. Johnston, R. K. Kremer, M. Troyer, X. Wang, A. Klümper, S. Bud'ko, A. Panchula, P. Canfield, *Phys. Rev. B*, 2000, **61**, 9558.
[5] Z. Mazej, E. Goreshnik, Z. Jagličić, B. Gaweł, W. Łasocha, D. Grzybowska, T. Jaroń, D. Kurzydłowski, P. J. Malinowski, W. Koźmiński, J. Szydłowska, P. J. Leszczyński, W. Grochala, *CrystEngComm* 2009, **11**, 1702.
[6] J. Tong, R. K. Kremer, J. Köhler, A. Simon, C. Lee, E. Kan, M.-H. Whangbo, *Z. Kristallogr.*, 2010, **225**, 498.
[7] D. Kurzydłowski, Z. Mazej, and W. Grochala, *Dalton Trans.*, 2013, **42**, 2167.

7. DFT+U calculations

	Experiment T = 80 K	DFT+U calculations
Symmetry	*Pnma*	*Pnma*
Energy per f.u. (eV)	n.a.	–17.351783
***a* (Å)**	6.382	6.577 (3%)
***b* (Å)**	8.254	8.425 (2%)
***c* (Å)**	6.058	6.197 (2%)
***α*. *β*. *γ* (°)**	90 90 90	90 90 90
***V* (Å^3)**	319.10	343.36 (8%)
$R_{Ag\text{-}F}^{\parallel}$ **(Å)**†	2.121	2.169 (2%)
$\delta_{Ag\text{-}F\text{-}Ag}^{\parallel}$ **(°)**†	153.2	152.4
$R_{Ag\text{-}F}^{\perp}$ **(Å)**‡	2.000 2.490	2.094 (5%) 2.553 (3%)

† Length of the Ag-F bonds and the Ag-F-Ag angle along the $[AgF_{2+2/2}]^-$ chains; ‡ length of the Ag-F bonds in the direction perpendicular to these chains; differences (in %) between the experimental and theoretical models are given in brackets.

Note that the calculated tilt angles of $[AgF_6]^{4-}$ octahedra in *Pnma* (13.1°/12.1°/4.3° for tilts about the ***a***/***b***/***c*** vectors) are in very good agreement with experimental values (13.1°/10.3°/3.0° at 80 K).

DFT+U calculations were performed in the formalism of Liechtenstein *et al.*[8] with the value of *U* equal to 5 eV. The Perdew-Burke-Ernzerhof exchange-correlation functional,[9] and the projector-augmented-wave method[10] were used as implemented in the VASP 5.2 code. The cut-off energy of the plane wave basis set was equal to 800 eV with a self-consistent-field convergence criterion of $1 \cdot 10^{-7}$ eV. The k-point mesh spacing was set to 0.16 Å^{-1}. Optimization of cell as well as atomic parameters was continued until the forces acting on individual atoms were less than 0.002 eV/Å. The geometry optimization were performed for magnetic models characterized by AFM ordering within the $[AgF_{2+2/2}]^-$ chains and inter-chain FM ordering, as it

[8] A. I. Liechtenstein, J. Zaanen, *Phys. Rev. B*, 1995, **52**, R5467.
[9] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
[10] P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953; G. Kresse, D. Joubert *Phys. Rev. B*, 1999, **59**, 1758.

has been shown that these are the lowest lying spin-ordered states of $KAgF_3$.[11] Structure visualization has been performed with the use of the VESTA software.[12]

For the *Pnma* structure of $KAgF_3$ one can define the coupling constant between nearest neighbours along the $[AgF_{2+2/2}]^-$ chain (J) as well as an inter-chain constant ($J\perp$). The values of these parameters were extracted from single point calculations on optimized structures with the use of the formulae given by Zhang *et al.*[11]. The obtained values of J and $J\perp$ (–125.4 meV and 2.6 meV, respectively) are in good agreement with those given by these authors (–136.0 meV / 5.8 meV) and indicate that $KAgF_3$ should exhibit quasi-1D AFM properties with strong intra-chain coupling.

[11] X. Zhang, G. Zhang, T. Jia, Y. Guo, Z. Zeng, and H. Q. Lin, *Phys. Lett. A*, 2011, **375**, 2456.
[12] K. Momma, F. Izumi, *J. Appl. Crystallogr.*, 2008, **41**, 653.