

Silverland: the Realm of Compounds of Divalent Silver—and Why They are Interesting

Wojciech Grochala¹ 

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Abstract In this personal account, the author takes readers on the journey to “Silverland,” i.e., the emerging field of electronic and magnetic materials based on divalent silver (Ag^{2+}). He blends historical background with the reasons which led him to become involved in this research, as well as to proposing (with Roald Hoffmann, 2001) that high- T_C superconductivity might ultimately be observed in doped Ag^{2+} fluorides. More recent experimental and theoretical findings related to novel compounds, and their electronic and magnetic structure, are presented.

Keywords Silver · Copper · Fluorine · Oxygen · Magnetic properties · Superconductivity

1 *Novecento*: Bits and Pieces of History

Together with isolation of elemental fluorine by Moissan in 1886 (Nobel Prize 1906) [1], entirely new chemistry became possible due to unusually high reactivity of this chemical element. Fluorine was fast recognized as “the most electronegative element” (or more precisely as the most electronegative among reactive elements); electronegativity is a desire for electrons from an atom’s surroundings. Thus, one

important advantage of fluorine is that it may force chemical elements into unusually high oxidation states; in other words, a larger number of valence electrons than these elements would normally donate to less aggressive nonmetals, may now be transferred to voracious electron-deficient fluorine atoms surrounding an element. Thus, some elements will exhibit more than one “typical” oxidation state in fluoride ion environment (SbF_5 vs. SbF_3 , TlF_3 vs. TlF , etc.). In most of these compounds, the *valence* electrons at the central atom differ in number, e.g., there are *two* (s and p) electrons in TlF but *none* in TlF_3 (assuming the ionic picture). Arguably, the most interesting cases are those when fluorine opens such electronic shell of an element, which is usually tightly closed. One good example is that of divalent silver (Ag^{2+}) compounds in which silver is pushed beyond the limit of classical “ionic” bonding (typical of monovalent silver, with its s and p shells predominantly involved in bonding). For example, in AgF_2 , silver opens its—otherwise very stable and quasi-core— d^{10} shell, which leads to electronic configuration of $4d^9$ at the central metal atom. In chemistry terms, fluorine degrades silver from a post-transition metal status to the genuine transition metal one, across the boundary between the 11th and 12th groups of the periodic table; thus, closed-shell Ag^{1+} is still like Cd^{2+} or Zn^{2+} (post-transition) but Ag^{2+} is already in one pot with Pd^{2+} , Cu^{2+} , or Ni^{1+} (d shell is now firmly open).

Obviously, the Ag^{2+} species are more rare than the common Ag^{1+} ones; currently, only about 100 compounds of Ag^{2+} and as many as over 16,000 of respective Ag^{1+} systems have been structurally characterized [2]. However, an effort paid to open the electronic 4d shell, and concomitant exoticism of Ag^{2+} species, come with a pleasant (but not unexpected) surprise: the involvement of a more contracted d shell in chemical bonding implies, by necessity, an increased covalence of chemical bonds, and that leads

This work commemorates the 150th birth anniversary of Maria Salomea Skłodowska (Madame Curie).

✉ Wojciech Grochala
w.grochala@cent.uw.edu.pl

¹ Centre of New Technologies, University of Warsaw, Żwirki i Wigury 93, 02-089, Warsaw, Poland

to a number of fascinating consequences for chemistry and physics of such species, as I will outline below.

The first compound of divalent silver, plain *silver difluoride* (AgF_2), has likely been prepared (but not recognized as having such stoichiometry) by Moissan himself; in 1891, he observed the formation of dark brown/black stains on the surface of silver metal treated with F_2 gas [3]. This observation is mentioned in later works [4]. However, a deeper insight into this reaction was gained ca. 40 years later, in 1933–1934 when Ebert et al. in the USA [4] and in parallel Ruff and Giese in Germany [5] prepared a larger batch of the product and correctly suggested the ratio of F to Ag atoms being 2:1. Aspects of preparative chemistry of AgF_2 were later summarized by Priest and Swinehart [6]. In the advent of the 2nd World War, an extremely talented and ambitious chemist, von Wartenberg, determined the heat of formation of AgF_2 and he confirmed that this compound is thermodynamically stable at ambient (p,T) conditions [7]. Determination of the crystal structure needed to wait for over 30 years though, i.e., until 1970 [8, 9], and the structure model [10] coming from a neutron study on a powder sample was confirmed another 20 years later by x-ray diffraction on a coincidentally obtained single crystal [11].

The strong fluorinating and oxidizing properties of AgF_2 were recognized early [4], but it was during and after the 2nd World War that reactivity of AgF_2 towards many materials was carefully tested [12]. Formation of AgF_2 (Fig. 1) may formally be viewed in ionic picture as a transfer of hole, \square , from p-type (on F atom) to d-type (on Ag atom):

$\text{AgF} + \text{F}^\square \rightarrow \text{Ag}^\square\text{F}_2$ (where F stands for fluorine atoms used in photochemical synthesis).

As expected for a process which is downhill in energy by as much as 2.4 eV (or 1.6 eV if undissociated F_2 molecules are used), the d hole in the AgF_2 product is less electron-hungry than the original p hole at the F atom, but nevertheless still very reactive—the fact which may be utilized in chemical synthesis. Formally, Ag^{2+} may be viewed as a free radical, similarly to an isolated F atom (Fig. 1); the

energy barriers for chemical reactions of free radicals are most often very low, which speeds up chemical reactions. Thus, AgF_2 was successfully applied as a fluorinating agent towards a range of inorganic and organic compounds, and it ranks second to none among common superior fluorine-transfer catalysts ($\text{AgF}_2 > \text{XeF}_2 > \text{CoF}_3 > \text{NiF}_2$, etc.) [13]. Such reactions may simply be conducted in a stream of F_2 gas, with a trace amount of Ag^{1+} as a catalyst precursor (AgF_2 forms in situ). However, many interesting chemical properties of AgF_2 were disclosed only after the 2nd World War [14], since strong fluorinating agents were used to prepare UF_6 for its further isotope separation during the Manhattan Project. Nowadays, AgF_2 finds wide use in laboratory synthesis (particularly in organic chemistry) with the annual production of ca. 100 kg worldwide, and being the only commercially available Ag^{2+} reagent. Some other compounds may be obtained on a 10–100-g scale [15], but usually, an extensive characterization of each new compound requires not more than 1 g of compound, and sometimes 100 mg may suffice.

The chemistry of Ag^{2+} derivatives has been beautifully developed in the post-war period 1950–2000, mostly by three groups: Hoppe and later Müller in Giessen, Bartlett and coworkers at Berkeley, and Žemva in Slovenia, the latter two in close collaboration (details are outlined in comprehensive review [16]). About 100 distinct chemical compounds evolved from this research, a great majority of them hosting only F atoms in the vicinity of a voracious Ag^{2+} center. Indeed, not many other atoms may withstand the request of Ag^{2+} to have its 4d shell filled back with electrons coming from its surroundings.

2 From Molecules to Solids

My own journey into Silverland has begun in 1999, without any knowledge of facts presented in the previous section, and it was quite unexpected for myself. Being brought up initially as a spectroscopist, and having defended my PhD thesis in surface-enhanced Raman spectroscopy in 1998, I was deeply fascinated by the phenomenon of vibronic coupling which is largely responsible for huge scattering enhancement in the resonance Raman effect. Simultaneously, it is also at the core of classical superconductivity as emphasized through the BCS model. The coupling of electronic and nuclear motion, dramatic breakdown of the Born–Oppenheimer approximation which as at the very core of chemistry (try to explain chemistry without actually drawing where nuclei and chemical bonds are. . .!), and the mathematical magic of *null* electric resistivity or *infinite* conductivity, jointly spelled a charm which I could not resist. You do not find *infinity* behind every corner. . .! One question which particularly baked my noodle at that time

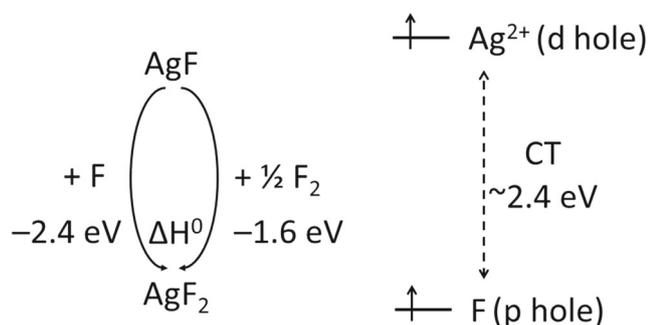


Fig. 1 (Left) Standard enthalpy of formation of AgF_2 (for two formation reactions) and (right) a crude picture of valence energy levels in Ag^{2+} fluorides

was to what extent could the electron–phonon coupling constant be enhanced, so it might lead to effective increase of the critical superconducting temperature, T_C (via exponential factor rather than linear pre-factor in the BCS equation for T_C). I was particularly interested whether there are any classes of chemical systems which are most worth looking at. However, the BCS theory does not have “materials aspect,” i.e., it uses vibronic coupling as a parameter rather than tells you how to maximize it in real systems. I could hardly find guidance from metals and alloys, since sometimes they show weak and sometimes stronger coupling, and this seems to be unrelated to their chemical composition in any obvious way. Only years later have I realized that the changing of an electron count (Matthias rules) may bring an alloy at the verge of lattice instability and helps to maximize the T_C value [17].

Under the patient tutorship of Roald Hoffmann (Nobel Prize 1981) at Cornell Univ., I largely truncated my original research project (single molecule detection with SERRS) planned for the first postdoctoral stay, and I started to look at simplistic triatomic systems—linear symmetric ABA molecules—for a very broad set of chemical elements, A and B. Such systems often contain an element with two different valencies; for example, NaClNa might formally be described as $(\text{Na}^+\text{Cl}^-)\text{Na}^0$, or rather a resonance between two such equivalent structures (for a symmetric molecule). I was interested whether valencies will tend to localize (this would indicate strong vibronic coupling) or rather stay at intermediate valence (this would point to an inverse scenario). These two situations may be viewed as a distant molecular model of a charge-density wave insulator, and of a metal, respectively. Localization would mean a tendency for a molecule to become asymmetric, i.e., A–B...A, and seen in the appearance of an *imaginary* antisymmetric stretching vibrational mode. The model was brutally simple; I enforced linear geometry, neglected any bending vibrons (even if imaginary), and used crude DFT functionals to calculate the force constant for the asymmetric stretching mode. This reductionism of this model was greatly criticized during the Hoffmann Group seminars, but I have stubbornly insisted that it contains all essential ingredients to understand vibronic coupling for electron-transfer processes via a bridge (it is similar to the Marcus model of electron transfer reactions, but again, this model has no “materials aspect” inbuilt). The simplicity of the triatomic model seemed also to appeal to Roald Hoffmann, great teacher and unreachable model-to-follow in popularization of science, my good mentor and friend, from whom I am learning to this day.

The following picture emerged: the most vibronically unstable molecules are free radicals which contain the most electronegative elements, preferably F, Cl, or H. Such systems are made up of relatively small atoms; their

valence electrons have a large binding energy and they reside in compact orbitals, and molecules consisting them very strongly tend to localize valencies. Another important observation was that A–B bonds should be covalent rather than ionic in order to increase propensity towards electron localization; thus, a B mediator mattered greatly for an electron transfer between two A centers. Those trends could be easily rationalized using the molecular orbital theory, even in its semiempirical extended Hückel theory version. Moreover, there seemed to be a natural link to successful copper oxides, where an undoped state is formally a free radical (Cu^{2+}), and there is excellent mixing of the Cu(3d) and O(2p) orbitals (hybridization, covalence). The strong mixing might actually generate a peculiar electronic situation where electronic bands of very different character cross at Cu–O separation which is within the reach of Cu–O stretching oscillations, thus leading to huge electron–phonon coupling, as first insightfully postulated by Burdett, a bright former coworker of Hoffmann [18]. This intuitive model, too, has served as a great inspiration in my quest [19]; so were interactions with the late Andy C. Albrecht, who knew a great deal of things about the vibronic coupling and used it to explain the resonance Raman effect.

These results of our research with Hoffmann were published in a series of five papers, which seem not to have inspired chemistry or materials science communities substantially [20]. Sadly, neither have Burdett’s beautiful ideas.

3 From Oxides to Fluorides

As I was already aware of many attempts at metallizing elemental H_2 , or achieving moderate T_C in hydrides (Pd, Th, etc.), with a large amount of literature available on this topic, and obviously an immense effort focused on copper oxides, I have turned my attention to rather unexplored fluoride systems. The question posed was whether one may find a suitable partner for fluorine, which could form sufficiently covalent bonding to it and even attempt to compete with it for electrons. Ideally, such a partner should be a free radical, i.e., have an odd number of valence electrons. It was clear that one must look for systems with large binding energy of valence electrons, since this is the most characteristic feature of electronegative fluorine.

I voiced the problem at the Hoffmann Group meetings, and the prevailing opinion was that there is no solution. Only genuine nonmetals were thought of as being capable of forming markedly covalent bonding to fluorine, with C–F bond being “the most peculiar of all bonds formed by carbon” (quoting Norman Goldberg). But there are no C–F–C links in nature, as F atom is always *terminal* at carbon. Similarly, many stable (CF_4 , XeF_2 , NF_3 , ClF_3) and even

thermodynamically unstable stoichiometries (OF_2 , O_2F_2) are known, but they all lack unpaired electron density, and these are molecular and not extended systems. The mixed-valence systems in this family are nearly unknown, but it is easy to imagine that they would be of the CDW type (say, a co-crystal of ClF_3 and ClF_5). In other words, the tendency for localization is too strong, and the chance for stabilizing a free radical in the crystal lattice is very small. Thus, to increase the chance for success, covalence should be somewhat decreased, e.g., by using electronegative metals as ingredients. Still, the remarkable molecules of which I then become aware (e.g., PtF_6 , the potent fluorinating agent which served to prepare the first noble gas compound) contained many F atoms crowded around a single metal center, and they formed molecular crystals (thus, they would be magnetic insulators at best).

For over month, I pursued a literature quest while looking for metal fluorides, in which metal centers could exhibit huge affinity for electrons and form extended lattices in which the metal–F–metal bridges would exist. I narrowed down the search to relatively low oxidation states (up to $3+$) so that extended networks might form instead of isolated molecules. Some systems were interesting for various reasons (TlF_3 , NiF_3 , CoF_3 , PdF_2 , etc., as outlined in a feature paper some years later [21]), but I was determined to find the best candidate of all.

4 From Smaller to Larger Electron Binding Energies

My quest was finally rewarded, when I came across beautiful papers by Bartlett, Žemva et al. [22]. These authors showed that a divalent silver cation is so potent an oxidizer that it may steal an electron from an O_2 molecule; thus, it is capable of doing the same trick as PtF_6 , but at a much lower formal oxidation state of a metal. None of the above-mentioned fluorides, possibly except NiF_3 , can have the same chemical reaction (but this has not been tried). It should be noted that the ionization potential of an O_2 molecule is as large as 12.2 eV, so the electron-acceptor species, Ag^{2+} , must show the electron affinity of at least the same size. This anomalous feature renders Ag^{2+} a very strong oxidizer in chemistry, one of the very few known [23]. Doing a careful literature search on Ag^{2+} systems, I have learned that they may form 0D, 1D, or even 2D lattices (thus, Ag–F–Ag bridges are found [16]) and that the second ionization potential of silver (which partly governs the formation of its compounds) approaches 21.5 eV in the gas phase, and it is by far the largest value among all metals (except, obviously, the alkali metals, which do not adopt divalent state in chemical compounds). Obviously, this value is reduced in solid state systems or in solution due

to the presence of electron pairs from the solvent or ligands (down probably to 9.0–12.5 eV, depending on a system, but these are huge values anyway). This unusual reactivity has inspired my mentor and friend, Roald Hoffmann, to write a popular-scientific account to *Scientific American* about higher fluorides of silver. In any case, the experimental observations assured me that Ag^{2+} compounds have partly filled valence orbitals at very large electron-binding energies, typical of nonmetals—just as requested in my search. While elemental silver is *not* the most noble metal, and it cannot compete with gold or platinum, yet its dication seemed to be apart from those of all other transition metals. Later, I have learned that quantum chemists have already been able to understand why Ag^{2+} is special, and wherefrom the stark differences between coinage metals originate [24].

5 From Hole on Metal to Hole on Nonmetal

An additional argument for studying Ag^{2+} fluorides came from ESR and optical studies of Moreno et al. on Ag^{2+} impurities in various crystalline hosts [25, 26]. It turns out that Ag^{2+} placed in ionic fluoride lattices shares a lot of its spin density with the neighboring F ligands. When placed in oxide, chloride, or bromide, matrices, it shifts most of the spin density to nonmetals, while attempting to fill the hole in its d^{10} set. This was a particularly dramatic exemplification of what divalent silver may do when surrounded by O or Cl atoms. These prototypical nonmetals seem not to be electronegative enough to withstand the presence of Ag^{2+} ! To put it another way: it is more fair to say that it is *magnetic chlorine or oxygen*, rather than *magnetic silver*, present in such impurity center. This explains the failure to dope copper oxides with Ag^{2+} in the early days of high- T_C superconductivity: diamagnetic Ag^{1+} was always the outcome, and O_2 was off [27]. Indeed, in Ag^{2+}/O systems, bond covalence and vibronic coupling are so strong that they lead either to electron-transfer process and/or to charge density wave—as for long-known AgO [28]. More recently, we have been able to show in theory and experiment that CDW does not disappear even at 100 GPa [29], which is quite a substantial pressure sufficient to metallize O_2 alone; related (as yet hypothetical) AuO should metallize at pressure as high as 330 GPa [30]. In the language of solid state physics, this means that the Mott–Hubbard on-site repulsion energy, U , is close to null or even negative in hypothetical Ag^{2+} oxides and chlorides (“negative U ” scenario). In any case, I have anticipated that the fluorine atom environment around Ag^{2+} is the only viable option for stable systems; this later proved to be correct albeit some metastable compounds bearing O or N atoms may be prepared quite easily.

6 From Colorless to Black

Metal fluorides are often colorless, as exemplified by broad band gap insulators such as NaF or CaF₂ (used as optical windows). The first hints that it is worth studying Ag²⁺ fluorides come from their color. While some are violet or blue (more on sky blue color anon) [31], those featuring direct Ag–F–Ag bridges are usually dark brown or nearly black. An intense color of AgF₂ should immediately suggest to Moissan that something very interesting is taking place. Indeed, most free radicals usually have low-lying electronic states, and Ag²⁺ has relatively low-lying d-d transitions at 1.5 eV and above. But charge-transfer states in these compounds are also found at anomalously low energies (as for fluoride materials). The thermodynamics of AgF₂ formation (assuming that the enthalpy of formation reflects mostly changes of electronic energy) leads one to an estimate of a CT gap between Ag and F of ca. 2.4 eV (Fig. 1). Coincidentally, this is similar to what is found in divalent copper oxides. We note here that while studying the optical spectra of many transition metal compounds, Jørgensen has introduced the concept of optical electronegativity (OEN) to explain the energies of CT bands [32]. Our analysis has shown that, remarkably, divalent silver fluorides and divalent copper oxides exhibit very similar difference of OEN between metal and nonmetal sites of 0.8–1.1 [16]. Thus, their CT gaps should be similar and rather narrow. This in turn suggests that metallization of Ag²⁺ fluorides via band closure might be facile, either by applying external pressure and/or possibly by doping.

7 From Thermally Stable to Unstable

The decisive argument for getting hands on Ag²⁺ fluorides came from previous studies of their hole-doped analogues, i.e., Ag³⁺ fluorides. While they do not have a free radical character (with one exception they contain low-spin Ag³⁺), they are likely even stronger oxidizers than their Ag²⁺ counterparts [33]. In fact, they are among the half dozen of the best oxidizers known to chemistry [23]. What is most striking, AgF₃ spontaneously decomposes thermally, while liberating F₂ at temperatures above –20 °C (!) [34] (again, only several chemical systems can do the same). This means that Ag³⁺ transfers its 4d holes back to F 2p manifold with enormous ease. Authors of [33] specifically state that in Ag³⁺ fluorides, the electronegativity of the metal center equals or surpasses that of the fluorine center. This is the kind of partner for fluorine which I was looking for from the very beginning...! What is more, this unusual behavior feature of Ag³⁺ is reminiscent of what happens upon hole doping to oxocuprates, where it was claimed by some authors that holes reside largely on O and not on Cu sites.

8 From Copper Oxides to Silver Fluorides

My literature quest for a “fluorine partner” has been unbiased, and it encompassed many different s-, p-, d-, and f-block elements, thus both main group as well as transition and post-transition metals. The fact that Ag²⁺—which is isoelectronic to Cu²⁺—has popped out seems to be a fortuitous but also fortunate coincidence, indeed. A similar electronic character of Ag²⁺ and Cu²⁺ (one hole in the d set) and those of F[–] and O^{2–} (s²p⁶ octet) as well as a similar energy difference of their valence electronic states (CT gap) suggested that many similarities may be expected in the electronic and magnetic structures between the two classes of materials: copper oxides and silver fluorides. We have already mentioned several of them. Indeed, chemistry freshmen are taught that to achieve similar chemical bonding one must provide that atomic orbitals have comparable energy differences, and comparable spatial overlap integrals. Guided by the expected similarity (Fig. 2), we have performed simple spin unpolarized density of states calculations for model Ag²⁺/F systems, and compared the results to those for Cu²⁺/O systems [16]. Numerous striking similarities were found including substantial hybridization of the d/p states and large dispersion (regions of low DOS) for the highest *e_g* bands for systems showing short Ag–F–Ag links. Moreover, Ag³⁺ systems showed even more pronounced hybridization.

All those similarities, taken together, helped us to build the claim that high-*T_C* superconductivity could be observed in doped fluorides of Ag²⁺ [16]. While this paper was in preparation, we had numerous thought exchanges with the late Müller, Bartlett, and Žemva (they are specifically

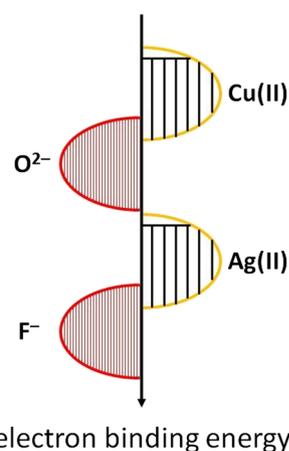


Fig. 2 Ideographic comparison of Ag²⁺/F[–] vs. Cu²⁺/O^{2–} analogy within the framework of spin-unpolarized MO theory applied for solids. The energy separation of Cu/O and Ag/F levels is similar; Cu²⁺/F[–] systems are ionic, while Ag²⁺/O^{2–} ones too covalent (and exhibit unfavorable redox reactivity as well as negative Mott–Hubbard *U* values)

quoted in [16]). It fast turned out that Bartlett, a very intuitive chemist, has considered the possibility that fluorides of silver may be superconducting. Knowledge that a very famous chemist had similar ideas (albeit without explicitly phrasing them in his papers) has served as a great encouragement to the (then) young postdoctoral associate. Regrettably, Neil Bartlett passed in 2008 and I could not benefit directly from his deep knowledge anymore. Anyway, I have firmly decided to focus my research on experimental investigations of these unusual materials.

9 “Paths of science are not always straight” (Roald Hoffmann)

Considering my second postdoctoral stay, I have been given an opportunity to join the group of Peter P. Edwards at the University of Birmingham (UK) in late 1999. Peter is the leading expert in metal-insulator transition (MIT) and superconductivity [35], now at Oxford; he ran at that time in Birmingham an ambitious inorganic chemistry group with access to diluted F_2 gas as a reagent and a nickel tube oven [36]. I have learned a great deal of hard and soft skills from Pete during his wise one-year guidance, and I appreciate the kindness which he and his wife Pat showed to my family during the stay in the UK.

While in Birmingham, I have pursued four main directions. (i) One was the preparation of $KAgF_3$ perovskite and attempts of its doping with Ba. (ii) Another was an attempt to generate $AgBeF_4$, hoping it would form a layered structure. (iii) The next one was search for experimental confirmation of marked covalence of chemical bonds in the Ag^{2+} fluoride systems. (iv) The last one was trying to understand electric and magnetic properties of Ag^{2+} fluorides.

(i) While doping of $KAgF_3$ perovskite has failed, I have learnt that Ag^{2+} fluorides are so reactive that they may corrode gold foil which I used to wrap the samples in. I recall showing the scraps of strongly corroded foil to Peter, who was greatly impressed, having dearly paid from his research funds for purchasing high-purity 5N foil. I have even observed red single crystals of what was presumably AuF_3 , and I was greatly impressed by the oxidizing ability of Ag^{2+} systems (about which I have previously only read). Losing part of Ag^{2+} from the $KAgF_3$ composition meant that the system becomes more KF-rich, and new phases may form. Indeed, I have observed the formation of $K_3Ag_2F_7$, as well as K_2AgF_4 double perovskite, the members of the so called Ruddsden–Popper series of layered intergrowth systems. Simultaneously, $KAgF_3$ was showed to be anti-ferromagnetic. The results of this research were published many years later [37], when a specialist in the Rietveld method, W. Łasocha, has proposed the models of the crystal

structures of $K_3Ag_2F_7$ and $KAgF_3$ based on powder x-ray data which I obtained in the UK. Simultaneously, the crystal structure of K_2AgF_4 was published coming from single-crystal x-ray diffraction [37]; this structure was later shown by us to be incorrect (more on double perovskites below).

(ii) The second direction led me to the preparation of black shiny polycrystalline and multi-phase samples (Fig. 3) which contained AgF_2 and various phases of BeF_2 (including an amorphous one), as well as unknown impurities. Many of these samples showed sudden drops of magnetic susceptibility upon cooling, reminiscent of the Meissner–Ochsenfeld effect [38] (<http://www.superconductors.org/64K.htm>). These dramatic changes of susceptibility were overlapped with the broad background typical of a weakly ferromagnetic AgF_2 precursor. Most samples showed anomalies at rather low temperature, 8–12 K, but some surpassed this range; the highest temperature for which the susceptibility drops were detected was 64 K. The volume fraction was very low (and impossible to determine, as suggested by Adrian Porch, since a possibly superconducting minority phase was embedded in the ferromagnetic host).

The chemical analyses (detection of trace elements with AAS) performed at the University of Nottingham have shown that the samples do not contain any meaningful copper impurities, and thus traces of oxocuprates can be ruled out. After a few years, W. Łasocha has managed to solve the crystal structure of the major impurity phase, which turned out to be Ag_2BeF_4 (isostructural to its Na analogue [39]). This, being a diamagnetic Ag^+ compound, could not be responsible for the observed magnetic anomalies. Moreover, the x-ray powder diffraction patterns showed the presence of very small reflections from yet another phase(s), which was(were) not identified to this day. An attempt to perform electron diffraction within the TEM at David’s Jefferson laboratory at the University of Cambridge has shown that all Ag-bearing compounds present in the sample get reduced to beautiful hexagonal nanocrystallites of silver metal when

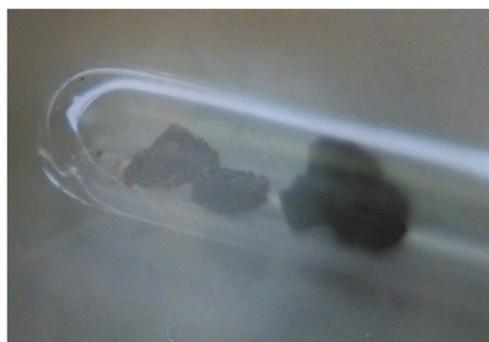


Fig. 3 Photograph of the AgF_2/BeF_2 sample showing the magnetic susceptibility anomaly at 64 K, and enclosed in dry quartz glass container

placed in the electron beam; use of the smallest nanocurrents available has not improved the situation, since the electron affinity of Ag^{2+} species towards unbound electrons is simply large. Anyway, the preliminary results on $\text{AgF}_2/\text{BeF}_2$ phases were published in 2004 [38] and encouraged me to further pursue the promising Ag^{2+} fluoride domain.

(iii) The experiments resulting in the corroded gold foil put in doubt any attempts to directly measure dc transport properties of Ag^{2+} compounds by attaching metal electrodes to them, since the electrode surface would react and become passivated by insulating metal fluorides (or so I thought at that time). This was similar to difficulties reported by Bartlett years later ([16] and references therein). Therefore, we have used the microwave cavity perturbation technique set up by Adrian Porch to assess the electronic properties of AgF_2 and KAgF_3 . The experiments have shown that AgF_2 is an insulator, and its conductivity decreases only slightly below the magnetic phase transition at 165 K [40]. Many years later (using impedance spectroscopy, i.e., an ac technique to tunnel the current through the insulating fluoride layers), we have shown that the actual activation energy for conductivity of bulk AgF_2 is ~ 0.6 eV and this may be partly attributed to ionic conductivity or to excitations from Ag^{1+} defects [41]. On the other hand, the resonance bandwidth measured for KAgF_3 showed a large change at the temperature of its magnetic transition (64 K) and it seemed that KAgF_3 could even be metallic close to or above its Néel point [40]. In view of our later findings, this conclusion seems now to be incorrect (more on this below) but the effects are certainly worth to be carefully reinvestigated and reinterpreted.

10 From Ionic to Covalent

(iv) The fourth direction pursued by me while in Birmingham were attempts of determining the covalence of the Ag–F bonding in silver fluorides, and thus verify the conclusions coming from my earlier DFT calculations [16]. While there are different measures of covalence, the absolute values are difficult to be assessed for extended solids, where broad electronic bands may be present. It seemed more sensible to systematically compare covalence in the series: Ag^{1+} , Ag^{2+} , and Ag^{3+} , hoping that trends may be more clearly seen. While AgF , silver monofluoride, and AgF_2 , silver difluoride, were commercially available, the last member of the trio was not. The preparation of Ag^{3+} salts required either using the high pressure of F_2 gas or performing photochemical reactions in anhydrous hydrogen fluoride (aHF); both methods are dangerous and require specialized equipment and extensive know-how, which is available in just a few laboratories in the world. Bartlett's lab

at Berkeley was already closed after he retired, and Müller was about to retire, so I have contacted Boris Žemva at Jožef Stefan Institute in Ljubljana. Žemva's laboratory has continued research traditions of his predecessor, Slivnik, who pursued fluorine chemistry and was involved in ambitious (and failed) Tito's plans to assure a nuclear bomb for the former Yugoslavia (hence fluorine chemists were desired).

It turned out that young research associate Zoran Mazej is interested in preparation of Ag^{3+} salts for my purpose. In Zoran, I have found a very careful, enthusiastic, and fearless researcher, a trusted collaborator, and ultimately a friend. All successes and failures of our preparative Ag^{2+} chemistry reported since 2003 [42] should be credited to our tight collaboration.

Mazej has suggested that preparation of AgF_3 is useless, due to its inherent lack of stability. The compound would decompose before it would be delivered to the UK. Instead, he proposed that we study KAgF_4 , still immensely reactive but more stable Ag^{3+} fluoride system. With KAgF_4 prepared, we could finally compare the three oxidation states of silver as planned. To gain insight into covalence, Edwards has contacted Russ Egdell at Oxford Univ.; Egdell is an expert in XPS spectroscopy and he proposed an experiment using the best-resolution machine at that time, available in Daresbury National Laboratory. I was afraid, though, that the experiment could fail because the samples might decompose fast, even if enclosed in the airtight container. Courier delivery was ruled out, the samples were too precious. Pete Edwards has provided the solution: he ordered an ultra-fast luxury transport service for myself and the samples. It was the only time in my life when I travelled in an immense VW limousine having a black suit-wearing chauffeur and feeling like royalty. After a 1.5-h drive, we reached Daresbury; the chauffeur opened the door and took the sample container with such distinction as if it contained Her Majesty's favorite cat. This is the kind of treatment one was getting from Peter! Russ and I could immediately transfer the samples into the XPS chamber using the argon-filled glove-bag. The whole operation from me loading the samples inside the glovebox in Birmingham to safely placing them inside XPS machine at Daresbury took no more than 2 h.

The XPS study [42] showed very good agreement with my previous DFT calculations, which was very encouraging. Specifically, we have observed that $\text{Ag}(4d)$ electrons mix with the $\text{F}(2p)$ ones quite weakly in AgF , as expected. Only 10% of $\text{Ag}(4d)$ states are found in the group of bands placed at higher binding energy (BE) (where mostly $\text{F}(2p)$ states are found). However, this dramatically changes when silver is pushed beyond the limit of classical “ionic” bonding via opening of the d shell. For AgF_2 , already 1/3 of the 4d states sit in the high-BE bands and they mix heavily with the $\text{F}(2p)$ states, which indicates marked covalence of Ag–F bonding (Fig. 4).

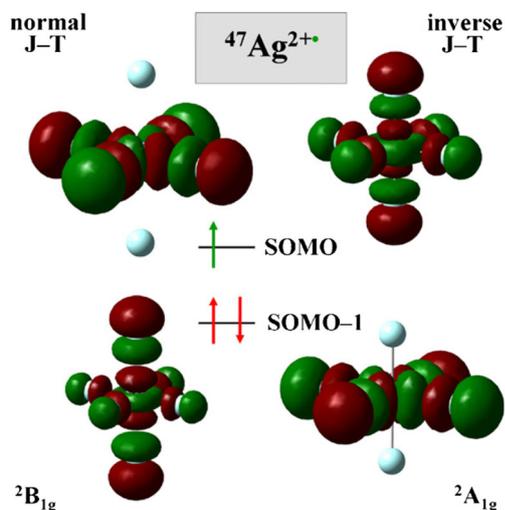


Fig. 4 Ag^{2+} cation shows a remarkable flexibility of its first coordination sphere and can exhibit either a normal or an inverse JT effect. The arrangement of the two uppermost d orbitals in the elongated O_h ($4 + 2$) ligand field (normal JT effect, left) and in the compressed O_h ($2 + 4$) ligand field (inverse JT effect, right). Note the transfer of a very large share of spin density on F atoms. Reproduced with permission from [43]

The most unusual result was seen for KAgF_4 ; it turns out that 60% of $\text{Ag}(4d)$ states go to higher BE bands, while only 40% remain in the lower BE region. This indicated that holes are largely transferred from Ag^{3+} to F^- , just as expected based on DFT calculations. The case of this Ag^{3+} salt is now quoted as a rare example of “inverse ligand field” in chemistry [44], certainly the first of its kind seen in experimental studies for *fluoride* materials. The effects seen before for Ag^{2+} and chloride, bromide, and oxide hosts [25, 26] belong to the same family of “inverse ligand field” systems.

11 From Blue to Sky Blue

In late 2000, I have returned to Warsaw, wishing to continue doing science in my homeland, and I started work at the University of Warsaw, my alma mater, in February 2001. Establishing my own laboratory at the Faculty of Chemistry has proved to be more difficult than preparing high-valence silver compounds, but in 2004, I submitted my habilitation thesis (D. Sc., an equivalent to tenure in the US system); since fall 2005 I could pursue fully independent research and promote PhDs.

My new laboratory was finally established at the *mathematical* institute and a supercomputer center (ICM, Interdisciplinary) thanks to the courageous vision of Lucjan Piela, my friend, and mutual agreement between Grzegorz Chałasiński, the Dean of the Faculty of Chemistry, and

Marek Niezgodka, the fearless director of ICM who did not mind hosting an experimental laboratory (!). The Laboratory of Technology of Novel Functional Materials which I am heading exists to this day (since 2012 within premises of the Center of New Technologies).

Still in 2003, I have finally visited my Slovenian colleagues in Ljubljana, and I have finally met Zoran Mazej in person. I could then observe the beautiful sky blue solution of Ag^{2+} hexafluoroantimonate, $\text{Ag}(\text{SbF}_6)_2$, in anhydrous HF solvent (Fig. 5). It was immensely similar to that of Cu^{2+} sulfate solution in water, known to all young chemistry adepts (as well as to the color of water in a beautiful Slovenian river, Soča). I have realized that the ligand field exerted by six O-terminated ligands on an isolated Cu^{2+} center, and the one imposed by six F-terminated ligands on Ag^{2+} , must be similar, and this adds to a large number of previously mentioned similarities between Cu/O and Ag/F systems. The subsequent research showed this surmise to be correct, with the parameters governing the splitting of d orbital sets being similar in both families of compounds [45]. Still, the Jahn–Teller effect is somewhat stronger in Ag^{2+} than in Cu^{2+} compounds, by a factor of up to 1.3 [45]. The stereochemical activity of the dz^2 lone pair is therefore larger for silver than for copper, and the vibronic effects for the hypothetical undistorted octahedral coordination also follow the same trend. The 10Dq factor is also somewhat larger for Ag^{2+} , by a factor of up to 1.5, but varies from one system to another.

12 From Low to High Pressure

Conscious of the impact which elevated pressure may have on the metal-insulator transition as well as generation of

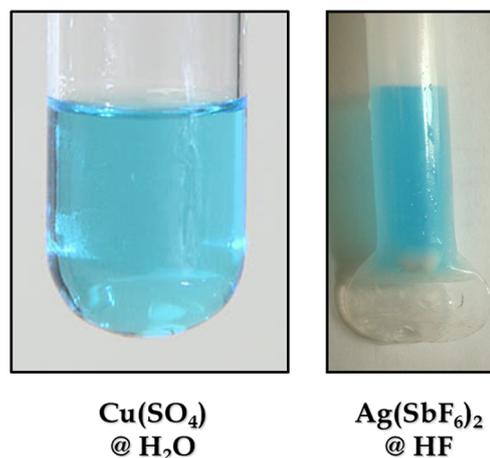


Fig. 5 Photographs of solutions of Cu^{2+} ions in water (glass tube) and Ag^{2+} ions in anhydrous HF (semitransparent fluoropolymer tube). Both ions are in homoleptic ligand environment, $[\text{MX}_6]$ (Color Online)

superconductivity, and aiming at metallization of Ag^{2+} fluorides, in June 2004, I have contacted several experts in the field of high pressure at the Geophysical Laboratory, Carnegie Institution of Washington (USA). One of them, Viktor V. Struzhkin, was very interested in pursuing the research for Ag^{2+} fluorides, and he invited me to visit GL in July 2004. Viktor proved to be an extremely patient, careful, and experienced researcher originating from the famous Russian school of high pressure research in Troitsk, and an extremely pleasant companion. Viktor was aware of the immense reactivity of Ag^{2+} materials but nevertheless was determined to confine them.

Our actual joint research commenced in 2006, when Viktor visited my laboratory in Warsaw to load the samples of AgF_2 into the diamond anvil cell (DAC). The painstaking research continued over a decade, with many samples of Ag^{2+} compounds loaded into DAC but turning into diamagnetic Ag^{1+} upon squeezing, in contact with the gasket material, diamond surface, and traces of humidity in the pressure medium. Pursuing this kind of research would definitely be impossible without Viktor's patience and persistence. Chemical reactivity greatly complicated x-ray diffraction patterns (diffraction reflections being broad anyway due to a certain pressure distribution), the samples containing two and up to five phases. Occasionally, we were successful in retrieving fundamental information about the behavior of some Ag^{2+} systems at high pressure; for example, we have learned that a strong Jahn–Teller effect persists in antiferromagnetic AgSO_4 up to at least 300,000 atm [46]. More recently, thanks largely to the involvement of my bright collaborator, theoretician Dr. Mariana Derzsi (who has been able to correctly predict the phonon-driven lattice instabilities), and hard detectivistic work of my PhD student, Adam Grzelak (who fitted the crystal structures to powder x-ray diffraction data), we have finally gained insight into the structural phase transitions and properties of high-pressure phases of AgO [29] and (after a decade of studies) of AgF_2 [47].

13 From Spin-Unpolarized Picture to Magnetic Ag^{2+} . . .

In 2006, an interesting paper was published by McLain et al. [48]. These authors have been able to show that Cs_2AgF_4 shows an antiferrodistortive pattern of elongated $[\text{AgF}_6]$ octahedra and thus it is a quasi-2D ferromagnet with a rather small value of the magnetic superexchange constant, J , around 5 meV. This work forced me to leave the comfortable premises of the spin-unpolarized MO theory [16] and think more deeply about magnetic properties of Ag^{2+} fluorides and the structure–property relationships. It seems that the $\text{Ag–F} \dots \text{Ag}$ bond length alternation within the $[\text{AgF}_2]$

sublattice, albeit seemingly small, is responsible for the observed FM rather than desired AFM spin ordering [49]. Our own studies of related double perovskite M_2AgF_4 systems conducted a decade later with the great help from experts on high-field ESR spectroscopy, Andrew Ozarowski and Steve Hill from MagLab in Tallahassee (USA), have shown that an antiferrodistortive order inevitably persists for $\text{M} = \text{K}, \text{Rb}, \text{Cs}$ [50]. Thus, these M_2AgF_4 systems are dissimilar to La_2CuO_4 in terms of crystal structure and magnetic properties. This may be expressed in the language of chemistry by saying that the formally neutral $[\text{MF}]$ charge reservoir layers found in M_2AgF_4 systems exhibit too high Lewis basicity, and this enables Ag^{2+} to coordinate F atoms from these layers very closely; given the propensity of Ag^{2+} cations towards the “normal” Jahn–Teller effect, this in turn induced the short–long bond pattern within the $[\text{AgF}_2]$ sheets and affects magnetic properties. On the other hand, the positively charged (LaO^+) layers do not release oxide anions and the adjacent $[\text{CuO}_2^-]$ sheets are anyway electron rich, hence apical O atoms in La_2CuO_4 are distant from the metal enter (or even absent in Nd_2CuO_4 or CaCuO_2), and the ferrodistortive order of $[\text{CuO}_6]$ octahedra persists leading to AFM ordering.

Despite these differences, the theoretical studies by many groups have led to the conclusion that the Mott–Hubbard U is of the order of 5 eV in Ag^{2+} fluorides. Given a much smaller CT gap of ca. 2.4 eV (Fig. 1), this clearly suggested that these materials are charge transfer insulators—similarly to copper oxides, but unlike most other magnetic metal fluorides, which are Mott–Hubbard insulators. The calculations for AgF_2 performed later by my talented PhD student, Dominik Kurzydłowski, have confirmed that indeed this is the case [45, 51]. A crude estimate of the CT gap may be obtained using the so-called standard redox potentials for the $\text{Ag}^{2+}/\text{Ag}^+$ (~ 1.98 V) and F^0/F^- (~ 3.87 V) one-electron redox pairs [23]; one obtains the value of ~ 1.9 eV which turns out to be similar to that measured for Cu^{2+} oxides (1.72.0 eV).

But how strong magnetic superexchange could be achieved in Ag^{2+} fluorides? To answer this question, we have focused our attention on AgF_2 , the only fluoride of Ag^{2+} which does not have any charge reservoir layers and does not exhibit alternation of the Ag–F bond length with its (puckered) $[\text{AgF}_2]$ sheets, which was the key for achieving 2D AFM ordering [49]. AgF_2 has been known for 40 years to exhibit strong 2D AFM interactions [8, 52, 53] with small spin canting [54], and it seemed to be a very promising system for this study. In late 2006, I asked my (then) MSc student Tomasz Jaroń to calculate the electronic and magnetic structure of the hypothetical flat-layer form of AgF_2 , which we anticipated from an earlier research could be adopted at high pressure. Given the very limited computational resources available to us at that time, we have

used standard DFT within the GGA approximation [55]. The result has surpassed my expectations: the flat layer form of AgF_2 was supposed to show an intra-sheet antiferromagnetic superexchange constant J of the order of 300 meV, and a huge reduction of magnetic moment down to $\sim 0.2 \mu_B$, as typical for strongly coupled AFM materials. These results were immensely promising, inspired our experimental search for strongly coupled AFM materials, and simply kept us going. They also prompted me to write a short poetic *laudatio* of Ag^{2+} fluorides which was refined with the help of my British PhD student, Andy Churchard, and first presented during the 2010 fluorine chemistry meeting in Ljubljana, and which is reproduced in [45].

After several years, when the supercomputer resources available to us at ICM have greatly improved, these calculations were repeated using the DFT+U method [51]. Quite recently, after hybrid DFT functionals such as HSE06 have been introduced to commercial DFT codes (VASP, etc.), the calculations were performed again. All results have shown that—as we have anticipated [55]—standard DFT exaggerates the strength of superexchange interactions in Ag^{2+} fluorides by the factor of 1.5–3.0 times (depending on the system), but the more realistic estimates still render the hypothetical flat-layer forms of AgF_2 the immensely strongly coupled 2D AFMs with intra-sheet J of 140–200 meV [56]. Clearly, these values are reminiscent of those measured for layered copper oxides, the well-known precursors of high- T_C superconductors. More on that anon.

14 . . . and Back Again to a Metal

But could Ag^{2+} fluorides be metallized and turned into a superconductor? Could the $\text{Ag}(4d)$ electrons in the x^2-y^2 band be itinerant rather than localized via magnetic interactions? Our early GGA calculations suggested the ease of metallization of AgF_2 already at a pressure as low as 38 GPa. This value, again, seems to reflect the limitations of the DFT in its standard GGA formulation, and must be considered as too optimistic. In view of our recent experimental and theoretical results [47], even pressure of ca. 80 GPa does not lead to metallization of AgF_2 but rather to its transformation to odd low-dimensional structures which should be magnetic insulators. Thus, direct pressure-induced metallization of undoped Ag^{2+} fluorides via band overlap seems currently to fall into the over 1-Mbar regime. However, if a sufficient amount of doping is achieved, the superconducting state might appear even in the underdoped regime, via application of external constraints, just like for Cu^{2+} oxides [57, 58]. However, all these predictions came from theoretical calculations. An experiment was desperately needed to confirm or refute them.

15 Doping: from Charge Density Wave to Intermediate Valence

So what about doping to Ag^{2+} fluorides? My preliminary analysis in 2001 [16] has detected several problems with the realizing of a genuine doping. The most important one comes from the fact that the first coordination spheres of Ag^{1+} , Ag^{2+} , and Ag^{3+} are usually very different from each other. Within the ramifications of the Marcus theory of electron transfer, this implies that the on-site “reorganization energy” will be large, and the defect may tend to localize. This would lead to the appearance of high-DOS states within the band gap at the Fermi level, but not to metallization. Two cases are known of mixed-valence silver fluorides ([16] and references therein), i.e., severely hole-overdoped Ag_2F_5 and Ag_3F_8 —both show CDW. Electron-doped systems were not known, but some were postulated based on preliminary DFT calculations [59]. They, too, correspond to excessive doping and are supposed to show disproportionated character. However, the first electron-doped Ag^{2+} complex fluoride, $\text{Ag}_3(\text{SbF}_6)_4$, was accidentally prepared by Dr. Mazej [60]. Interestingly, it seemed at the beginning that the Ag^{2+} and Ag^{1+} cations occupy the same crystallographic position, which would render the system metallic; yet no metallic shine was observed. It turns out that this is in fact a CDW paramagnetic system with disorder, and a large energy of the inter-valence CT excitation (ca. 3.1 eV). It will not be easy to metallize this kind of system by applying external pressure.

16 From Theory to Experiment

The first decade of the twenty-first century has witnessed great positive changes in Poland, and an increased funding for science. In 2009, I have received TEAM grant from the Foundation for Polish Science (FNP), and managed to gather sufficient manpower to continue experimental research. Moreover, in 2010, my laboratory was among those which greatly benefited from large structural funds coming from the European Union (CEPT project). The combined experimental/theoretical team (senior researcher Dr. P. Leszczyński; postdoctoral associates Dr. M. Derzsi, Dr. A. Budzianowski; PhD students P. Malinowski, D. Kurzydłowski, and several MSc students) focused their attention on compounds of Ag^{2+} in F [61, 62], O [63, 64], N [65], and Cl [66] environment, by reinvestigating several poorly known systems and preparing or theoretically hypothesizing a few novel ones. The continued funding was later assured by the newly formed (2010) national state agency for funding of scientific research, Polish National Science Center (NCN), via grants OPUS and HARMONIA, with more enthusiastic young researchers onboard (P.

Połczyński, T. Gilewski, T. Michałowski, J. Gawraczyński, A. Grzelak, and others).

The first nice result was the theoretical prediction by M. Derzsi in 2009 that AgSO_4 should consist of genuine Ag^{2+} rather than being CDW, in contrast to AgO , its more Lewis-basic analogue (the results were published a year later [63]). Indeed, the first preparation of AgSO_4 was achieved in 2010 by P. Malinowski [64]. This compound showed a range of peculiar properties, but the most important one in the context of Ag^{2+} research was the observation of the well-developed maximum of the magnetic susceptibility. Zvonko Jagličič, the Slovenian physicist who was involved in this research, has fitted the susceptibility to the Bonner–Fischer model of a 1D AFM and obtained the magnetic superexchange constant of ca. 18 meV. This was an appreciable value, similar to that for NiO , but more impressive given that (i) Ni^{2+} has two unpaired electrons per site and not one, as Ag^{2+} , and (ii) the superexchange pathway in NiO consists of a monoatomic O bridge at a favorable angle, 180° , while AgSO_4 exhibits much longer and bent $-\text{OSO}-$ bridges. This was clearly a promising result. In the meantime, we learnt that the 2D system containing pyrazine, an organic ligand (one of the very few compounds which may be achieved via wet chemistry methods), exhibits J of ca. 4 meV [67]. This is a large value given that the superexchange propagates via the complex σ MO manifold of the ligand ($-\text{NCCN}-$). Our own results (P. Leszczyński) showed that the as-obtained compound is unstable and it slowly decays in time [65]. It was necessary to turn back to the smallest monoatomic bridge withstanding the presence of Ag^{2+} —fluorine.

Attempts to form $\text{KAgF}_3/\text{KZnF}_3$ intergrowth structures gave an unexpected result. Double perovskite, K_2AgF_4 , turned out to be metastable, and it readily collapsed to quasi-1D polymorph upon heating [61]; see also [50]. The 1D polymorph was not useful from the viewpoint of fluoroargentate(II)/oxocuprate(II) analogy, and our attention has turned to KAgF_3 . Our previous results have indicated that it adopts a distorted quasi-3D perovskite lattice, was antiferromagnetic, and exhibited huge spin polarization at F sites [37]. However, its preparation method suffered from the formation of an undesirable FM K_2AgF_4 minority phase (due to an excess of KF formed in situ just like in early experiments described in Section 8); this affected the precise determination of magnetic susceptibility in the high- T regime, where a constant Pauli-paramagnet-like dependence was previously observed [40]. I have come up with a new synthetic method which involved the preparation of a pure KAgF_4 salt of Ag^{3+} and its controlled thermal decomposition. Zoran Mazej has immediately tested this simple idea, and it proved to lead to satisfactory results: a very pure KAgF_3 specimen was obtained. My PhD student, D. Kurzydłowski, has used our brand new and very sensitive vibrating SQUID magnetometer and observed that

magnetic susceptibility actually *rises* as T is increased in the high- T region. This was the very tail of the Bonner–Fischer maximum, from which an approximate value of the superexchange constant was estimated to reach ~ 100 meV [62]. This was a large value, indeed, and its order of magnitude finally fell into the range of our early optimistic estimates [55]. Moreover, computational resources then available allowed us to calculate J more precisely, and the satisfactory agreement with the experimental value was readily obtained. KAgF_3 was soon described as the most strongly coupled system featuring the monoatomic F bridge [68].

Following the Goodenough–Kanamori rules, D. Kurzydłowski has insightfully proposed to look at Rb and Cs analogues of KAgF_3 , since they should exhibit Ag–F–Ag links closer to linearity than the one seen for K salt [51]. This, indeed, was a good and straightforward concept and a further increase of J by up to 60% could be expected [51]. However, I had an alternative but also simple idea for an even stronger J value.

17 From Large Covalence to Strong Magnetic Superexchange

The geometry of the first coordination sphere around a metal cation depends on many, sometimes mutually opposite factors, involving Coulombic effects, bond covalence (orbital overlap), steric repulsion of lone pairs on ligands approaching the metal center, etc. However, a simple final picture usually results, in which the increase of the coordination number (CN) leads to an elongation of all bonds on the average. This may be illustrated by the tabularized ionic radii of selected metal cations, say Li^+ . For a CN of 4, the ionic radius of Li^+ (R_4) is 0.73 Å, but it systematically increases for larger CNs ($R_6 = 0.90$ Å, $R_8 = 1.06$ Å). One is tempted to say that a smaller number of stronger interactions is equivalent to a larger number of weaker interactions. Another way of saying that is that an electron-deficient metal center ensures a certain quasi-constant electronic density from ligands, in an attempt to equalize its chemical potential with the environment.

There are many manifestations of this rule, including, inter alia, so-called hypervalent bonding [70], *trans* effect [71], and Jahn–Teller effect [72]. All result in a characteristic plot of the respected bond lengths resembling a hyperbola, just like in the famous case of the “plasticity” of the coordination sphere of Cu^{2+} [72]. Ag^{2+} is obviously no different (Fig. 6) [69].

Considering that a typical coordination sphere of Ag^{2+} takes the form of a distorted octahedron, in order to provide the shortest bond lengths possible (and thus the strongest electronic and magnetic interactions), one must focus on

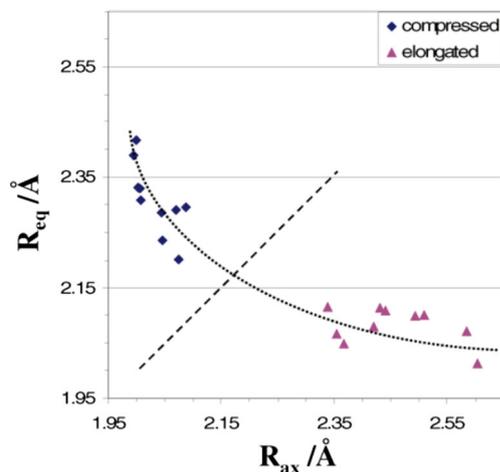


Fig. 6 Dependence between R_{eq} and R_{ax} Ag–F bond lengths for about 20 fluorides of Ag^{2+} . The broken line is drawn for $R_{ax} = R_{eq}$; the dotted line is a guide to the eye. Reproduced with permission from [69]; for an update, cf. [45]

the 2(+4) case (compressed O_h) rather than the 4(+2) case (elongated O_h). Indeed, the Ag^{2+} fluorides showing the 2(+4) coordination have the short Ag–F bond lengths of about 2.0 Å, while the shortest bonds in the 4(+2) case are usually by 10% longer. Overlap and hopping integrals strongly depend on the Ag–F distance, so $\sim 10\%$ difference is large (recall *huge* dispersion of the $d(z^2)$ band seen in spin unpolarized calculations [16]). I tend to phrase this as a *Two legs good, four legs bad* (aka *anti-Orwell*) scenario.

Obviously, the extended case of the two-partner case may be realized only in a 1D material (Fig. 7), while the four-partner one may be featured in both 1D and 2D materials. However, one particular disadvantage of 1D systems featuring the unpaired electron density in the x^2-y^2 orbital is that large spin polarization is seen at two F centers which do not participate in bonding in the direction of chain propagation; thus, some spin density is “lost” and cannot interact effectively through orbitals with the one on neighboring sites. This is why, I thought, the $d(z^2)^1$ systems are preferred for hosting strong superexchange.

In the case of Ag^{2+} fluorides, the uppermost point in Fig. 6 which corresponds to two very short Ag–F bonds, four very long secondary Ag...F interactions (thus the most pronounced inverse Jahn–Teller effect), and fortunately a nearly linear Ag–F–Ag bridge, belongs to $AgFBF_4$. This compound contains the 1D AgF^+ chain (Fig. 7) and auxiliary BF_4^- anions.

When challenged by me with the proposal of $AgFBF_4$ as a host of huge J , my coworker D. Kurzydłowski rushed to calculate the magnetic superexchange constant. His preliminary results using the GGA+U method have shown that J should be larger than that calculated for $CsAgF_3$, and it may reach as much as 300 meV; if confirmed in

the experiment, this would constitute the actual record of this parameter for all known chemical compounds. The more careful calculations using the hybrid HSE06 potential gave an even larger value, but their parametrization to the known systems resulted in a very similar scaled value of J as for the DFT+U calculations [73]. Simultaneously, the expected magnetic anisotropy seemed to be very pronounced, as well [74]. The calculations have shown that $d(z^2)^1$ systems showed, on average, larger magnetic anisotropy than their $(x^2-y^2)^1$ counterparts [74]. Simultaneously, the former exhibit more dramatic J dependence on the Ag–F–Ag angle, which is not unexpected [73]; bending of the F bridge in the $d(z^2)^1$ system leads to a dramatic loss of overlap of “linear” $d(z^2)$ and $p(z)$ valence orbitals. However, old data from Bartlett and colleagues [75] pointed to the metallic nature of $AgFBF_4$ and Pauli paramagnetism at high temperatures. It seemed that this case may be similar to that of $KAgF_3$ (described above) which was erroneously considered to be metallic but turned out to be very strongly coupled 1D AFM; in any case, the discrepancy called for an explanation.

18 From Chemistry to Physics

Wishing to confirm the large predicted J values in experiment, I tried to learn methods which could be helpful in this respect. Numerous experiments were performed since 2013 for a large batch of $AgFBF_4$ synthesized laboriously and rigorously by Zoran Mazej, in collaboration with several excellent physicists from the UK and USA, but they failed to deliver the expected result. In late 2016, I have turned to optical methods, in which I was trained since my MSc and PhD studies; they have previously proved effective

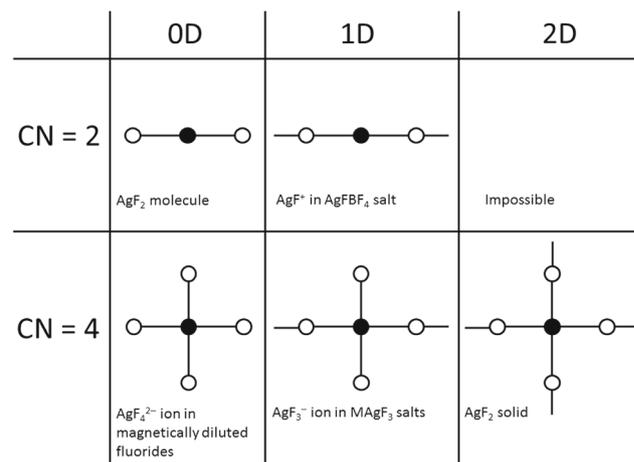


Fig. 7 Bonding scenarios for two- and four-partner interactions in 0, 1 and 2 dimensions

in establishing the J values for oxocuprates in both 1D [76] and 2D [77, 78] systems. In early 2017, I have contacted José Lorenzana, excellent theoretical physicist of Argentinian origin working in Italy, and with his guidance, our experimental data collected by my hardworking PhD student, Jakub Gawraczyński, for 1D AgFBF₄ and for 2D AgF₂, could finally be rationalized and will be published soon.

19 The Prospect

A chemist's viewpoint on the fascinating phenomenon of superconductivity is not necessarily different from those of his physics colleagues—it is simply expressed using a different language. Physics is certainly chemistry's "older sister" among sciences, but both fields have developed their own languages to describe matter. But the key differences between these two strongly related branches of science may be reduced to language, as well as to preference for real space (chemistry) vs. reciprocal space (physics) formulations. Yet superconductivity often arises at the intermediate doping levels where both points of view are fuzzy but nevertheless they should eventually meet.

It is relatively easy to think how to maximize T_C in a known class of materials. However, a scientist trying to come up with an entirely novel family of superconductors faces a wall of problems. The key one is that physical theories usually do not have a materials aspect, i.e., there are no obvious prescriptions what particular blend of chemical elements and in which structural arrangement should generate the desired properties contributing to high- T_C SC. As Neil Ashcroft used to joke (quoting one of his collaborators), all theories of high- T_C SC contain at least one parameter: the T_C value. So one simple idea is to use a bigger hammer and scale things up: get to more strongly bound electrons at deeply lying Fermi levels, provide the ingredients and environment where vibronic coupling may be strong, and set these heavy electrons into motion.

Within the BCS theory, in order to maximize T_C , metallic precursors are needed showing high DOS at the Fermi level and simultaneously very strong vibronic effects. However, the existence of such materials is limited by the maximum hardness principle [79–81] since such metals would be electronically very soft [82] and prone to lattice distortions which minimize DOS or even open the band gap [83, 84]. These problems may partially be circumvented by the application of external pressure [85], but metastability of such materials at 1 atm conditions is questionable.

Here, I have presented an account of my personal involvement into the chemistry and physics of Ag²⁺ compounds, notably Ag²⁺ fluorides, from the perspective of the nearly two decades of research in the field. I have outlined

the reasons for interest in these materials and how I have come to explore them. Having studied diverse Ag²⁺ systems, I am still amazed at what physicochemical properties they have and how many applications they might find if only their chemical reactivity was easier to tame. One important application which comes to mind is introducing Ag²⁺ as a spin polarizer in Ln³⁺ systems with the goal in mind to generate more persistent magnetic memory—this line will now be pursued in collaboration with Zoran Mazej as well as Paul Kögerler (Germany).

Obviously, the ultimate goal is to achieve moderate doping levels to stiff 2D Ag²⁺ fluoride lattices, and—while benefiting from both lattice and spin degrees of freedom [2, 16, 18]—possibly fulfill a dream of the high- T_C superconductivity in these materials. AgF₂ here could be considered—in oxocuprate notation—as a (001) material which lacks any other chemical ingredients except those which make up [CuO₂]-like sheets. One pathway to pursue is to generate complex stoichiometries where the [AgF₂] sheets could preferably be made flat, kind of intergrowth structures [86, 87], and dope them chemically. Another is to explore thin (maybe even monoatomic) layers of AgF₂ on appropriate substrate materials, say with molecular beam epitaxy, and attempt an electric field-driven charge-injection. The list of substrates which will resist the presence of Ag²⁺ is very narrow, but some are very promising [88]. One might also try to introduce a substantial number of defects into AgF₂ via irradiation with a large-energy electromagnetic wave and/or ionic bombardment; some of this has already been tried [89]. One may also try to dope AgF₂ directly (or one of its high-pressure forms, if it could be quenched [47]). Ag²⁺ fluoride materials are certainly a promising candidate to thoroughly investigate within some kind of "materials genome" initiative [90].

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The quantum mechanical calculations were performed at first using a small Unix machine in Roald Hoffmann's lab at Cornell, and since 2002 at the supercomputers of the ICM, Univ. of Warsaw, Poland, most recently from ADVANCE PLUS project (GA67-13).

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