Prediction of giant antiferromagnetic coupling in exotic fluorides of Ag$^{II}$

Tomasz Jaroń$^1$ and Wojciech Grochala$^{1,2}$

$^1$ Faculty of Chemistry, The University of Warsaw, Pasteur 1, 02-093 Warsaw, Poland
$^2$ ICM, The University of Warsaw, Pawińskiego 5a, 02-106 Warsaw, Poland

Received 20 November 2007, revised 16 January 2007, accepted 16 January 2007
Published online 18 January 2008

PACS 61.50.–f, 61.66.Fn, 71.30.+h, 71.70.Ej, 74.10.+v, 75.50.Ee

We show, using Density Functional Theory (DFT) calculations, that compressed AgF$_2$ should turn above 17 GPa into a layered narrow-gap material with a huge intralayer antiferromagnetic (AFM) coupling constant, reminiscent of those seen for parent copper (II) oxides (e.g., La$_2$CuO$_4$). Compressed AgF$_2$ is thus the first candidate for the non-oxocuprate two-dimensional antiferromagnet. Calculations indicate that AgF$_2$ could subsequently be metallised above 38 GPa, likely giving rise to superconductivity (SC).
Prediction of giant antiferromagnetic coupling in exotic fluorides of Ag II*

Tomasz Jaroń1 and Wojciech Grochala**, 1, 2

1 Faculty of Chemistry, The University of Warsaw, Pasteur 1, 02-093 Warsaw, Poland
2 ICM, The University of Warsaw, Pawinskiego 5a, 02-106 Warsaw, Poland

Received 20 November 2007, revised 16 January 2007, accepted 16 January 2007
Published online 18 January 2008

PACS 61.50.–f, 61.66.Fn, 71.30.+h, 71.70.Ej, 74.10.+v, 75.50.Ee

* To Arndt Simon, in recognition of his outstanding contribution to the chemistry of novel superconductors [1].
** Corresponding author: e-mail wg22@cornell.edu, Phone: +48-22-5540828, Fax: +48-22-5540801

We show, using Density Functional Theory (DFT) calculations, that compressed AgF₂ should turn above 17 GPa into a layered narrow-gap material with a huge intralayer antiferromagnetic (AFM) coupling constant, reminiscent of those seen for parent copper (II) oxides (e.g., La₂CuO₄). Compressed AgF₂ is thus the first candidate for the non-oxocuprate two-dimensional antiferromagnet. Calculations indicate that AgF₂ could subsequently be metallised above 38 GPa, likely giving rise to superconductivity (SC).

The second ionization potential of silver is huge, 2070 kJ mol⁻¹ (typical of non-metals like Xe), ranking Ag the first among all metals, except for the alkalis (Fig. 1). The compounds of divalent silver rank among the strongest oxidizers currently known. Ag II is stable only in the fluoride ligand environment [2] and yet its bonding to F⁻ shows an unprecedented degree of covalence [2, 3].

Unusual chemistry of Ag II has prompted authors [2] to draw numerous analogies between oxides of Cu II (parent compounds of oxocuprate superconductors) and fluorides of Ag II (see also SI). Notably, an intriguing possibility was discussed that charge- or self-doped fluorides of Ag II might exhibit high-temperature SC.

McLain et al. have recently reported that Cs₂AgF₄ below 15 K is a strongly correlated 2D Heisenberg ferromagnet (FM) with a moderate intralayer magnetic constant J of +5.0 meV [4]. The nature of magnetic interactions in this compound has been theorized independently by Kasinathan et al. [5] and by Dai et al. [6]. Unfortunately, both groups have used an incorrect I4mm structure type, initially deposited by McLain et al. at the preprint server [7]. More careful examination published later [4] has led the authors to the lower-symmetry Bbcm structure. Both types differ considerably: the tetragonal one contains compressed [AgF₆] octahedra, with their short axes aligned perpendicularly to the [AgF₂] sheets, while the orthorhombic one has elongated [AgF₆] octahedra, with their long axes lying perpendicularly to each other yet within the [AgF₂] sheets. Distortion of the Bbcm structure from I4mm, albeit small, must have large impact on magnetic ordering [8], and calls for a theoretical reinvestigation of magnetic interactions in this compound.

Our Generalized Gradient Approximation (GGA) DFT calculations [9] using the Bbcm structure [4] show that Cs₂AgF₄ is indeed FM. The magnetic coupling constant, J, estimated from the energy difference between the FM and AFM configurations per one Ag center [6] reaches +17.7 meV (Table 1). Our value is nearly 40% smaller than the one derived by Dai et al. [6], which shows that the use of the orthorhombic structure is indispensable to better reproduce the experimentally derived value. However, J is still too large, by a factor of 3.5, as compared to the experimental value (+5.0 meV [4]). This result is not unexpected since the DFT methods usually overestimate magnetic interactions [5, 6].
The calculated magnetic moments of Ag and F atoms (Table 1) are similar to the previously published results [5, 6, 10] and confirm a substantial share of holes in the F(2p) states [2, 3]. There are two marked qualitative differences between our results and those of [5, 6]: (i) in our calculations a direct band gap of 0.42 eV opens at the Fermi level, and (ii) relative position of the d(x^2−y^2) and d(z^2) states is in agreement with the elongated O_2 ligand environment of the Jahn–Teller d^3 cation [11]. Thus, the half-metallic character discussed in [5] and substantial part of the earlier considerations on the origin of FM ordering in 144mm Cs$_2$AgF$_4$ [6], are irrelevant to the Bbcm structure. Our calculations thus yield similar results to those by Wu and Khomskii and by Kan et al. [10], who have pointed out the energy preference for the orthorhombic vs. the tetragonal phase while our manuscript was in preparation.

Oxocuprates (II) are distinctive in having [CuO$_2$] planes with strong AFM ordering. Search for similarly large AFM interactions in magnetic insulators with other spin-1/2 transition metal atoms, and for related SC [12] has not been successful to date. Ferromagnetic (FM) ordering predominates the magnetic behaviour of fluoroargentates (II) [2, 4]: binary AgF$_2$ is itself a spin-canted FM, with the appreciable Curie temperature of 163 K [13]. Ferromagnetism is usually considered to be detrimental for the appearance of superconductivity (SC) [14]. We will now discuss the AFM order, namely that of pressure-induced metalization [15], which is very large and negative (~227 meV to ~298 meV) indicating strong AFM coupling [16], this is due to the presence of nearly linear AgF$_2$ bridges in the crystal structure of δ-AgF$_2$ [11]. They are similar to the Cu–O–Cu linkers in the crystal structure of oxocuprates, although the former ones are bent from 180°, while the latter are perfectly linear. Since DFT exaggerates the strength of magnetic interactions, it is fair to rescale the calculated J values by the factor of 3.5. The derived values of ~64 meV to ~84 meV are still large, and comparable with typical values found for the undoped compounds of the oxocuprate SCs [17] like La$_2$CuO$_4$ (~100 meV [18]). According to some theories of SC, this feature alone makes δ-AgF$_2$ a plausible candidate for the parent compound of a new high-temperature SC.

SC is usually generated in AFM oxocuprates (II) by an electron- or hole-doping. Chemical doping is very difficult for fluoroargentates, because it results in the localization of an extra charge in form of Ag$_I$ or Ag$_{III}$, respectively [2]. We therefore follow an alternative path of the frustration of the AFM order, namely that of pressure-induced metallization [19]. High pressures have been spectacularly applied to turn elemental B, S and O$_2$ into SCs [20] and even to force slightly underdoped cuprates into the SC state [21].

**Table 1** Calculated values of the intralayer magnetic coupling constant, J, and of the magnetic moments on metal and nonmetal atoms, $\mu_{Ag}$ and $\mu_{F}$, respectively, for Cs$_2$AgF$_4$ and δ-AgF$_2$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$J$ (meV)</th>
<th>$\mu_{Ag}/\mu_{F}$</th>
<th>$\mu_{F}/\mu_{F}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs$_2$AgF$_4$ (144mm)</td>
<td>+28.0$^a$</td>
<td>+0.50$^a$</td>
<td>0.10, 0.0$^b$</td>
</tr>
<tr>
<td>Cs$_2$AgF$_4$ (Bbcm)$^c$</td>
<td>+17.7</td>
<td>0.53, 0.56</td>
<td>0.10, 0.0</td>
</tr>
<tr>
<td>δ-AgF$_2$ (17 GPa)$^d$</td>
<td>−227.1</td>
<td>±0.23</td>
<td>±0.01</td>
</tr>
<tr>
<td>δ-AgF$_2$ (1 GPa)$^d$</td>
<td>−298.3</td>
<td>±0.21</td>
<td>0.0</td>
</tr>
</tbody>
</table>

$^a$ Ref. [6], $^b$ Ref. [5], $^c$ this work.

Recent theoretical work [15] has elucidated the pressure-induced transformations of AgF$_2$. Phase transition to the orthorhombic δ-AgF$_2$ (Abma) infinite-layer form at ca. 15 GPa was predicted from DFT calculations. Here we utilize the previously derived structural data [15] to calculate the magnetic properties of δ-AgF$_2$ in the 0–54 GPa pressure range.

The values of J for δ-AgF$_2$ at two distinct pressures are given in Table 1. Pressure of 17 GPa is slightly larger than the onset of the phase transition [15], while 1 GPa corresponds to quenching of δ-AgF$_2$ to the near-ambient pressure conditions. The computed J is very large and negative (~227 meV to ~298 meV) indicating strong AFM coupling [16]; this is due to the presence of nearly linear AgF$_2$ bridges in the crystal structure of δ-AgF$_2$ [11]. They are similar to the Cu–O–Cu linkers in the crystal structure of oxocuprates, although the former ones are bent from 180°, while the latter are perfectly linear. Since DFT exaggerates the strength of magnetic interactions, it is fair to rescale the calculated J values by the factor of 3.5. The derived values of ~64 meV to ~84 meV are still large, and comparable with typical values found for the undoped compounds of the oxocuprate SCs [17] like La$_2$CuO$_4$ (~100 meV [18]). According to some theories of SC, this feature alone makes δ-AgF$_2$ a plausible candidate for the parent compound of a new high-temperature SC.

SC is usually generated in AFM oxocuprates (II) by an electron- or hole-doping. Chemical doping is very difficult for fluoroargentates, because it results in the localization of an extra charge in form of Ag$_I$ or Ag$_{III}$, respectively [2]. We therefore follow an alternative path of the frustration of the AFM order, namely that of pressure-induced metallization [19]. High pressures have been spectacularly applied to turn elemental B, S and O$_2$ into SCs [20] and even to force slightly underdoped cuprates into the SC state [21].

![Figure 1](www.pss-rapid.com) Comparison of the values of the second ionization potential for several metallic and non-metallic elements.

![Figure 2](www.pss-rapid.com) Electronic band structure close to $E_F$ (note two d(x^2−y^2) bands) and atomic DOS for δ-AgF$_2$ at (A) 17 GPa (AFM semiconductor) and (B) 38 GPa (metal). Partial DOS for one Ag and one F atom is shown in (A).
Figure 3 Two direct electronic band gaps at the Fermi level, \( \Delta E_f \), for the \( \delta\)-AgF\textsubscript{2} as a function of pressure, \( \rho \). Fractional coordinates of two high symmetry points in the Brillouin zone are shown in the inset.

In Fig. 2 we show the electronic band structure and the density of states (DOS) zoomed at the \( d(x^2-y^2) \) bands in the vicinity of the Fermi level, for the AFM \( \delta\)-AgF\textsubscript{2} in its primitive cell \( (Z = 2) \) at 17 GPa and 38 GPa.

The band structure of \( \delta\)-AgF\textsubscript{2} at 17 GPa confirms the electronic two-dimensionality of this compound, with some bands nearly flat along selected directions. Two direct electronic band gaps of similar size (0.25 eV) open at some bands nearly flat along selected directions. Two di-electronic two-dimensionality of this compound, with x via self-doping, i.e. delocalization of a d\textsubscript{xy} hole within the AgF\textsubscript{2} lattice. Ease of hole introduction into the fluoride band by the powerful oxidizer, Ag\textsuperscript{+\textsuperscript{0}}, provides for this [2].

In conclusion, the high pressure \( d \) form of AgF\textsubscript{2} \( (\rho > 17 \text{ GPa}) \) is a layered material with giant AFM ordering, as seen for the parent compounds of high-temperature oxocarbides SCs. \( \delta\)-AgF\textsubscript{2} is the first viable candidate for the non-oxocarbide transition-metal AFM; it could be turned into two-dimensional metal or possibly a superconductor, at accessible pressures of \( \sim 40 \text{ GPa} \).

Acknowledgements We thank KBN for the grant N204 167 32/4321 and acknowledge ICM for access to VASP.

References

[10] For consistency with the previously published results [2, 5, 6] we have applied DFT methods (VASP). We have used the Generalized Gradient Approximation with the PBE functional, 600 eV cutoff and \( k \)-point grids of \( 6 \times 6 \times 6 \) (Ca\textsubscript{2}AgF\textsubscript{4}) and \( 8 \times 12 \times 6 \) (AgF\textsubscript{2}) for the primitive cells of Ca\textsubscript{2}AgF\textsubscript{4} and of \( \delta\)-AgF\textsubscript{2} \( (Z = 2) \), see SI), and \( 6 \times 6 \times 10 \) for the \( \sqrt{2} \times \sqrt{2} \times 2 \) cell of CaCuO\textsubscript{2}. Spin polarization was enforced for the AFM and FM calculations. The recommended Wigner–Seitz radii of 1.34 Å (Ag) and 0.72 Å (F) were used.
[17] FM is not necessarily incompatible with SC:
[19] We note substantial reduction of the magnetic moment on Ag center in comparison with Ca\textsubscript{2}AgF\textsubscript{4}.
[20] The DFT methods based on Local Spin Density Approximation cannot reproduce the AFM ground state for CaCuO\textsubscript{2}; nevertheless, the correct results are obtained with the B3LYP functional or with the LSDA–U approaches. Compare: D. Singh et al., Physica C, 162–164 1431 (1989); H. Wu et al., J. Phys.: Condens. Matter 11, 4637 (1999); X.-B. Feng and N. M. Harrison, Phys. Rev. B 69, 132502 (2004). Our GGA calculations for CaCuO\textsubscript{2} have converged to the ‘nonmagnetic metal’ ground state, with the FM solution over 0.5 eV/Cu above. The difference between CaCuO\textsubscript{2} and \( \delta\)-AgF\textsubscript{2} suggests that the reasons beyond the AFM ordering of both materials may be of different nature.
[27] DFT tends to underestimate the electronic bandgap, but the highest-energy optical phonon (at about 70 meV for \( \alpha\)-AgF\textsubscript{2} at ambient pressure and even stiffer at \( \delta\)-AgF\textsubscript{2}; at increased pressure) might facilitate delocalization. Both effects affecting the metallization pressure, are likely to cancel.
[28] Pressure-induced metallization of oxocarbides has been successful only for partially chemically-doped systems: T. Cuk et al., APS March Meeting 2007, abstract #P13.007.