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The Theoretical Quest for Sulfate of Ag^{2+}: Genuine Ag(II)SO$_4$, Diamagnetic Ag(I)$_2$S$_2$O$_8$, or Rather Mixed-Valence Ag(I)[Ag(III)(SO$_4$)$_2$]?

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In an attempt to extend the chemistry of Ag^{II} compounds to novel ligand environments, we have examined various polymorphs of an as yet unknown compound of AgSO$_4$ stoichiometry by means of a quantum chemistry DFT approach. Since AgSO$_4$ has not yet been prepared, we were interested whether genuine divalent silver, Ag^{II}, could be stabilized in the presence of sulfate (SO$_4{}^{2-}$) anions or whether it would rather have a tendency toward disproportionation to Ag^{I}/Ag^{III} (as known from binary oxide, "AgO") or maybe toward the formation of peroxodisulfate (S$_2$O$_8{}^{2-}$) of Ag^{I}. Considering all important electromeric forms, Ag^{II}SO$_4$, Ag^{I}Ag^{III}(SO$_4$)$_2$, and Ag$^{I}{}_2$S$_2$O$_8$, in a variety of crystal structures, we examined their dynamical (vibrational) stability and discussed the most stable phases from the point of view of structural features thought to be crucial for appearance of high-T_C superconductivity. We show that a compound of a nominal stoichiometry, AgSO$_4$, should most likely be a genuine paramagnetic sulfate of divalent silver which forms 3D ...Ag−O−S(O$_2$)−O... networks, and—unlike CuSO$_4$—shows no direct connections of paramagnetic Ag^{II} centers via Ag−O bridges. This must lead to low electronic dimensionality and concomitant low potential for the appearance of high-T_C superconductivity. Finally, we discuss structural features of the most stable phase of AgSO$_4$ predicted here in a broader context of crystal structures of group 11 metals.

Introduction

The chemistry of Ag^{II} is an exciting and still largely unexplored research field. It is especially the chemistry of Ag^{II} fluorides [fluoroargentates(II)] that has been developing vividly for a couple of decades.[1] The main interest in these systems since 2001 comes from realizing their potential for crystal-engineering of novel high-T_C superconducting (SC) materials.[2] Most striking are their similarities to the well-known SC oxocuprates, namely, that (i) the rather exotic spin-1/2 4d^9 Ag^{II} and s^{2}p^6 F$^-$ are isoelectronic with more common Cu^{II} and O^{2-}, respectively, (ii) Ag−F bonds exhibit considerably covalent character[3] similar to the Cu−O frameworks, and (iii) fluoroargentates(II) often form either infinite [AgF]$^+$ chains or [AgF$_2$] sheets, the latter being in close structural relation to the [CuO$_2$]$^{\delta-}$ sheets found in SC oxocuprates.

Although the exact mechanism of high-T_C SC is still unknown, it is generally believed that strong 2D antiferromagnetism (AFM) within the [CuO$_2$]$^{\delta-}$ layers is one of the essential aspects of the phenomenon.[4] It has been experimentally shown that fluoroargetates(II) can exhibit very diverse magnetic behavior ranging from para-, to ferro-, to antiferromagnetism due to an odd number of d electrons at silver occupying σ* orbitals, substantial covalence of Ag−F bonding, and a diverse topology of [AgF$_x$] frameworks.[3,5] One of the most recent theoretical findings concerns the simplest among fluorides of Ag^{II}, binary AgF$_2$. The Density Functional Theory (DFT) calculations suggest that AgF$_2$ should undergo a phase transition at ~15 GPa from the α structure showing infinite puckered sheets into the δ one consisting of flat [AgF$_2$] layers; the 2D topology of the high-pressure polymorph favors extremely strong AFM superexchange (J = −298 meV).[6] It has been predicted that δ-AgF$_2$ should become metallic or possibly even SC under

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elevated pressure (> 40 GPa) via self-doping.[5,7,8] This is an exciting result indicating that chemical doping (nonstoichiometry) may not be necessary for reaching SC in simple fluoroargentates(II), just like in the case of self-doped superconducting MgB_2.[9]

Unfortunately, high pressure experiments for AgF_2 and crystal engineering of layered 2D AFM fluoroargentates(II) remain a great challenge since these compounds are very strong oxidizers capable of oxidizing components of the diamond anvil cell; they are also extremely sensitive to moisture.[10] A natural question thus arises, whether the chemistry of Ag^{II} could be extended beyond fluoroargentates in the context of achieving high-T_C SC.

Keeping in mind the large oxidizing power of Ag^{II} as a limiting factor in the preparation of novel compounds of divalent silver, one might use oxide and chloride as ligands of choice next to fluoride. Unfortunately, it turns out that Ag^{II} easily oxidizes chloride ligands,[11] while it readily disproportionates to Ag^I and Ag^{III} in an oxide environment.[12] Our attention has thus concentrated on a ternary anionic oxa ligand—sulfate (SO_4^{2-}). The first question which awaits answering is whether Ag^{II} can indeed be stabilized in this ligand environment and, if not, what would be the preferred oxidation state of silver. Recent analysis of thermodynamic data suggests that SO_4^{2-} should be resistant to oxidation by Ag^{II}.[13] However, it is still unclear if the experimentally observed inertness of many sulfates to AgF_2 even at 300 °C[10] is a purely kinetic or rather a thermodynamic effect. The issue is even more complicated when recalling the preference of silver for a mixed valence state in simple oxides ($Ag^IAg^{III}O_2$). In other words, it is unclear if a compound of nominal stoichiometry "$AgSO_4$" would be a genuine paramagnetic $Ag^{II}SO_4$, a diamagnetic $Ag^I{}_2S_2O_8$ (silver(I) peroxodisulfate), or rather a mixed-valence $Ag^I[Ag^{III}(SO_4)_2]$ (silver(I) disulfatoargentate(III)).

Attempting to address these issues, we have applied a solid state quantum chemistry approach for the prediction of crystal structure and selected properties of the as yet unknown "$AgSO_4$". We have analyzed close to 20 hypothetical polymorphs of this compound taking into consideration all important electromeric forms: $Ag^I{}_2S_2O_8$, $Ag^{II}SO_4$, and $Ag^IAg^{III}(SO_4)_2$. We discuss here these phases from the point of view of structural and electronic features thought to be crucial for the appearance of high-T_C SC. All polymorphs have been tested for dynamic stability via calculations of their phonon dispersion.

Theoretical Calculations

Results presented in this study are based on solid-state calculations done within the DFT framework using the projector-augmented wave method (PAW)[14] as implemented in the Vienna *ab initio* Simulation Package (VASP).[15] For the exchange-correlation part of the Hamiltonian, the generalized gradient approximation (GGA)[16] has been applied. Full geometry optimization was performed with the SCF convergence criterion set to 10^{-5} eV. The ionic relaxation was continued until the forces on individual atoms were less than 0.02 eV/Å. The spacing between the k-points for the k-point mesh generation was *ca.* 0.5 $Å^{-1}$. In the initial step, the valence electrons were described by plane waves with a kinetic energy cutoff of 400 eV; all dynamically stable output structures were then recalculated with a higher cutoff of 600 eV yielding a good energy convergence of 1 meV/atom.

We have observed that allowing for spin polarization does not lead to remarkable modifications of structural features or the energy of polymorphs studied here; this can be understood if one recalls that magnetic coupling usually constitutes a very small contribution to electronic energy. Indeed, calculations for two benchmark systems, paramagnetic $CuSO_4$ and diamagnetic $AuSO_4$ (see section 3), have showed that their experimental structures indeed constitute the lowest energy polymorphs of these compounds. In addition, the first coordination spheres of both cations are nicely reproduced by our calculations (cf. the Supporting Information, SI) with the shortest transition metal−oxygen distances overestimated by a factor of 3%, as typical for GGA calculations. Similar good accuracy has been obtained for a prototypical mixed-valence system, $Ag(I)Ag(III)O_2$ (see SI). As a consequence, all results reported here have origins in non-spin-polarized GGA calculations.[17,18]

Ultrasoft Vanderbildt type pseudopotentials have been used to describe atomic cores. Test calculations for $AuSO_4$ have shown that the Au−Au bond length, a good sensor of relativistic effects, has been overestimated in our calculations by a mere 2.2%.

The energy landscape of a solid at given stoichiometry may be very complex, so a multitude of chemically reasonable minima should be probed. The strategy of obtaining the dynamically stable structures used in this work relies not only on a rich selection of starting structures (this has been

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(17) In systems with unpaired and d electrons, spin polarization and strong electronic correlations play an important role. Although in $Ag(II)SO_4$ with its one unpaired d electron both factors come into play, their inclusion is crucial when reproducing electronic and magnetic structure but not necessarily crystal structure. Our spin-polarized GGA+U calculations support this fact, showing that electron polarization and strong correlations indeed do not cause considerable structural changes to the structures studied here. Since our work is focused on finding the characteristic structural features of $AgSO_4$, we have omitted spin polarization as well as strong electronic correlations from the current calculations.

(18) It should be realized that spin-unrestricted calculations may in principle favor low-spin structures, such as diamagnetic Ag(I) (d^{10})/Ag(III) (low spin d^8) and Ag(I)/peroxo ones. However, since the main conclusion of this work is that these electromeric forms are disfavoured with respect to Ag(II) sulfate, then adding spin polarization might only stabilize the Ag(II) formulation even more, thus supporting our conclusion.

Table 1. The Most Important Features of the Dynamically Stable Polymorphs of $AgSO_4$[a]

no.	E_r	$(E+ZPE)_r$	coord.[b]	d(Ag−O)[c]			O_T	N_O	N_{SO2}	type
1	0	0	sp	**2× 2.189** **2× 2.181**	**2× 2.156** **2× 2.239**		0	0	3	$Ag^IAg^{III}O_2$
2	4.8	3.7	sp (O_e)	**2× 2.180**	**2× 2.229**	2× 2.987	0	0	3	$PdSO_4$
3a	5.3	3.9	sp (O_e)	**2× 2.217**	**2× 2.221**	2× 2.670	1	1	2	$CuSO_4$
3b[d]										$K^IAl^{III}(SO_4)_2$
4	6.4	7.1	sp (O_e)	**2× 2.103** **2× 2.233**	**2× 2.216** 2× 2.353	2× 2.964 2× 2.898	0	0	3	$Ag^ICu^{III}O_2$
5	7.0	6.3	sp (O_e)	**2× 2.195**	**2× 2.217**	2.839, 2.855	1	1	2	$AgSO_3F$
6	7.7	6.9	sp (O_e)	**2× 2.211**	**2× 2.233**	2× 2.729	1	1	2	$AgHSO_4$
7	11.1	10.0	sp (O_e)	**4× 2.286**		2× 2.511	2	1	2	$NiSO_4$
8	15.8	14.2	def-sp (O_e)	**2.201, 2.199, 2.240, 2.263**		2.656, 2.763	1	0	2	$AgMnO_4$
9	19.0	17.2	butterfly	**2× 2.214**	2× 2.338	2x 2.509	2	0	1	Ag_2SO_4
10	20.7	21.0	sp [$AgAgO_3$]	**2.098, 2.105, 2.195**		2.668, 2.813	1	0	2	$AuSO_4$
11	21.1	19.6	butterfly	**2.209, 2.212**	**2× 2.231**	-	2	1	2	$ThSiO_4$
12	22.7	20.9	linear (O_c)	**2× 2.170**	2.388, 2.887	2× 2.535	2	0	1	Ag_2CrO_4
13	23.4	21.2	butterfly	2× 2.307	2× 2.310	2× 2.481	0	0	3	$CdSO_4$
14	27.1	25.3	T-shaped	**2.285**, 2.457, 2.546, 2.856		**2× 2.184**	2	0	1	$LiSO_3F$
15	32.4	31.3	butterfly	**2.140, 2.142**	2. 366, 2.388		2	0	1	$KReO_4$
16	41.9	41.3	Ag^I: [AgO_8] Ag^{III}: sp		8× 2.715 (Ag^I) **4× 2.076** (Ag^{III})		2	0	0	$K^IBr^{III}F_4$
17	53.3	52.6	[AgO_6]		6× (2.415−2.780) (Ag^I)		3	0	0	$K_2S_2O_8$

[a] Relative energy per one formula unit $E_r = (E_i - E_0)$ [kJ/mol] where E_i is total energy of the ith polymorph and E_0 is the energy of the energetically most stable polymorph, relative $(E+ZPE)_r$ [kJ/mol] (calculated in an analogous way to E_r but the ZPE correction was additionally applied), type of coordination around silver (coord.), Ag−O distances within the 3 Å[26] coordination sphere of Ag (d(Ag−O) [Å]), number of terminal oxygen atoms in the sulfate group (O_T), and number of dimensions in which the $(Ag-O-)_\infty$ chains (N_O) and $(Ag-O-S-O-)_\infty$ network (N_{SO2}) propagate (cf. text for details). The last column shows the structure type, from which the respective polymorph was derived. Note, there are two non-equivalent Ag atoms in structure No. 4. [b] sp, square planar; def-sp, deformed square planar; O_e, elongated octahedron; O_c, compressed octahedron. [c] The Ag−O distances shorter than 2.3 Å have been marked in bold fonts. [d] Entries for polytype 3b are essentially identical to those for 3a, and they have been omitted.

frequently used in the past[19]) but also on following vectors of those normal modes which exhibit imaginary frequencies in their calculated phonon spectra.

Dynamical stability was probed by phonon calculations. The phonon dispersion curves and values of zero−point energy (ZPE) corrections were obtained using the direct method as implemented in the PHONON program.[20] Only for the calculation of E_{ZPE} ($= 1/2\,h\nu$) for $^3O_2$ have we used the experimental value of its stretching frequency, 1580 cm^{-1}.

An analogous approach has been successfully applied in the past for AuF,[21] XeAuF,[22] and SiH_4.[23]

Constructing Structural Models

Since $Ag^{II}SO_4$ has not yet been prepared, we have searched crystallographic databases for various known compounds of the ABO_4 stoichiometry, which could possibly lead us to the desired structure. Following criteria usually applied in such a search (similarities in ionic radii, coordination spheres, oxidation states, etc.), we have selected 10 structure types ($NiSO_4$, $PdSO_4$, $CuSO_4$, $AuSO_4$, $CdSO_4$, $AgMnO_4$, $ThSiO_4$, $KReO_4$, $LiSO_3F$, and $AgSO_3F$) and built the initial models by atomic substitutions (Ni, Pd, Cu, Au, Cd, Th, K, Li → Ag; Mn, Si, Re → S; F → O). Three other models were obtained by introducing ordered defects in the crystal structures of three compounds of Ag^I: Ag_2SO_4, Ag_2CrO_4 (removing half of the silver atoms), and $AgHSO_4$ (removing all protons). We have also considered the peroxo connection of Ag^I (one distinct model, $K_2S_2O_8$[24]) and few mixed valence Ag^IAg^{III} species (four different models were obtained from $K^IAl^{III}(SO_4)_2$, $Ag^IAg^{III}O_2$, $Ag^ICu^{III}O_2$, and $K^IBr^{III}F_4$ structure types by atomic substitutions, for example, K → Ag, $O^{2-} \rightarrow SO_4^{2-}$, and $2F^{1-} \rightarrow SO_4^{2-}$, wherever applicable, and concomitant expansion of the unit cell).

In this way, we have screened a broad spectrum of distinct structure types containing Ag atoms in various bonding environments and exhibiting coordination numbers from 2 to 8.

Results and Discussion

1. Dynamically Stable Polymorphs. We have begun screening of the potential energy surface of $AgSO_4$ with 18 starting structure models of $AgSO_4$, and every model led to one dynamically stable polymorph. Some structure types required many steps of optimization and consecutive calculations of phonon dispersion; some others showed dynamic stability already in the first step. Interestingly, appreciably different $KAl(SO_4)_2$- and $CuSO_4$-type input structures, representing, respectively, mixed valence and intermediate valence forms of $AgSO_4$, resulted in an identical output structure with one unique silver atom per formula unit (FU; entries 3a and 3b in Table 1). The ZPE-corrected energies of all polymorphs

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[19] The GGA-PAW with ultrasoft relativistic pseudopotentials and plane wave basis is now a method of choice for screening various polymorphs of the known and as-yet unknown compounds. For BeH_2 and SiO_2, see: Hantsch, U.; Winkler, B.; Milman, V. *Chem. Phys. Lett.* **2003**, *378*, 343−348. For $LiAlH_4$ and Li_3AlH_6 see: Løvvik, O. M.; Opalka, S. M.; Brinks, H. W.; Hauback, B. C. *Phys. Rev. B* **2004**, *69*, 134117. For AlH_3 at high pressure, see: Vajeeston, P.; Ravindran, P.; Fjellvåg, H. *Chem. Mater.* **2008**, *20*, 5997−6002.

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[24] Note that a "sulfate anion-radical" $M(I)(SO_4^{-\bullet})$ formula is one reasonable electromeric form of $AgSO_4$. Indeed, such a possibility is the most likely one for an isolated $AgSO_4$ molecule in the gas phase (Grochala, W. *Inorg. Chem. Commun.* **2008**, *11*, 155–158). However, formation of a direct O−O peroxo bond in the solid state (or even in a molecular dimer) will certainly be favored due to stability of the O−O bond. Therefore, the $M(I)(SO_4^{-\bullet})$ formulation is represented in this work by the $M(I)_2(S_2O_8)$ one.

Table 2. Crystallographic Data for the 17 Dynamically Stable Polymorphs of $AgSO_4$[a]

no.	type	SG	D (g/cm^3)	a (Å)	b (Å)	c (Å)	α, β, γ (deg)
1	$Ag^{I}Ag^{III}O_2$	$I41_a$	3.70	10.560	10.560	13.115	
2	$PdSO_4$	$C2/c$	3.62	8.148	5.655	8.176	96.4
3	$CuSO_4$	$Pmna$	3.90	8.775	7.446	5.290	
4	$Ag^{I}Cu^{III}O_2$	$P2_1/c$	3.70	8.722	4.881	9.561	59.7
5	$AgSO_3F$	$P2_1/m$	3.95	5.497	7.558	8.333	82.1
6	$AgHSO_4$	$Pnma$	4.00	16.557	7.473	5.477	
7	$NiSO_4$	$Pca2_1$	4.08	10.476	7.233	8.759	
8	$AgMnO_4$	$P1$	3.99	10.751	8.167	8.861	60.8
9	Ag_2SO_4	$Fdd2$	3.87	12.046	5.500	10.566	
10	$AuSO_4$	$Pbca$	3.67	9.182	8.618	9.334	
11	$ThSiO_4$	$P\bar{1}$	3.79	5.969	5.637	6.339	102.8, 82.0, 63.4
12	Ag_2CrO_4	$Pnma$	4.19	9.390	6.632	5.187	
13	$CdSO_4$	$Pmn2_1$	4.26	6.587	4.894	4.929	
14	$LiSO_3F$	$C2/c$	4.03	8.874	8.056	10.016	110.0
15	$KReO_4$	$P4_1$	4.09	4.593	4.593	15.708	
16	$K^{I}Br^{III}F_4$	$I4/mcm$	3.68	6.169	6.169	19.357	
17	$K_2S_2O_8$	$P\bar{1}$	3.96	5.858	4.932	6.310	102.8, 78.7, 82.2

[a] Space group (SG), calculated density (D), and cell parameters (a, b, c, α, β, γ). Angles are not listed whenever equal to 90°. For fractional atomic coordinates see the .cif files (SI).

Table 3. Silver Coordination Types and Respective Ag−O Distances in Known Silver Oxides[a]

cation type	structure	coordination	d(Ag−O) [Å]
Ag^{I}	Ag^{I}_2O	linear	2× 2.047[27]
	$Ag^{I}Ag^{III}O_2$		2× 2.179[28]
	$Ag^{I}Cu^{III}O_2$		2× 2.178[29]
	$Ag^{I}_2Cu^{II}_2O_3$		2× 2.073[30]
Ag^{II}	$Ag^{II}(Ag^{III}O_2)_2$	deformed square planar	2.052, 2.055, 2.075, 2.086[31]
Ag^{III}	$Ag^{II}(Ag^{III}O_2)_2$	square planar	2× 2.021, 2× 2.041[24]
	$Ag^{III}_2O_3$	square planar	1.98, 2× 2.03, 2.04[32]
	$Ag^{I}Ag^{III}O_2$	square planar	2× 2.013, 2× 2.054[21]

[a] Only the shortest Ag−O distances are listed.

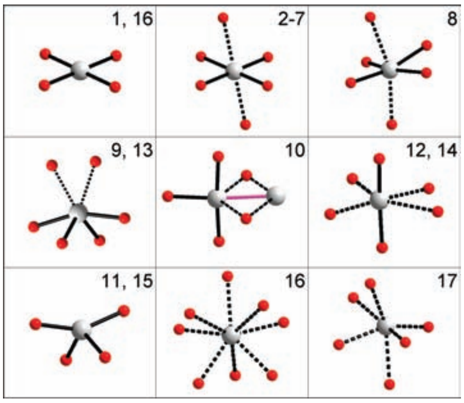

Figure 1. Coordination sphere (< 3 Å) around silver atoms observed in the dynamically stable polymorphs: silver, large gray atoms; oxygen, small red atoms. The Arabic numbers refer to the numbering of polymorphs with respect to their energies (cf. Table 1). Full line, short Ag−O distances (< 2.3 Å); dashed line, long Ag···O contacts (> 2.3 Å).

are similar (Table 1), the energy difference between the most and the least stable forms being *ca.* 53 kJ/mol per FU; the seven most stable polymorphs fall within the narrow 10 kJ/mol energy window, thus within the error margin of the method. In the analysis to follow, we will concentrate predominantly on these seven lowest energy structures.

1.a. The First Coordination Sphere and the Oxidation State of Ag. It is very instructive to examine first the coordination sphere of silver and its relationship to metal's oxidation state for all dynamically stable polymorphs of $AgSO_4$ (Table 2).[25]

We note here that a nice correlation exists between the oxidation state of silver and the shape of its first coordination sphere (Table 3). While large Ag^{I} is usually coordinated linearly by its ligands, smaller Ag^{II} and Ag^{III} prefer a square planar (i.e., a considerably distorted octahedral) coordination. These preferences are of value for analysis of the possible electromerism for $AgSO_4$: Ag^{II}/O^{2-} vs $Ag^{I}_{0.5}Ag^{III}_{0.5}/O^{2-}$ vs Ag^{I}/O^{1-}, as they will help us to detect the presence of Ag^{I} in selected polymorphs.

In Figure 1, we show all types of Ag coordination spheres observed in dynamically stable polymorphs studied here (nos. 1−17). Since the polymorphs are arranged in the order of increasing energy, it is clear from Figure 1 that, as the coordination sphere around the silver atom deforms from square planar, the energy of the respective polymorph increases. First, the equatorial $[AgO_4]$ coordination changes from nearly ideal square planar (nos. 1−7) to nonplanar, and the axial O−Ag−O axis starts to bend (no. 8). Next, it changes to a 2 + 2 + 2 coordination type (no. 9), and then more exotic Ag coordination spheres evolve. For example, in polymorph no. 10, each silver atom is square-planarly coordinated by three oxygens and one silver atom and more weakly by two additional oxygens (shared by two Ag atoms) in a plane perpendicular to that of the $[O_3Ag{-}Ag]$ unit. This coordination is then followed by an even less energetically stable contracted octahedron with positions of equatorial oxygens very much deformed from the square plane (nos. 12 and 14), then by the $[AgO_4]$ butterfly (no. 11 and 15), and finally by the $[AgO_8]$ polyhedron (no. 16); for the highest energy polymorph, a coordination far from octahedral $[AgO_6]$ is seen (no. 17).

In the case of polymorph no. 10, pairs of silver atoms form an unusual $Ag^{II}{-}Ag^{II}$ chemical bond with d(Ag−Ag) = 2.637 Å, just like for its $Au^{II}SO_4$ precursor where the short $Au^{II}{-}Au^{II}$ bond has been experimentally

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(25) As a reviewer correctly reminds us, using just the coordination geometry and bond lengths for assigning oxidation states may sometimes lead to pitfalls and misassignments. However, in the case of $AgSO_4$ stoichiometry, this task is simpler, since the presence of Ag(III) requires the presence of an equal stoichiometric amount of Ag(I) (with its most characteristic dumbbell coordination sphere). In other words, if there is no Ag(I) in the structure, there is not Ag(III) either, and the oxidation state of silver may safely be assigned as Ag(II).

(26) A majority of coordination spheres of Ag(II) listed here as "square planar" may in fact be classified as "elongated octahedral", with axial distances ranging from 2.51 to 3.40 Å. Here, we omit very weak secondary bonding (> 3 Å) for the sake of brevity. Note that the Jahn−Teller effect is usually much stronger for Ag(II) than for Cu(II) (*cf.* Grochala, W. *Phys. Stat. Sol. B* **2006**, *243*, R81–R83). Indeed, square-planar coordination is found for selected compounds of Ag(II), such as $BaAgF_4$ and related systems (ref 2).

(27) Niggli, P. *Z. Kristallogr.* **1922**, *57*, 253–299.

(28) McMillan, J. A. *J. Inorg. Nucl. Chem.* **1960**, *13*, 28–31.

(29) Curda, J.; Klein, W.; Jansen, M. *J. Solid State Chem.* **2001**, *162*, 220–224. Curda, J.; Klein, W.; Liu, H.; Jansen, M. *J. Alloys Compd.* **2002**, *338*, 99–103. Munoz-Rojas, D.; Oro, J.; Gomez-Romero, P.; Fraxedas, J.; Casan-Pastor, N. *Electrochem. Commun.* **2002**, *4*, 684–689.

(30) Gomez-Romero, P.; Tejada-Rosales, E.; Palacin, M. R. *Angew. Chem., Int. Ed.* **1999**, *38*, 524–525. Munoz-Rojas, D.; Fraxedas, J.; Oro, J.; Gomez-Romero, P.; Casan-Pastor, N. *Cryst. Eng.* **2002**, *5*, 459–467.

(31) Standke, B.; Jansen, M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 77–78. Standke, B.; Jansen, M. *J. Solid State Chem.* **1987**, *67*, 278–284.

observed. Our calculations indicate that divalent silver cations of $AgSO_4$ are also capable of adopting this coordination type, but it comes with an energy price of over 0.2 eV per FU with respect to the most stable polymorph.

Another interesting polymorph (no. 16) contains silver atoms with two very different coordination spheres. Half of the silver atoms are coordinated by eight oxygens with long Ag−O distances of 2.715 Å (this range of distances is typical for Ag^{I} in a cubic oxide environment[33,34]), while the other half are coordinated square-planarly with very short Ag−O distances of 2.076 Å (characteristic for Ag^{III}). This implies that polymorph no. 16 is a mixed valence (+1,+3) species. Indeed, this is the only mixed-valence polymorph of $AgSO_4$ we have detected in our calculations. Its high energy compared to the most stable computed polymorph (ca. +0.4 eV per FU) suggests that, interestingly, $AgSO_4$ will not have a tendency to disproportionation, in striking contrast to the more basic "AgO" = $Ag^{I}Ag^{III}O_2$ oxide.

Finally, unique polymorph no. 17 contains peroxo bridges with a characteristic O−O bond length of 1.525 Å and six O atoms quite far from Ag (at 2.415−2.780 Å). This is the least stable form of "$AgSO_4$" detected in our calculations. This computational result suggests that Ag^{II} is not sufficiently a strong oxidizer to oxidize the SO_4^{2-} anion to peroxodisulfate species; indeed, the reverse process (oxidation of Ag^{I} by $S_2O_8^{2-}$) is often observed in experiments.[35]

For the seven lowest energy polymorphs (out of total 17), Ag atoms are square-planarly coordinated by oxygen atoms (Figure 1) with typical Ag−O bond lengths of 2.10−2.29 Å. Somewhat shorter distances around Ag^{II} (2.05−2.09 Å) are found experimentally for $Ag^{II}[Ag^{III}O_2]$ (note that GGA usually overestimates bond lengths by up to 3%, corresponding here to ∼0.06 Å, which explains the observed discrepancy). For six of these seven polymorphs, silver is additionally coordinated by two oxygens found at an appreciable distance from Ag (2.68−2.99 Å) and completing an elongated octahedron (4 + 2). Such a first coordination sphere of silver must correspond to the second oxidation state of this metal.

In summary of this section, we should say that the vast majority of our starting models, including the mixed valence ones, converged to polymorphs containing divalent silver (oxidation state +2). Only the $KBrF_4$-type structure stabilized the mixed-valence $Ag^{I}Ag^{III}$ oxidation states, but it is energetically much less stable (by over 0.4 eV per FU) than the most stable polymorph containing the intermediate oxidation state of Ag^{II}. In addition, the peroxodisulfate form of Ag^{I} has turned out to be unfavorable as the $K_2S_2O_8$-type polymorph has the highest energy of all polymorphs used in the calculations.

In conclusion, the compound with a stoichiometry of $AgSO_4$—if synthesized—should be genuine paramagnetic sulfate of divalent silver. While thinking of physical properties that this compound might have, one must first inspect the topology of interatomic connections between neighboring paramagnetic Ag^{II} cations.

1.b. Bonding Topology of the Seven Most Stable Polymorphs. The seven lowest energy polymorphs, which exhibit the square planar $[AgO_4]$ units, form crystal structures that can be divided into three distinct topological families. In the first family of structures (Nos. 1, 2, and 4, Figure 2A) each of the four oxygen atoms of the sulfate anion is coordinating a different Ag atom in such a way that one O−S−O link exists between every pair of neighboring Ag atoms. Every $[SO_4]$ unit thus links four silver atoms, and every silver atom is linked to four $[SO_4]$ units. The structures within this first group can thus be viewed as infinite three-dimensional ...−Ag−O−S−O−... networks. The shortest Ag···Ag separation in these structures is as large as 4.6 Å (no. 4),[36] suggesting that the magnetic ordering temperature should be very low for these polymorphs.

The second family of structures (Figure 2B; nos. 3, 5, and 6) contains infinite one-dimensional $(Ag-O-)_\infty$ zigzag chains running parallel to each other. Here, each $[SO_4]$ unit provides only one O atom to bridge two Ag atoms in one such chain. The S atom and other two O atoms form O−S−O links between these two Ag atoms and another two from a neighboring chain. The O−S−O links extend in two directions, thus creating a two-dimensional ...−Ag−O−S−O−... network (layer) containing the zigzag ...−Ag−O−... chains (Figure 2B, top). The relative orientation of two such layers is shown in Figure 2B, bottom. Here, as in the first group of structures, every silver atom is linked to four distinct $[SO_4]$ units and they to four distinct silver atoms, but contrary to the first group, one of the $[SO_4]$ oxygens links directly to two Ag atoms and one SO_4 oxygen atom is terminal. The shortest Ag···Ag separation is only 3.7 Å, which should provide for moderate magnetic $Ag^{2+\bullet}\cdots Ag^{2+\bullet}$ coupling via oxide bridges.

The third family (no. 7 and no. 11 have a similar topology) is represented by a sandwich-like structure (Figure 2C). The interior of a sandwich is filled by two layers of $[SO_2]$ fragments coming from the $[SO_4]$ tetrahedra where the terminal oxygens of both layers are pointing toward the van der Waals space; every second $[SO_2]$ fragment is sticking above and the other half below the $[AgO_2]$ layer (Figure 2C, top). The remaining two oxygens of the $[SO_4]$ tetrahedra link Ag atoms into infinite $(O_2Ag-)_\infty$ chains running parallel to each other (every two Ag atoms within a chain are interconnected by

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(32) Standke, B.; Jansen, M. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 118–119. Standke, B.; Jansen, M. *Z. Anorg. Allg. Chem.* **1986**, *535*, 39–46.

(33) The sum of the ionic Shannon−Prewitt radii of Ag (CN = 8) and O^{2-} (CN = 4) equals 2.72 Å (www.webelements.com). Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751. Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr.* **1969**, *B25*, 925. Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr.* **1970**, *B26*, 1046.

(34) The eight coordinate Ag(I) is not as unusual as one might think, and it is typical for ligands which form highly ionic bonding to Ag(I). One good example of 8-coordinated Ag(I) is $AgTaF_6$ (Matsumoto, K.; Hagiwara, R.; Ito, Y.; Tamada, O. *J. Fluor. Chem.* **2001**, *110*, 117−122); another one is the β form of AgF_2 (i.e., $Ag(I)AgF_4$) (Romiszewski, J.; Stolarczyk, L.; Grochala, W. *J. Phys. Cond. Matter.* **2007**, *19*, 116206-1−116206-13). Even 10-coordinated Ag(I) is found for $AgBF_4$, $AgPF_6$, $AgAsF_6$, etc. (Goreshnik, E.; Mazej, Z. *Solid State Sci.* **2005**, *7*, 1225−1229).

(35) Matthews, R. W.; Walton, R. A. *Inorg. Chem.* **1971**, *10*, 1433–1438.

(36) It is interesting that polymorph no. 13 also forms a 3D ...−Ag−O−S−O−... network, but it differs from the polymorphs no. 1, 2, and 4 by the presence of weak Ag···O···Ag contacts forming a 2D network and of a deformed 2 × 2 × 2 Ag−O coordination sphere. These differences come with an energy cost of 17 kJ/mol per FU. Within the Ag···O···Ag contacts, short and long Ag−O distances (2.31 and 2.48 Å) alternate. The shortest Ag···Ag separation in this polymorph is 4.3 Å.

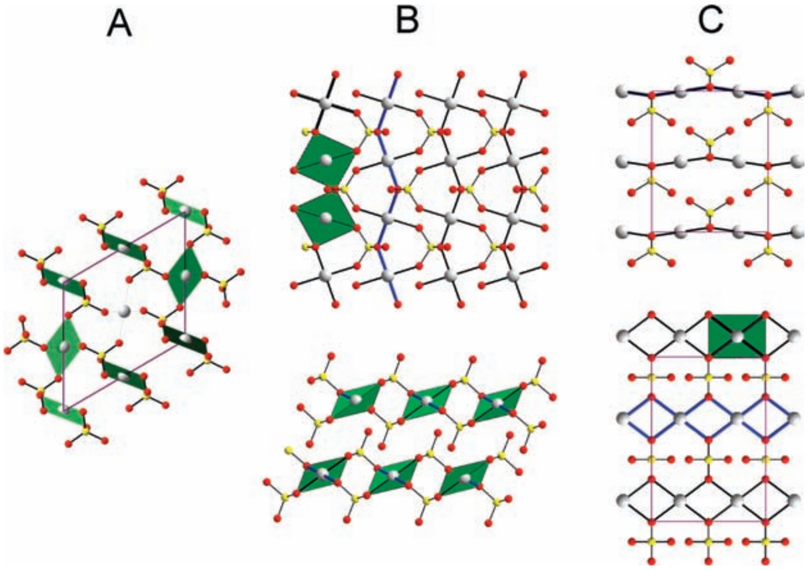

Figure 2. Representatives of three families of topologies to which the seven lowest energy polymorphs of $AgSO_4$ belong: polymorph nos. 1, 2, and 4 (A); nos. 3, 5, and 6 (B); and no. 7 (C).

two oxygen bridges), and these chains are further interconnected by O−S−O bridges, thus forming a 2D ...−Ag−O−S−O−... network (as in the second structural group). However, only one O−S−O link exists between every four nearest-neighbor silver atoms, and every sulfate anion provides two of its oxygens to two distinct parallel $[O_2Ag{=}]_\infty$ chains (Figure 2C, bottom). The shortest Ag···Ag separation is as short as 3.6 Å but still slightly over twice the van der Waals radius of Ag (3.44 Å), which excludes direct Ag−Ag bonding. Also, for this family of structures, substantial 1D magnetic coupling via two oxide bridges may be anticipated.

Interconnection of quasi-octahedral coordination spheres of the neighboring Ag atoms is directly related to the formation of the Ag−O_x−Ag chains ($x = 1, 2$) and also defines the main difference between the seven most stable polymorphs in question. In all cases, one or two oxygen atoms are common for coordination spheres of every two neighboring silver atoms. In the first topological family, some oxygen atoms coordinate one Ag atom axially and, at the same time, other ones equatorially; thus the long Ag_1−O distances alternate with the short O−Ag_2 ones (Figure 3A). In the second topological family, two nearest Ag atoms share two oxygens in their coordination spheres. One of them coordinates both Ag atoms equatorially, and the two Ag−O distances related to it are short enough (~ 2.2 Å) for the oxygen to be considered as a bridging ligand (Figure 3B). The second common oxygen coordinates both silvers axially, and the respective Ag−O distances are quite long (2.68−2.86 Å). The short O bridges link neighboring silver cations in one direction in an infinite zigzag fashion. In the third family of structures, the situation is still different since two oxygens coordinate the two silver atoms equatorially (Figure 3C), thus leading to the propagation of 1D doubly bridged $(O_2Ag-)_\infty$ chains.

Summarizing this section, we notice that the lowest energy polymorphs of $Ag^{II}SO_4$ exhibit rather poor connectivity of paramagnetic Ag^{II} centers via short Ag−O bridges (null for structure nos. 1, 2, and 4, and 1D for structures 3, 5, 6, and 7). The presence of direct Ag−O_x−Ag links for the lowest-energy structures nos. 1, 2, and 4 is of course important in terms of the through-bond interactions.[37] The topology of the lowest energy polymorphs of $AgSO_4$ is such that it must lead to low electronic dimensionality (0−1D) and concomitant low dimensional (at best 1D) magnetism or metallicity of this compound.

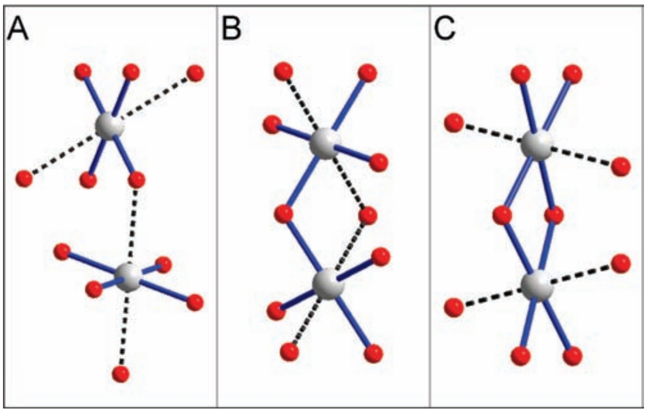

Figure 3. Interconnection of quasi-octahedral coordination spheres (<3 Å) of two neighboring Ag atoms for the seven lowest energy polymorphs showing an elongated octahedral coordination of Ag: (A) nos. 1, 2, and 4; (B) nos. 3, 5, and 6; (C) no. 7 (also polymorph nos. 8 and 11 show similar topology). Full and dashed lines define short and long Ag−O contacts, as in Figure 1.

1c. Bonding Topology of the Stable Polymorphs vs Energy. The characteristic structural features of the most stable polymorphs of $AgSO_4$ discussed in the previous section may now be related to the calculated energies of all polymorphs.

The lowest energy polymorphs (the first family of structures: nos. 1, 2, and 4) create a 3D ...−Ag−O−S−O−... network; they contain magnetically isolated Ag^{II} cations, have no terminal oxygens, and do not exhibit the 1D $[O_xAg]_\infty$ chains ($x = 1, 2$). These chains appear only for the five polymorphs of slightly higher energies.

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[37] Hoffmann, R. *Acc. Chem. Res.* **1971**, *4*, 1–9.

As the energy of the polymorphs grows, the dimensionality of the ...−Ag−O−S−O−... network also decreases and the number of terminal oxygen atoms (S=O) increases (cf. Table 1). First, the ...−Ag−O−S−O−... network changes from 3D into a 2D one. The 1D $[\mathrm{O}_x\mathrm{Ag}]_\infty$ chains may be seen only for the lowest energy 2D ...−Ag−O−S−O−... networks, first as singly −O− (nos. 3, 5, and 6 with one terminal oxygen) and then as doubly −O− bridged Ag chains (nos. 7 and 11 with two terminal oxygens). With growing energy, these chains break into O_2−Ag−O_2−Ag−O_2 islands interconnected by SO_4 units into a 2D network (no. 8). As energy rises further, these islands are replaced by Ag^{2+}−Ag^{2+} bimetallic pairs (with their unique Ag−Ag chemical bond, no. 10). No direct oxide connections between silver atoms are observed for this polymorph of $AgSO_4$ nor for the eight remaining higher-energy ones, and the shape of the coordination sphere of Ag becomes rather exotic. The 2D networks break down to 1D ones (nos. 9, 12, 14, and 15); in these chain structures, two oxygens of the sulfate anion are involved in the formation of a ...Ag−O−S−O... chain, and two others are terminal.

Finally, the two highest energy polymorphs are zero-dimensional (nos. 16 and 17). For the mixed valence polymorph no. 16 and for the peroxo-type no. 17, all Ag atoms are isolated from each other. The sulfate groups have two and three terminal oxygens, respectively.

As we can see, there is a nice progression from 3D via 2D and 1D structures to the 0D ones (with a concomitant increase of the number of terminal O atoms of the sulfate group from 0, via 1 and 2, up to 3) as the energy of the $AgSO_4$ polymorphs rises. This is certainly connected with substantial Lewis acidity of the electron-hungry Ag^{II}, which attempts to utilize all surrounding oxide anions for bonding in the lowest energy polymorphs. Thus, these polymorphs do not contain terminal O atoms.

2. $Ag^{II}SO_4$ vs Sulfates of Cu(II) and Au(II)—All Different! Anhydrous white Cu(II)SO_4 is the most meticulously characterized sulfate of a coinage group metal,[38] but also the heaviest homologue, Au(II)SO_4, has been synthesized during this decade.[39] Thus, $Ag^{II}SO_4$ remains the only member of the family of group 11. sulfates which has not yet been prepared in the laboratory. Although all these compounds are chemically related (transition metal cations come from the same group of the periodic table of elements, and the oxidation state of the metal is the same), yet it is fascinating how different from one another the structures of all these compounds may be.

Let us recall the presence of a unique chemical Au−Au bond in $AuSO_4$ and the lack of a similar bond in $CuSO_4$.[40] Our calculations indicate that divalent silver cations of $AgSO_4$ as well as Cu^{2+} cations of $CuSO_4$ are capable of adopting a coordination similar to that of Au^{2+} found for $AuSO_4$, but it comes with an energy price of over 0.2 eV per FU (Figure 4) with respect to the most stable polymorph (where the Ag^{II}−Ag^{II}/Cu^{II}−Cu^{II} dimers are absent).

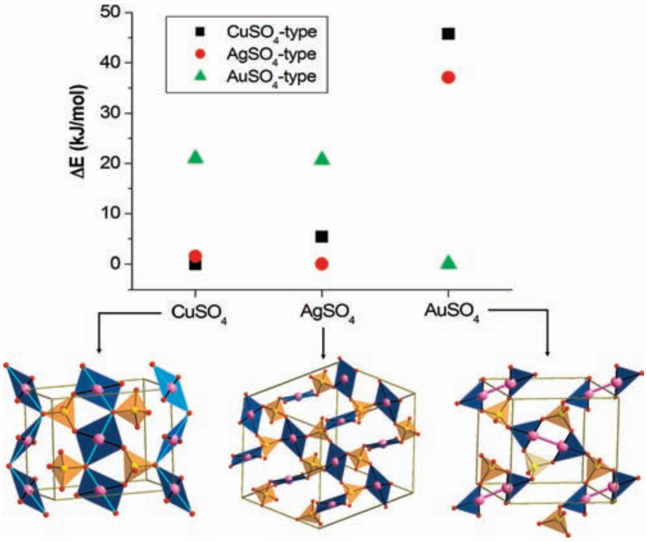

Figure 4. Relative energy per formula unit (top) of XSO_4 (X = Cu, Ag, Au) calculated for (bottom) three structural types: $CuSO_4$, $AuSO_4$, and the theoretically predicted lowest energy polymorph of $AgSO_4$ (no. 1); sulfate units (brown), planar coordination around X (blue), X ions (pink), sulfur (yellow), oxygen (red). Infinite ...Cu−O−Cu... chains are highlighted with light blue zigzag lines and the Au^{II}−Au^{II} chemical bonds with pink lines.

It seems that $AgSO_4$ could more readily adopt the $CuSO_4$-type structure since four initial structures (the $CuSO_4$, $KAl(SO_4)_2$, $AgSO_3F$, and defected $AgHSO_4$ type) converged to output structures showing striking structural similarities to $CuSO_4$, and all of them are found among the seven lowest energy polymorphs (nos. 3, 5, and 6 in Table 1). Let us recollect that the $CuSO_4$ structure is characterized by the presence of three-dimensional networks, where Cu ions are interconnected in two dimensions through O−S−O links and also, in the third dimension, via direct oxide bridges. Short oxygen bridges link the neighboring Cu atoms into infinite zigzag $(CuO)_\infty$ chains propagating parallel to each other. The energy difference between the lowest energy polymorph of $AgSO_4$ found (no. 1) and the $CuSO_4$-type structure is a mere 0.04 per FU. This result means that divalent silver resembles divalent copper—but not divalent gold—in sulfate connections.[41,42]

It is apparent from Figure 4 that divalent gold shows the most pronounced dissimilarities from the lighter members of group 11 (Cu ∼ Ag ≠ Au) since there are large energy penalties for $AuSO_4$ to adopt crystal structures of the $CuSO_4$ and $AgSO_4$ types; in addition, $CuSO_4$ and $AgSO_4$ would not readily take the $AuSO_4$-type structure. The large impact of relativistic effects on the

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(38) Szilagyi, R. K.; Frank, P.; George, S. D.; Hedman, B.; Hodgson, K. O. *Inorg. Chem.* **2004**, *43*, 8318–8329.

(39) Wickleder, M. S. *Z. Anorg. Allg. Chem.* **2001**, *627*, 2112–2114.

(40) Covalence of the Cu−O bonds may be quantitatively estimated with X-ray absorption spectroscopy. For example, copper L-edge XAS of anhydrous $CuSO_4$ revealed that 56% of the Cu(II) 3d hole is delocalized onto the sulfate ligand (Szilagyi, R. K.; Frank, P.; George, S. D.; Hedman, B.; Ho, K. O. *Inorg. Chem.* **2004**, *43*, 8318−8329). It is expected that this number will be even larger for $AgSO_4$, due to much stronger oxidizing properties of Ag(II) as compared with Cu(II). Recall that the E^0 values for the M(II)/M(I) redox pairs are as high as +2.27 V in anhydrous HF for Ag and only 0.16 V for Cu, cf. Bailar, J. C.; Emeleus, H. J.; Nyholm, R.; Trotman-Dickenson, A. F. *Comprehensive Inorganic Chemistry*; Oxford: Pergamon Press, 1973; p 1053.

(41) Recall that AgF_2 and CuF_2 in the solid state also have a similar bonding topology.

(42) It is interesting to note that $CuSO_4$-type structure of $AgSO_4$ is somewhat better packed than the best-energy structure (No. 1), as follows from analysis of the calculated density of these polymorphs (cf. Table 2). This means that the $CuSO_4$ type might be adopted by $AgSO_4$ under an increased external pressure.

Table 4. Calculated Enthalpy, *H*, and Gibbs Free Energy, *G*, at 0 K and at 273 K, for Reactants of Chemical Reactions I and II

compound	$H^{0K} = G^{0K}$ [kJ/mol]	H^{273K} [kJ/mol]	G^{273K} [kJ/mol]
$AgSO_4$ (no. 1)	−3071.4	−3056.1	−3087.4
$^3O_2$	−465.9	−463.7	−519.7
$Ag_2S_2O_7$	−5641.6	−5615.5	−5669.6
Ag_2SO_4	−3394.3	−3370.9	−3424.6
γ-SO_3	−2204.1	−2195.8	−2212.9

chemistry of gold is to be held responsible for the marked differences between copper and silver on one side and gold on the other.[43]

3. Thermodynamic Stability of $AgSO_4$. When predicting the existence of any new compound, one should certainly address the issue of its thermodynamic stability. Given the large oxidizing potential of Ag^{2+}, it is reasonable to assume that $AgSO_4$ would decompose into Ag_2SO_4, SO_3, and O_2 in two steps:[44]

$$AgSO_4 \rightarrow \frac{1}{2}Ag_2S_2O_7 + \frac{1}{4}O_2 \qquad \text{(I)}$$

$$\frac{1}{2}Ag_2S_2O_7 \rightarrow \frac{1}{2}Ag_2SO_4 + \frac{1}{2}SO_3 \qquad \text{(II)}$$

$$AgSO_{4(s)} \rightarrow \frac{1}{2}Ag_2SO_{4(s)} + \frac{1}{2}SO_{3(s)} + \frac{1}{4}O_{2(g)} \qquad \text{(I + II)}$$

We have calculated theoretical values of enthalpy, ΔH_i, and Gibbs free energy, ΔG_i, i = I and II, for the reactions (I) and (II) at 0 K and at 273 K. The values of H and G calculated for individual substrates and products are given in Table 4. We have assumed that $AgSO_4$ adopts the crystal structure of the lowest energy polymorph detected in this work (no. 1). According to our calculations, $Ag_2S_2O_7$ (not yet characterized structurally) would adopt the related $Na_2S_2O_7$-type structure rather than the $K_2S_2O_7$ type. For $SO_{3(s)}$, our calculations predict the lowest energy for one of the experimentally known (α, β, γ) polymorphs (γ , $P2_1/c$), and this monoclinic structure has been applied to thermodynamic calculations.

On the basis of the DFT calculations, we predict that $AgSO_4$, if crystallizing in the $AgAgO_2$-type structure (no. 1), should be a thermodynamically stable compound at ambient temperature, since positive values of Gibbs free energy were obtained for both decomposition pathways:

$$\Delta G_{I}{}^{273K} = 145.3 \text{kJ/mol} \qquad \text{(I)}$$

$$\Delta G_{II}{}^{273K} = 16.1 \text{kJ/mol} \qquad \text{(II)}$$

$$\Delta G_{I+II}{}^{273K} = 161.4 \text{kJ/mol} \qquad \text{(I + II)}$$

Despite its qualitative nature, these results are important because they suggests that $AgSO_4$ could indeed be obtained and characterized under ambient conditions.

4. Conclusions. We have examined close to 20 dynamically stable hypothetical polymorphs of $AgSO_4$, taking into consideration all important electromeric forms: $Ag^{I}{}_2S_2O_8$, $Ag^{II}SO_4$, and $Ag^{I}Ag^{III}(SO_4)_2$. Our DFT calculations indicate that, if crystalline, this compound should be genuine paramagnetic sulfate of divalent silver. The most likely coordination of Ag^{II} is a square planar $[AgO_4]$, with no or only a very poor connectivity of paramagnetic Ag^{II} centers via short Ag−O bridges (0D or at best 1D, respectively). The most stable polymorph of $AgSO_4$ (tetragonal, $I4_1/a$) is structurally related to "AgO", and it forms 3D ...−Ag−O−S(O_2)−O−... networks. The electron-hungry Ag^{II} cation exhibits substantial Lewis acidity, and it attempts to utilize all surrounding O anions of the $SO_4{}^{2-}$ Lewis base for bonding. The absence of direct Ag−O−Ag links in the most stable polymorph of $AgSO_4$ detected must lead to low electronic dimensionality and to concomitant low dimensional magnetism (or metallicity) of $AgSO_4$.

Positive values of the Gibbs free energy of reaction are calculated for various pathways of chemical decomposition of the lowest energy polymorph of $AgSO_4$, which suggests that $AgSO_4$ should be a thermodynamically stable compound under ambient temperature and pressure conditions.

In the future, we will study effects of external pressure on the structure and properties of $AgSO_4$, and we will also report our experimental findings for various sulfate phases of Ag^{2+}.[45]

Acknowledgment. This work is dedicated to Professor Martin Jansen, in recognition of his marvelous contributions to inorganic chemistry, and to the chemistry of oxoargentates in particular. The project 'Quest for superconductivity in crystal-engineered higher fluorides of silver' is operated within the Foundation for Polish Science 'TEAM' Program cofinanced by the EU European Regional Development Fund. Calculations have been performed at ICM supercomputers.

Supporting Information Available: Crystallographic information files (CIF) for all polymorphs of $AgSO_4$ calculated in this work.This material is available free of charge via the Internet at http://pubs.acs.org.

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(43) Pyykkö, P. *Angew. Chem., Int. Ed. Engl.* **2004**, *43*, 4412–4456.

(44) Malinowski, P.; Mazej, Z.; Gaweł, B.; Łasocha, W.; Grochala, W. Attempts to use fluorides of Ag(II) as precursors towards elusive Ag(II)SO_4.*19th International Symposium on Fluoride Chemistry*, Jackson Hole, WY, August 23−28, 2009.

(45) Malinowski, P. J.; Derzsi, M.; Gaweł, B.; Łasocha, W.; Jagličić, Z.; Mazej, Z.; Grochala, W. *Angew. Chem., Int. Ed. Engl.* **2009**, in press. DOI: 10.1002/anie.201000368.