Mateusz A. Domański* and Wojciech Grochala*

Superexchange interactions in AgMF₄ (M = Co, Ni, Cu) polymorphs

https://doi.org/10.1515/znb-2021-0124
Received August 27, 2021; accepted September 23, 2021; published online October 8, 2021

Abstract: Magnetic properties of silver(II) compounds have been of interest in recent years. In covalent compounds, the main mechanism of interaction between paramagnetic sites is the superexchange via the connecting ligand. To date, little is known of magnetic interactions between Ag(II) cations and other paramagnetic centres. It is because only a few compounds bearing a Ag(II) cation and other paramagnetic transition metal cation are known from experimental work. Recently the high-pressure synthesis of ternary silver(II) fluoridometallates with 3d metal cations AgMF₄ (M = Co, Ni, Cu) was predicted to be feasible. Here, we investigate the magnetic properties of these compounds in their diverse polymorphic forms. Using well-established computational methods we predict superexchange pathways in AgMF₄ compounds, evaluate coupling constants and calculate the impact of the Ag(II) presence on superexchange between the other cations. The results indicate that the low-pressure form of AgCuF₄, the only one composed of stacked layers like the parent AgF₂, would show mainly Ag–Ag and Cu–Cu superexchange interactions. Upon compression, or with the nickel(II) cation, the Ag–M interactions in AgMF₄ compounds are intensified, which is emphasized by an increase of Ag–M superexchange coupling constants and Ag–F–M angles. All the strongest Ag–M superexchange pathways are quasi-linear, leading to the formation of antiferromagnetic chains along the crystallographic directions. The impact of Ag(II) on M–M superexchange turns out to be moderate, due to factors connected to the crystal structure.

Keywords: density functional theory; magnetic ordering; silver fluoridometallates; superexchange; theoretical modelling.

1 Introduction

The quest for materials exhibiting large magnetic superexchange (SE) and semiconducting properties abides, especially in the field of rapidly advancing antiferromagnetic spintronics. Such materials are in demand due to their high-frequency response and insensitivity to data-consuming perturbations [1]. However, designing new materials with strong antiferromagnetic coupling is not trivial. The magnetic coupling strength drops sharply with increasing the distance between magnetic centres (due to weakening of the orbital overlap) but also with the departure from linear bonding, the angle bending causing the wrong phases of orbitals to overlap [2]. These factors influence the most important feature of antiferromagnetic semiconductors i.e. SE interactions between ligand p orbitals and magnetic centre d orbitals, as in the case of oxocuprates [3]. Both of these issues are influenced by the structure of the material and may be engineered to some extent e.g. by using cations with differing radii (like in the series of 1D antiferromagnets bearing silver(II)) [4]) or by enforcing the epitaxial growth of single layers [5].

But what are other pathways towards a large magnetic SE constant, J? Apart from structural changes, commonly two main ways of enhancing the (anti-)ferromagnetic SE interaction are utilized. The first one called radical-bridged SE consists of placing a free radical between interacting magnetic centres [6]. These centres may be connected by paramagnetic (often organic) linkers with a single unpaired electron, which strengthens the direct interactions between metal-based centres. Such significantly localized radicals improve J through the mechanism of SE, mediating the wavefunctions of the magnetic centres, or through the hopping mechanism [7].

However, the existence of stable and localized radicals is not necessary, and a formally closed-shell ligand may also do a similar job. The alternative route to increase J is the so-called redox non-innocence of ligands, which may be considered as a halfway to the above-mentioned situation of a radical. Here, a redox-active metal centre interacts with the bridging ligand through a strong p-d or s-d (in case of a hydride [8]) hybridization resulting in a partial spin transfer to the ligand. It appears that such small and non-localized magnetic moments induced on a non-metal can
greatly affect the magnetic properties of the whole system, mediating (even the long-range) interactions between localized spins [9]. In particular, ferromagnetic semiconductors are an example of such strongly p-d hybridized systems. They are well described with the theory proposed by Dietl et al. [9], and find applications in modern spintronics. In certain cases, ferroelasticity may appear [10, 11]. However, this way also has its limits – in an extreme situation, such a spin transfer may push the system on the verge of stability, eventually when a half electron will be transferred to each second unit, the whole system may collapse due to phonon instability [12].

The peculiar and attractive materials in this context are fluorides, which have been recently investigated in the context of spintronics. These materials can exhibit considerable anisotropy of the spin-electronic properties like MnF$_3$ [13] or [AgF][BF$_4$] [14]. The latter is particularly important as low-dimensional $d^3$ fluoride system with 1/2 spin, which shows large exchange anisotropies within an antiferromagnetic ground state [16]. Divalent silver is known to be a strongly spin-polarizing agent, known to polarize even such hard anions like fluoride, where this ligand holds an uncompensated spin density, as shown on the DFT + U level [15].

Therefore, in the present work we considered ternary fluoride stoichiometries which may host strongly coupled AgF$_2$ sheets. Among compounds of the type Ag$^{2+}$M$_n$F$_y$, many transition metal systems have been prepared so far [16], but the great majority of these compounds have closed-shell or low-spin cations. Therefore, we combined silver(II) fluoride with high-spin 3d metal (M = Co, Ni, Cu) fluorides in order to examine their magnetic properties, and to check what the influence of 1/2 spin Ag(II) on the M–M magnetic interactions would be. Naturally, we are also interested in the strength of the Ag(II)–M magnetic interactions, which have not yet been studied for any one among dozens of Ag(II)–TM systems known [16]. In recent work it has been shown, that phases with AgMF$_4$ composition (M = Co, Ni, Cu) can be synthesized under high pressure conditions, and should be metastable after decompression [17]. Here, we focus on an analysis of the magnetic interactions inside these yet unknown compounds of AgMF$_4$ composition, with particular attention paid to magnetic SE and to the influence of the Ag(II) spin polaron on M–M interactions.

## 2 Methods

This theoretical study is based on periodic electronic-structure calculations carried out with the VASP 5.4.4 software using the projector augmented wave method [18, 19]. We used the potentials set recommended by VASP with a 520 eV energy cut-off. The energy was calculated using a collinearly spin-polarized DFT method using the GGA functional PBEsol, i.e. the solid-revised Perdew, Burke and Ernzerhof correlation-exchange functional [20]. The on-site electronic correlation was included with Coulomb and exchange repulsion terms with a +U Dudarev’s approach [21, 22]. In this approach only effective U is taken into account, thus we used $U_{eff}$ equal to 6 eV (for Ag, Ni), 5 eV (Co) and 8 eV (Cu). These values were used earlier and validated in respective systems with +U oxidation states [17, 23–26]. We have also cross-checked the applied DFT + U parameters with other DFT approaches, namely the SCAN meta-GGA functional and the HSE06 hybrid functional, obtaining qualitatively the same results. Therefore they are not provided in this work. Geometry optimizations were done on DFT + U with fine parameters of 0.02 Å wave vector spacing and conjugate-gradient algorithm relaxation with convergence thresholds of $10^{-7}$ eV (electronic) and $10^{-3}$ (ionic step).

Magnetic SE coupling constants were calculated using the broken symmetry method [30–33]. In this method the Heisenberg magnetic interactions between spins are described with broken symmetry high-spin states. Using DFT based methods, the magnetic interaction energy may be calculated with the classic Ising model Hamiltonian considering only collinear magnetic moments for any spin value [32]. It was shown that using the broken-symmetry method, the eigenvalues of the Ising model Hamiltonian correspond to those obtained from the Heisenberg Hamiltonian [30, 32]. The Ising model Hamiltonian was used in the form $H = -\sum_{ij} J_{ij} S_i S_j$ (with $J_{ij} = J_{ji}$), where $J_{ij}$ is the antiferromagnetic coupling constant between the closest neighbouring magnetic centres i and j when $J_{ij} < 0$. Then, by assuming that all the interactions are additive, all magnetic interaction constants $J_{ij}$ can be extracted solving the system of equations derived from different spin states [30]. In the case of inconsistencies in a linear system of equations, the solutions were calculated using the least-squares method [34]. To include interactions over longer distances, the single-point of different spin states was calculated in $2 \times 2 \times 2$ supercells. Using this method we have obtained coupling constants for the binary fluorides: CuF$_2$, NiF$_2$ and AgF$_2$ (discussed in the main text). The values for CuF$_2$ and NiF$_2$ agree well with those found in the literature [27–29]. The VESTA [35] software was used for the visualization of structures.

## 3 Results

In the present work, we investigate the magnetic properties of the proposed ternary fluorides which contain the spin-polarizing Ag(II) cation. Using the well-established computational methods we want to illustrate the influence of the Ag(II) cation on magnetic SE interactions inside the proposed ternary fluorides, which have been proven recently to show stability under high pressures [17]. To do so, (i) first we briefly describe the structure of the ternary fluorides with formulae AgMF$_4$, (ii) next we analyse and calculate the magnitude of magnetic interactions of these compounds and (iii) finally we investigate whether the presence of Ag(II) influences the strength of spin-spin interactions.
3.1 Crystal structure of ternary silver(II) fluorides and SE pathways

Since ternary silver(II) fluorides with 3d metal cations prefer monoclinically distorted AgF₂ type structures [17], the parent silver(II) fluoride is a reference essential for the purpose of a comparison with the ternary fluorides. In the experimentally known orthorhombic structure of AgF₂ [36, 37] (Figure 1a) we distinguish three different magnetic interaction paths named $J_{2D}$, $J_1$ and $J_2$ within distances of about 4.0 Å, following the work of Kurzydlo et al. [23] (Figure 1b). Even though all three interactions are essentially two-dimensional, the $J_{2D}$ is reserved for the strongest interaction within the covalently bound AgF₂ layers within the $ac$ plane. $J_1$ and $J_2$ indicate interactions within the $bc$ and $ab$ planes, respectively (i.e. interlayer interactions).

The ground state of orthorhombic AgF₂ holds strong antiferromagnetic interactions within the $ac$ plane as revealed by a highly negative $J_{2D}$ value equal $-60.5$ meV on a DFT + $U$ level (this study). Both $J_1$ and $J_2$ are over one order of magnitude smaller and positive [37]. Values for $J_{2D}$ calculated here on different levels of theory correspond well to the theoretical ($-71$ meV for SCAN functional [23], $-56$ meV for DFT+$U$ [38]) as well as experimental ($-70$ meV [38]) values found in the literature.

The structures of ternary fluorides having 3d cations, proposed in our previous work [17], differ in three major aspects with respect to that of the parent AgF₂. The first one is the presence of the 3d transition metal cation M(II), which implies differentiating two general types of magnetic interactions namely the mixed magnetic coupling constants $J^{mix}$ between Ag(II) and M(II), and the magnetic constants $J^M$ between two M(II) sites (Figure 2a). The second difference is that the considered structures of the ternary fluorides AgMF₄ are monoclinically distorted with values $\beta > 90^\circ$ being chosen. Due to this distortion, the $ac$ face of a monoclinic unit cell is stretched, causing the original $J_{12}$ interaction (originally parallel to the $ab$ plane) to transform from two-dimensional into two distinct linear interactions, which are labelled as $J^{mix}_1$ and $J^{mix}_4$ in Figure 2b. This distortion is present in all AgMF₄ ternary fluorides and manifests itself in two different values for Ag–M distances parallel to the $ac$ plane (distances for $J^{mix}_3$ and $J^{mix}_6$ in Table 1). The third difference arises because in ternary fluorides there are two distinct types of Ag–F–M bridges along the shortest Ag–M distance parallel to the $ab$ planes (corresponding to $J_{12}$ parallel to the $bc$ plane in the parent AgF₂). For example, in the AgNiF₄ LP structure for an Ag–Ni distance of 3.715 Å there is one Ag–F–Ni bridge with an angle of 137.7° with short bonds, and the second with a 120.1° angle with longer bonds (cf. Table S3). Thus, these two types of bridges are split here into two distinct interactions (i.e. to interaction paths $J^{mix}_1$ and $J^{mix}_2$, see Figure 2b and c), for the same distance between the interacting sites.

Moreover, the layered structure of AgF₂ is preserved only in the LP-AgCuF₄ structure, which consists of corrugated layers for each difluoride and alternating along the $x$ axis. In all other fluoridometallates found, the primary connectivity pattern from AgF₂ changes to a lattice, where strong covalent bonds occur along all three lattice directions or their combinations. This change in connectivity implies the greater significance of the Ag–M magnetic interactions as compared to those within single-metal layers. This structural difference, however, does not require a different model for the magnetic interactions, as the positions of the transition metal cations do not change in all the structures of ternary fluorides presented here, and they all represent the monoclinically distorted AgF₂ structure type.

Overall, we considered all interactions within a distance of about 6.0 Å (slightly varying with the formula, see Tables S1–S5), resulting in 13 different coupling constants included in the model Hamiltonian. In the model, we recognize: (1) Ag(II) sheets coupled with $J_{2D}^{Ag}$; (2, 3, 4) Ag(II) chains coupled along subsequent lattice vectors i.e. $J_y^{Ag}$, $J_z^{Ag}$, $J_y^{Ag}$; (5, 6, 7, 8) the same for M(II) with coupling constants $J_{2D}^{M}$, $J_y^{M}$, $J_z^{M}$, $J_x^{M}$; (9) Ag(II)–M(II) chains along the [110] or [−110] directions coupled with $J^M_{mix}$ along the Ag–F–M bridges with a more obtuse angle and shorter bonds; (10)

![Figure 1](image-url): (a) Crystal structure of orthorhombic AgF₂ at ambient pressure, and (b) magnetic interaction pathways between the constituting Ag(II) sites. Grey colour for silver atoms, green for fluorine.
Ag(II)–M(II) chains along the [110] or [−110] directions coupled with $J_{mix}^4$ along the Ag–F–M bridges with a smaller angle and longer bonds [39]; (11) Ag(II)–M(II) chains along the [101] direction coupled with $J_{mix}^3$; (12) Ag(II)–M(II) chains along the [−101] direction coupled with $J_{mix}^3$; (13) Ag(II)–M(II) sheets within the (−101) plane coupled with $J_{mix}^5$ without a direct SE route.

### 3.2 Magnetic interactions in AgMF₄ systems

After determination of the key SE pathways, we calculated the energies of the possible magnetic configurations of each structure and constructed a system of equations applying the Ising Hamiltonian for each of the structures (provided in points 2. and 3. in the Supplementary Material available online). Since each of the considered systems of equations was overdetermined, we applied a least-squares statistical method to obtain the solutions.

Systems that have been successfully analysed are AgCuF₄ and AgNiF₄ for both the low-pressure and the high-pressure polymorphs after their decompression to standard pressure (i.e. following reoptimization of the structure at $p = 0$ GPa). In the case of the AgCoF₄ system, owing to the instability of the magnetic configuration combined with the proximity of the intrinsic redox reaction we could not obtain reliable results applying the Ising Hamiltonian, a biquadratic exchange or four-spin ring interactions. The lack of a reliable solution manifested itself in large differences (over 0.1 eV, cf. with results from point 3. in the Supplementary Material available online) between the energy values obtained with DFT and the energy calculated using the Ising Hamiltonian, or a modified Hamiltonian including the mentioned interactions. This is why we focus exclusively on the cases of M = Ni and Cu.

The magnetic exchange in LP-AgCuF₄ resembles the situation in the parent AgF₂ since the strongest interactions are calculated to be the intralayer ones ($J_A^{2D}$ and $J_C^{2D}$), with weak ferromagnetic interactions between the layers ($J_{mix}^1$, $J_{mix}^3$). The key change in comparison with AgF₂ is that the result of inserting [CuF₂] layers is a relative flattening of the [CuF₂] layers (140.8° in LP-AgCuF₄, but 131.7° in pure CuF₂) and buckling of the [AgF₂] sheets (decrease of the angle from 129.0 to 122.2°, cf. Table S1), since Cu(II) has a much smaller ionic radius than Ag(II). Along with the increased buckling in the [AgF₂] sheets, the intralayer antiferromagnetic exchange decreases for $J_A^{2D}$ (−60.5 meV for AgF₂ vs. −37.4 meV for LP-AgCuF₄) in accordance with the Goodenough-Kanamori-Anderson (GKA) rules [2, 40, 41]. In both cations, mainly $d$ holes are occupying the $d_{x^2−y^2}$ orbitals as usual for strongly coupled antiferromagnetic layers (Figure 3a). The obtained spin density projections have been deposited in the NoMAD database (https://nomad-lab.eu/).

The core features of the HP-AgCuF₄ structure are preserved after decompression, but the topology of the SE interactions differs dramatically. The ground state of this structure is ferrimagnetic, with Ag(II) sites having opposite spins to Cu(II) sites, resulting in a small net magnetic
Table 1: Magnetic SE constants calculated for each ternary silver(II) fluorometallate system, as well as for the reference AgF₂, provided in meV, and metal-metal separations at the corresponding SE pathways. Distances d are provided in Ångstroms, and coupling constants J in meV.

| Interaction | AgF₂ | AgCuF₄ | AgNiF₄ | AgCoF₄ |
|-------------|------|--------|--------|--------|
|             | LP   | LP     | HP     | LP     | HP     | LP     |
| J₂D         | d    | J      | d      | J      | d      | J      |
|             | 3.743 | −60.5 | 3.616 | −37.4 | 3.731 | 0.8    | 3.715 | −6.3 | 3.633 | −26.8 | 3.740 | − |
|             | Jₐ   | 3.851  | 5.6    | 3.810 | 4.8   | 3.662 | −45.9 | 3.695 | −32.8 | 3.642 | −33.3 | 3.731 | − |
|             | J₂   | 3.997  | 2.4    | 3.453 | 3.3   | 3.529 | −16.4 | 3.354 | 6.1   | 3.406 | −7.3  | 3.402 | − |

*Interactions J₁ and J₂ are identical in the AgF₂ structure, and equivalent to J₁. ²Interactions J₄ and J₅ are identical in the AgF₂ structure, and equivalent to J₂. ³Not determined as explained in the text.

The moment of about +0.022 µ₀ due to different moments on both cations. In HP-AgCuF₄, the covalent layers of [CuF₂] and [AgF₂] cannot be distinguished, what is further confirmed by weak interactions along the bc planes, J₄ and J₅. In HP-AgCuF₄, the strongest interactions and the shortest Ag–F–Cu bridges are J₄ mix along the directions [110] (or [−110]), these directions are alternating along the c vector, and J₃ mix along [10−1]. Holes on both Ag(II) and Cu(II) sites still sit mainly in dₓ²−ᵧ² orbitals as in the LP structure (Figure 3b).

**Figure 3:** The SE pathways along the strongest and the second-strongest magnetic coupling interactions in LP-AgCuF₄ (a) and HP-AgCuF₄ (b), as well as in LP-AgNiF₄ (c) and HP-AgNiF₄ (d). Spin densities are projected on isosurfaces with a value 0.030 e Å⁻³, with pink for spin-down and yellow for spin-up densities. The spin densities are projected for the ground state magnetic configuration for each system. Grey colour for silver, green for fluorine, blue for copper, and orange for nickel atoms.
The interactions along the chains dominate also in the LP-AgNiF₄ structure. The strongest Ag–Ni interactions are oriented along the directions [110] (or [−110]), namely \( J_{1}^{\text{mix}} \). In Figure 3c the projected spin density suggests that in this case \( d \) holes in Ag(II) consist mainly of the \( d_{z}^{2} \) orbital, enhancing the interaction along the \( J_{1}^{\text{mix}} \) path. Here, the interactions along the path \( J_{2}^{\text{mix}} \) are relatively strong, resulting in the fact that the constant \( J_{2}^{\text{mix}} \) is the second-largest among all that have been calculated. Unlike in HP-AgCuF₄, \( J_{3}^{\text{mix}} \) is positive in this case thus indicating a ferromagnetic character, because of a double Ag–F–Ni bridge having the angle of about 103° (Table S3), whereas usually values of about 90° favour ferromagnetic exchange according to the GKA rules (vide ultra).

In the last determined system i.e. the HP-AgNiF₄ structure, the Ag(II) cations tend to interact within the bc plane, which is revealed by an increase of \( J_{2}^{\text{Ag}} \) from −6.3 meV in the LP structure up to −26.8 meV in the HP structure, which is about half of the value found for parent AgF₂. This structural transition is linked with an axial elongation of the Ag(II) coordination octahedra and location of the spin densities mainly in \( d_{z}^{2} \), \( s^{2} \) orbitals, just like in parent AgF₂ or LP-AgCuF₄. Here, however, still the Ag–Ni interaction \( J_{1}^{\text{mix}} \) is the strongest one like in the LP-AgNiF₄ structure, suggesting that it may play a crucial role in the predicted stability of AgNiF₄.

### 3.3 Ag(II) influence on M–M SE coupling

Our key aim was to scrutinize, whether the presence of the Ag(II) cation has an impact on the magnetic SE between the neighbouring 3d metal cations inside the structures of the proposed ternary fluorides. Therefore, we have conducted a theoretical experiment of substituting paramagnetic Ag(II) for a diamagnetic cation with similar charge and ionic radius, Cd(II). In order to investigate the influence of the electronic properties of Ag(II) only, we have not reoptimized the structures featuring Cd(II). Next, we recalculated the coupling constants \( J_{1,2}^{\text{M}} \) as well as others of the \( J_{1,2,3}^{\text{mix}} \) type, and compared them in Table 2.

The Ag(II) spin polarizer influences the M–M spin interactions in two basic ways: (i) by inducing the redox non-innocence of the ligands, resulting in an increase of the magnetization of the fluorine atoms within the \([MF_{2}]\) layers, or (ii) through two consecutive SE paths leading via Ag(II) cations such as M′–Ag–M″ (e.g. through \( J_{1}^{\text{mix}} \), \( J_{2}^{\text{mix}} \) and \( J_{3}^{\text{mix}} \) in Figures 2b and 3), resembling a free radical-bridged next-nearest-neighbour superexchange. (iii) However, one may anticipate a suppression of the orthogonal M–M SE when major interactions are of the mixed Ag–M type, as e.g. when \( J_{2}^{\text{mix}} \) is orthogonal to \( J_{1}^{\text{mix}} \) (Figure 2). In such a case, since the active orbitals of Ag(II) are oriented along the M–Ag–M paths, their impact on the M–M SE pathways is very small or even weakening. (iv) Also, the influence of Ag(II) would be small, if both Ag(II) and M(II) are significantly separated and interactions between Ag(II) and M(II) are weak.

The results presented in Table 2 indicate a moderate impact of Ag(II) on the shortest M–M SE interaction, \( J_{2}^{\text{Ag}} \), ranging between 38 and 106% of the value typical of Cd-substituted compounds. In the LP-AgCuF₄ structure, probably the enhancement effect (i) dominates but is suppressed owing to the substantial separation of the layers (iv). In all other structures, the mixed Ag–M SE interactions predominate, which is revealed by large \( J_{\text{mix}} \) constants given in Table 1, thus the effect (iii) is operational and the shortest interactions \( J_{2}^{\text{M}} \) are weakened. On the other hand, the influence of Ag(II) on longer and weaker M–M SE interactions \( J_{1,2}^{\text{M}} \), and \( J_{1,2}^{\text{mix}} \) is generally much larger (up to over 2000%), but of course minor in terms of absolute changes, since these interactions are weak anyway. In these cases, probably the mechanism of double SE (ii) or a radical-bridging mechanism (i) is essential, and may even cause a change of character of the interaction, i.e. from ferromagnetic to antiferromagnetic or vice versa, as manifested by the minus sign at the percent values listed in Table 2.

### 4 Conclusions

In this work, the magnetic properties of ternary silver(II) fluoridometallates with nickel and copper were scrutinized. Using the DFT + U computational methods we have predicted SE pathways in ternary silver(II) fluorides, evaluated coupling constants and calculated the impact of the presence of Ag(II) on the SE between the other cations. The model of magnetic interactions described by the Ising Hamiltonian requires 13 different coupling constants to obtain a satisfactorily converged solution. The results indicate that the low-pressure form of AgCuF₄, the only one composed of stacked layers similar to that of the parent AgF₂, holds mainly \( J_{2}^{\text{Ag}} \) and \( J_{2}^{\text{M}} \) interactions, which are weakened due to different sizes of the Ag(II) and Cu(II) cations causing a geometry strain. Upon compression in HP-AgCuF₄, as well as in both the LP and HP structures with nickel(II) cations, the linear Ag–M antiferromagnetic interactions are dominating, what is emphasized by
substantially negative SE coupling constants and obtuse Ag–F–M angles. The most pronounced antiferromagnetic Ag–Cu SE constant is predicted to be substantial, about −45.9 meV, while the Ag–Ni one is about −33.3 meV. All the strongest Ag–M SE interactions are close-to-linear, leading to the formation of antiferromagnetic chains along the crystallographic directions. Other SE interactions are minor, except for the HP-AgNiF₄ structure, where J₂⁴ is −26.8 meV, still half of the value for the parent AgF₂. Moreover, the influence of Ag(II) on M–M SE is rather moderate, due to limiting factors such as structurally unfavourable SE pathways, or excessively strong competing Ag–M interactions. However, the presence of Ag(II) cations strongly influences most of the weak SE coupling constants of these systems, as compared to the case of diamagnetic Cd(II) replacing Ag(II). It remains to be seen whether Ag(II) could exert strong effects in molecular rather than solid state systems.

5 Supporting information

Additional structural data regarding ligand bridges, details of the obtained magnetic configurations and constructed sets of equations with detailed results are given as supplementary material available online (https://doi.org/10.1515/znb-2021-0124).

Acknowledgements: This work was supported by Polish National Science Center (NCN) within Beethoven project (2016/23/G/ST5/04320). The research was carried out using supercomputers of Interdisciplinary Centre for Mathematical and Computational Modelling (ICM), University of Warsaw, under grants ADVANCE++ and SAPPHIRE, number GA76-19 and GA83-34.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Table 2: Magnetic exchange constants calculated for each ternary silver(II) fluoridometallate system with silver cations J(Ag) and after substitution with cadmium cations J(Cd), and the ratio between them.

| System       | J(Ag)/meV | J(Cd)/meV | J(Ag)/J(Cd)/% |
|--------------|-----------|-----------|---------------|
|              | Jₓ²⁰      | Jₓ        | Jₓ²          | Jₓ²          | Jₓ²        | Jₓ²        | Jₓ²        |
| LP-AgCuF₄   | −18.9     | −0.1      | −1.5         | −0.1         | −17.8      | −0.1      | −0.9       | 106         | 99          | 162          | 2084       |
| HP-AgCuF₄   | 0.2       | 0.6       | −0.8         | 0.4          | 0.6        | −0.1      | −0.1       | 38          | −841        | 628          | −219       |
| LP-AgNiF₄   | −4.7      | −0.1      | −0.4         | −0.2         | −5.1       | 0.0       | −0.1       | 91          | −626        | 319          | 87         |
| HP-AgNiF₄   | −3.9      | 0.0       | 1.0          | 0.5          | −5.1       | 0.0       | −0.1       | 75          | −29         | −753         | −453       |

Research funding: This work was supported by Polish National Science Center (NCN) within Beethoven project (2016/23/G/ST5/04320).

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Jungwirth T., Martí X., Wadley P., Wunderlich J. Nat. Nanotechnol. 2016, 11, 231–241.
2. Anderson P. W. Phys. Rev. 1950, 79, 350–356.
3. Norman M. R. Rep. Prog. Phys. 2016, 79, 074502.
4. Mazej Z., Kurzydlowski D., Grochala W. In Photoptic and Electronic Properties of Fluoride Materials; Tressaud A., Poeppelmeier K., Eds. Elsevier: Boston, 2016, pp. 231–260.
5. Grzelak A., Su H., Yang X., Kurzydlowski D., Lorenzana J., Grochala W. Phys. Rev. Mater. 2020, 4, 084405.
6. Hua C., DeGayner J. A., Harris T. D. Inorg. Chem. 2019, 58, 7044–7053.
7. Lambert C., Noll G., Schelter J. Nat. Mater. 2002, 1, 69–73.
8. Jaroń T., Grochala W., Hoffmann R. J. Mol. Model. 2007, 13, 769–774.
9. Dietl T., Ohno H., Matsukura F., Cibert J., Ferrand D. Science 2000, 287, 1019–1022.
10. Xu X., Ma Y., Zhang T., Lei C., Huang B., Dai Y. Nanoscale Horiz. 2020, 5, 1386–1393.
11. Sánchez-Movellán I., Moreno-Ceballos J., Garcia-Fernández P., Aramburu J. A., Moreno M. Chem. Eur. J. 2021, 27, 13582–13590.
12. Grochala W., Hoffmann R., Edwards P. P. Phys. Rev. B 2021, 94, 134405.
13. Jiao Y., Ma F., Zhang C., Bell J., Sanvito S., Du A. Phys. Rev. Lett. 2017, 119, 016403.
14. Kurzydlowski D., Grochala W. Phys. Rev. B 2017, 96, 155140.
15. Mazej Z., Goreshnik E., Jagličič Z., Gavel B., Lašoča W., Grzybowska D., Jaroń T., Kurzydlowski D., Malinowski P., Koźmiński W., Szydłowska J., Leszczyński P., Grochala W. CrystEngComm 2009, 11, 1702–1710.
16. Grochala W., Hoffmann R. Angew. Chem. Int. Ed. 2001, 40, 2742–2781.
17. Domański M. A., Derzi M., Grochala W. RSC Adv. 2021, 11, 25801–25810.
18. Kresse G., Furthmüller J. Phys. Rev. B 1996, 54, 11169–11186.
19. Kresse G., Joubert D. Phys. Rev. B 1999, 59, 1758–1775.
20. Perdew J. P., Ruzsinszky A., Csonka G. I., Vydrov O. A., Scuseria G. E., Constantin L. A., Zhou X., Burke K. Phys. Rev. Lett. 2008, 100, 136406.
21. Liechtenstein A. I., Anisimov V. I., Zaanen J. Phys. Rev. B 1995, 52, R5467–R5470.
22. Dudarev S. L., Botton G. A., Savrasov S. Y., Humphreys C. J., Sutton A. P. Phys. Rev. B 1998, 57, 1505–1509.
23. Kurzydlowski D., Derzsi M., Barone P., Grzelak A., Struzhkin V., Lorenzana J., Grochala W. Chem. Commun. 2018, 54, 10252–10255.
24. Barreda-Argüeso J. A., López-Moreno S., Sanz-Ortiz M. N., Aguado F., Valiente R., González J., Rodríguez F., Romero A. H., Muñoz A., Natal L., Baudelet F. Phys. Rev. B 2013, 88, 214108.
25. Cococcioni M., de Gironcoli S. Phys. Rev. B 2005, 71, 035105.
26. Miller C., Botana A. S. Phys. Rev. B 2020, 101, 195116.
27. Reinhardt P., de P. R. Moreira I., de Graaf C., Dovesi R., Illas F. Chem. Phys. Lett. 2000, 319, 625–630.
28. Hutchings M. T., Thorpe M. F., Birgeneau R. J., Fleury P. A., Guggenheim H. J. Phys. Rev. B 1970, 2, 1362–1373.
29. de P. R. Moreira I., Dovesi R., Roetti C., Saunders V. R., Orlando R. Phys. Rev. B 2000, 62, 7816–7823.
30. Illas F., Moreira I. P. R., de Graaf C., Barone V. Theor. Chem. Accounts 2000, 104, 265–272.
31. Dai D., Whangbo M.-H. J. Chem. Phys. 2001, 114, 2887–2893.
32. Dai D., Whangbo M.-H. J. Chem. Phys. 2002, 118, 29–39.
33. Whangbo M.-H., Koo H.-J., Dai D. J. Solid State Chem. 2003, 176, 417–481.
34. Press W. H., Teukolsky S. A., Flannery B. P., Vetterling W. T. Numerical Recipes in FORTRAN 77: Volume 1, Volume 1 of Fortran Numerical Recipes: The Art of Scientific Computing; Cambridge University Press: Cambridge, 1992.
35. Momma K., Izumi F. J. Appl. Crystallogr. 2011, 44, 1272–1276.
36. Fischer P., Schwarzenbach D., Rietveld H. M. J. Phys. Chem. Solid. 1971, 32, 543–550.
37. Fischer P., Roul G., Schwarzenbach D. J. Phys. Chem. Solid. 1971, 32, 1641–1647.
38. Gawraczyński J., Kurzydlowski D., Ewings R. A., Bandaru S., Gadomski W., Mazej Z., Ruanı G., Bergenti I., Jaroń T., Ozarowski A., Hill S., Leszczyński P. J., Tokár K., Derzsi M., Barone P., Wohlfeld K., Lorenzana J., Grochala W. Proc. Natl. Acad. Sci. U. S. A. 2019, 116, 1495–1500.
39. $J_1^{\text{mix}}$ and $J_1^{\text{mix}}$ lie within the same plane and have the same Ag-M distances but are distinguished due to different superexchange paths as explained before., n.d.
40. Goodenough J. B. Phys. Rev. 1960, 120, 67–83.
41. Kanamori J. J. Phys. Chem. Solid. 1959, 10, 87–98.

Supplementary Material: The online version of this article offers supplementary material (https://doi.org/10.1515/znb-2021-0124).