

Crystal and electronic structures and high-pressure behavior of AgSO_4 , a unique narrow band gap antiferromagnetic semiconductor: LDA(+U) picture

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Received: 15 September 2010 / Accepted: 29 December 2010 / Published online: 26 January 2011
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Abstract We demonstrate that DFT calculations performed with the local density approximation (LDA) allow for significantly better reproduction of lattice constants, the unit cell volume and the density of Ag(II)SO_4 than those done with generalized gradient approximation (GGA). The LDA+U scheme, which accounts for electronic correlation effects, enables the accurate prediction of the magnetic superexchange constant of this strongly correlated material and its band gap at the Fermi level. The character of the band gap places the compound on the borderline between a Mott insulator and a charge transfer insulator. The size of the band gap (0.82 eV) indicates that AgSO_4 is a ferrimagnetic semiconductor, and possibly an attractive material for spintronics. A bulk modulus of 27.0 GPa and a compressibility of 0.037 GPa^{-1} were determined for AgSO_4 from the third-order Birch–Murnaghan isothermal equation of state up to 20 GPa. Several polymorphic types compete with the ambient pressure P-1 phase as the external pressure is increased. The P-1 phase is predicted to resist pressure-induced metallization up to at least 20 GPa.

Keywords Density functional theory · Sulfate · Mixed valence · Silver · Solid state

Introduction

The chemistry of Ag(II) compounds is currently undergoing rapid development [1–3]. Of particular interest are the derivatives of divalent silver that exhibit an antiferromagnetic (AFM) ground state, as they could potentially serve as precursors of high-temperature superconductors [4]. Ag(II)SO_4 , recently prepared for the first time [5], shows many unusual properties that set it apart from all other sulfates of transition metals. First, its crystal structure is very different from those of all other sulfates, as it exhibits a triclinic 3D lattice without terminal O atoms at sulfate groups, and consists of distinct 1D Ag–OSO–Ag chains (Fig. 1). Second, it exhibits unusually strong 1D AFM ordering (with a magnetic superexchange constant, J_{SE} , of the order of -10 meV) that persists right up to the thermal decomposition of the compound (at ca. 400 K). Third, it was suggested that the compound possesses a very small ($> 0.18 \text{ eV}$) electronic band gap, which is consistent with its deep black color [5].

A recent study [5] showed that many important properties of AgSO_4 can be qualitatively reproduced using GGA(+U) calculations. In this contribution, we show that the LDA(+U) scheme leads to significantly better, quantitative agreement with experiment for many important micro- and macroscopic properties of this compound, and we also predict its bulk modulus and compressibility. In addition, driven by the partial charge-transfer character of the electronic band gap of AgSO_4 , we analyze the impact of external pressure and isoelectronic substitutions ($\text{S} \rightarrow \text{Se}$, $\text{S} \rightarrow \text{Cr}$) on the electronic properties of this material.

Dedicated to the memory of Professor Andrzej Sadlej, an outstanding Polish quantum chemist.

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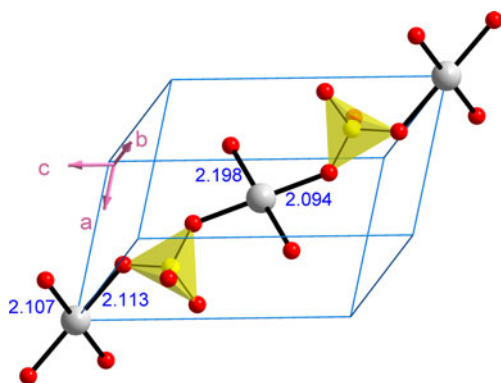


Fig. 1 Experimental triclinic unit cell of Ag(II)SO₄. For lattice constants, see Table 2. Reproduced from [3] with permission

Methods

Our spin-nonpolarized optimizations (LDA or GGA) used the projector-augmented wave method (PAW) [6] as implemented in the Vienna Ab Initio Simulation Package (VASP) [7]. In the case of PAW-GGA, both of the available functionals (PBE and PW91) were tested. The parameters for full unit cell relaxation were: electronic convergence 1×10^{-6} eV, ionic convergence 5×10^{-4} eV/Å, forces on atoms <0.02 eV/Å, k-point mesh at $\sim 0.5 \text{ \AA}^{-1}$ (using the Monkhorst–Pack scheme). Valence electrons were described by plane waves with an kinetic energy cutoff of 600 eV, providing good convergence of electronic energy. Spin-polarized calculations of magnetic properties and the electronic band structure for the experimental unit cell utilized the LDA+U and GGA+U (i.e., PBE+U) methods with electronic convergence of 10^{-7} eV/atom, $U(\text{Ag}_{4d})=U(\text{O}_{2p})=4$ eV, $U(\text{S}_{3p})=U(\text{Se}_{3p})=U(\text{Cr}_{3d})=2$ eV, and $J_{\text{H}}(\text{all atoms})=1$ eV [5]. We can see that the inclusion of U for S_{3p} electrons has a negligible effect on the band gap (Table 1), in agreement with the very small spin density on an S center [5]. However, allowing correlation for O_{2p} electrons has a somewhat larger effect (a band gap increase of 0.10 eV).¹ The

¹ U is a quasi-arbitrary parameter. It is a common practice to vary U over a broad energy range when trying to reproduce either a crystal structure, magnetic moments, or a band gap, etc. Unfortunately, different U values will perform best for each of these properties. In addition, in most cases, unrealistically large values of U are needed to make the band gap broad enough to match the experimental value. With this in mind, we have decided to use certain arbitrarily chosen U values. A typical value for Cu(II) is 9–10 eV, and it is reduced considerably if one moves to the next period (larger, softer cation). The values of U and J used in this paper for Ag(II) have in the past yielded reliable results for other compounds of Ag(II), such as KAgF₃ and both polymorphic forms of K₂AgF₄ [8, 9]. In particular, the crystal and electronic structures of Cs₂AgF₄ have been screened very carefully by a number of theoretical groups, and the values of U and J used in these works for Ag match our values well. Concerning the oxide dianion, it is reasonable to assume that strong correlations are comparable to those for the isoelectronic fluoride one. In this way, we can improve the description of electronic correlation compared to that usually employed for, say, oxocuprates, where U is typically set for a transition metal only.

Table 1 Influence of the Mott–Hubbard U , applied to Ag_{4d}, O_{2p} and S_{3p}, on the electronic band gap ΔE_{F} of Ag(II)SO₄. $J_{\text{H}}=1$ eV for all electrons when $U \neq 0$, otherwise $J_{\text{H}}=0$. The values of ΔE_{F} were obtained from single-point LDA+U calculations for AFM-ordered structure using the unit cell optimized at the LDA level

$U(\text{Ag}_{4d})$ (eV)	$U(\text{O}_{2p})$ (eV)	$U(\text{S}_{3p})$ (eV)	ΔE_{F} (eV)
0	0	0	0.00
4	0	0	0.70
4	4	0	0.80
4	4	2	0.82

magnetic superexchange constant, J_{SE} , has been estimated from the energy difference in the AFM and FM configurations on the basis of a 1D coupling model [5] using the broken symmetry approach [10]. The sign of the preferred magnetic ordering for AgMO₄ (M=Se, Cr) has been tested via explicit single-point calculations.

Results

Unit cell, density and equation of state

It turns out that PBE systematically overestimates the unit cell volumes of several hypothetical polymorphs of AgSO₄ [11] by 13–16% as compared to the LDA results.² Importantly, LDA is superior to PBE and PW91 in predicting the volume and density of the experimental P - I unit cell (Table 2). The LDA-predicted density is smaller than the experimental one by just 1.1%, while the corresponding GGA values are over 16% smaller.³ The GGA functionals are very erroneous, which disqualifies them from being used to predict mechanical properties and lattice dynamics. Correct density predictions are also crucial for estimating pressure-dependent properties such as enthalpy, and the pressures of phase transitions and metallization. In the following text, only the LDA and PBE results will be discussed (PBE will be referred to as the GGA functional), since both PBE and PW91 yield similar values for crystal parameters.

The LDA-calculated $V(p)$ behavior in the 0–20 GPa pressure range (Fig. 2, left) is well described by the third-order Birch–Murnaghan equation of state [13, 14], with a bulk modulus B_0 of 27.0(3) GPa and a B_0' value of 7.1(1). The bulk modulus is 3–4 times smaller than the typical

² Sometimes LDA outperforms GGA in the prediction of lattice constants and dynamic properties, as found, for example, for alkali metal hydrides [12].

³ It also turns out that also the phonon spectra of AgSO₄ are reproduced by LDA calculations with excellent accuracy (Derzsi M et al., submitted to *Vibr Spectrosc*).

Table 2 Selected microscopic and macroscopic parameters for AgSO₄: comparison between experimental values and GGA and LDA calculations. *NA* not available, *FU* formula unit. For details, see text

Property	Experiment [5]	LDA	PBE	PW91
<i>a</i> (Å)	8.0125	8.1347	8.4768	8.4409
<i>b</i> (Å)	4.7535	4.5754	4.9343	4.9291
<i>c</i> (Å)	4.6923	4.6915	4.8296	4.8437
α (°)	76.5	71.6	73.7	72.8
β (°)	103.4	96.8	97.1	96.7
γ (°)	118.1	112.1	111.5	110.3
<i>V</i> (Å ³)	151.76	153.5	180.3	180.6
<i>d</i> (g/cm ³)	4.46	4.41	3.75	3.74
<i>B</i> ₀ (GPa)	NA	27.1±0.3	17.9±0.3	NA
κ (GPa ⁻¹)	NA	0.037	0.056	NA
<i>J</i> _{SE} (meV/2 FU)	-9.5	-8.6*	-6.2* [5]	NA
ΔE_F (eV)	> 0.18**	0.82***	0.49***	NA
μ_{Ag} (μ _B)*	NA	+0.447, -0.436	+0.443, -0.390	NA

* Values obtained with the LDA+U approach for the state of an unrelaxed experimental AFM unit cell

** Optical absorption edge. The band gap is larger than this value

*** Values obtained with the LDA+U/GGA+U approach for the fully relaxed AFM unit cell at the +U level.

values measured for oxocuprate superconductors [15], and even smaller than those for silicate glasses (35–55 GPa), making Ag(II)SO₄ a rather soft material. Indeed, our LDA calculations place the bulk modulus of AgSO₄ between those of NaCl (32.6 GPa) and KCl (24.9 GPa). Since LDA exaggerates the value of the bulk modulus by as much as 30%, we can realistically expect the experimental bulk modulus of AgSO₄ to be around 20 GPa.

The compressibility of the lattice constants of AgSO₄ (Fig. 2, right) is quite anisotropic in the low-pressure regime up to 5 GPa, with a substantial decrease in the *b* constant (by over 6%), a moderate decrease in the *c* constant (by ca. 4%), and a small but significant expansion of the *a* vector (by 0.5%). For pressures larger than 5 GPa, all of the lattice constants decrease, but *a* clearly changes far less than the remaining two vectors. Anisotropy of

compressibility has also been predicted for AgF₂, another derivative of Ag(II) [16].

Character of the electronic band gap and the value of the magnetic superexchange constant, *J*_{SE}

The electronic structure of semiconducting AgSO₄ cannot be described correctly without including electronic correlation effects [5] (Table 1). Indeed, both GGA and LDA calculations converge to a metallic solution, even if we start with the AFM one with exaggerated magnetic moments on the Ag atoms. The inclusion of the Mott–Hubbard *U* dramatically changes the situation, leading to band-gap opening at the Fermi level (Tables 1 and 2). The metallic solution is pushed up in energy and simultaneously the AFM solution becomes the ground state.

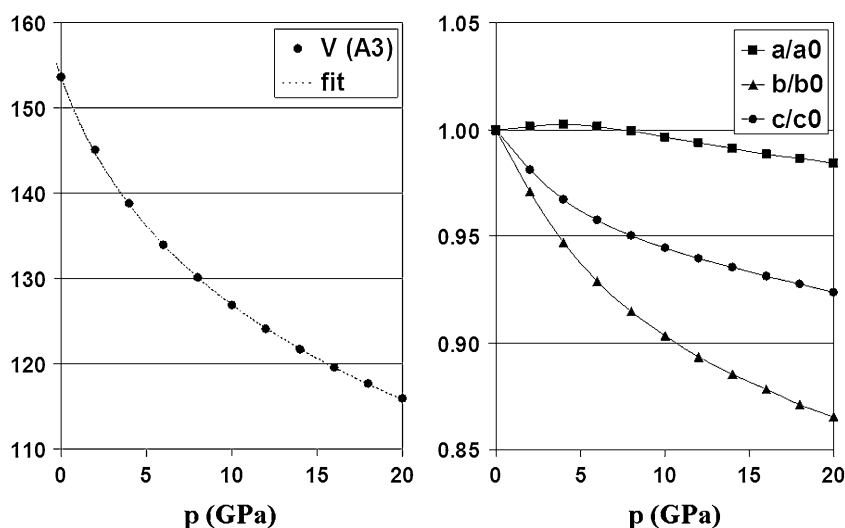


Fig. 2 LDA-calculated equation of state of Ag(II)SO₄ and the fit to the Birch–Murnaghan equation (dotted line, left); compressibility of lattice vectors related to those at 0 GPa (right)

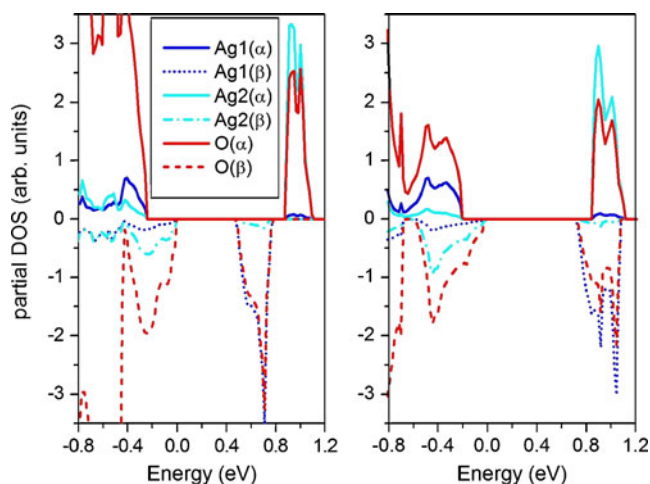


Fig. 3 GGA+U (*left*) and LDA+U (*right*) calculated the partial DOS near the Fermi level of Ag(II)SO₄ for the AFM *P*-1 cell optimized at the spin-polarized +U level. Fermi levels were set to zero. The contributions from all O atoms have been summed

The value of the energy band gap at the Fermi level, ΔE_F , is difficult to estimate from experimental data. The IR optical absorption edge occurs at 0.18 eV, but the value of ΔE_F is certainly larger than the edge value; unfortunately, strong absorption by phonon excitations at ca. 1100 cm⁻¹ precludes the precise estimation of ΔE_F . In addition, it is not certain whether the experimentally observed optical absorption around 0.2 eV corresponds to an electronic transition across the band gap of AgSO₄ (the impacts of impurities, lattice defects and color centers on the optical absorption in this spectral region are unknown at present). Our theoretical estimates (from calculations using the fully relaxed magnetic unit cell at the +U level) indicated that ΔE_F lies between 0.49 eV (GGA+U) and 0.73 eV (LDA+U). Ag(II)SO₄ is thus a narrow band gap semiconductor, similar to elemental germanium ($\Delta E_F=0.64$ eV), but it is unique due to its magnetism. These features make ferromagnetic semiconducting AgSO₄ an attractive material for spintronics [17].

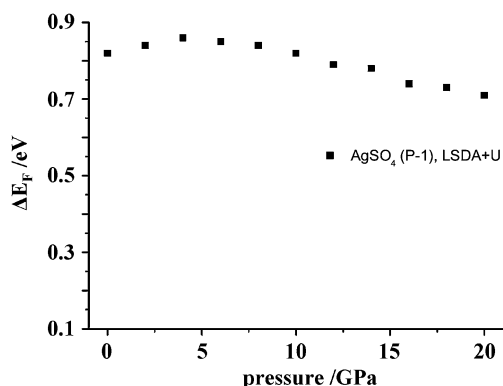


Fig. 4 LDA+U calculated dependence of the electronic band gap in Ag(II)SO₄ at the Fermi level, ΔE_F , on the external pressure, p

Table 3 The LDA-calculated densities, d , of several hypothetical polymorphic forms of AgSO₄ as compared to that of the *P*-1 structure

Type	d (g cm ⁻³)	Type	d (g cm ⁻³)
Ag ₂ O ₂ (I4 ₁ /a)	4.280	ZrSiO ₄ (I4 ₁ /amd)	4.736
Exp. (<i>P</i> -1)	4.408	KReO ₄ (P4 ₁)	4.756
CuSO ₄ (Pnma)	4.441	BaWO ₄ (C2/c)	4.926
CoSO ₄ (P2 ₁ /m)	4.563	LaPO ₄ (P2 ₁ /n)	4.955
CrVO ₄ (Cmcm)	4.575	CaWO ₄ (I4 ₁ /a)	5.041

What is the character of the electronic band gap? Since it is the electronic correlation for the 4*d* electrons that opens the band gap, it could be anticipated that Ag(II)SO₄ is a Mott insulator. However, detailed analysis of the partial density of states (Fig. 3) reveals that the states below the Fermi level are dominated by the contribution from the sulfate O atoms admixed with the 4*d* states of Ag, while those above the Fermi level have more pronounced Ag(*d*) character. In other words, the strongly correlated character of Ag(II)SO₄ and the substantial Ag(4*d*)/O(2*p*) mixing place this material on the borderline between a Mott insulator and a charge transfer insulator, just like Ni(II)O [18].

Importantly, LDA+U is superior to GGA+U in its ability to reproduce the magnetic superexchange constant, J_{SE} (Table 2). While the LDA+U picture accounts for ~90% of the experimental value, the GGA+U picture accounts only for 65% [19]. The LDA+U value of $J_{SE}=-8.6$ meV per pair of interacting Ag(II) centers is close to the value of -9.5 meV derived experimentally using the 1D Bonner–Fisher model [5].

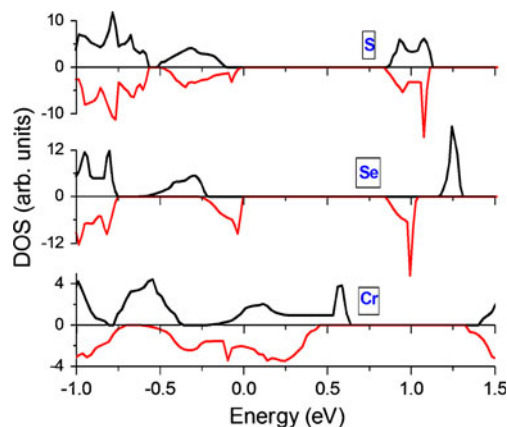


Fig. 5 LDA+U calculated total alpha (*black*) and beta (*red*) densities of states for AFM Ag(II)SO₄ (*top*), Ag(II)SeO₄ (*middle*) and Ag(II)CrO₄ (*bottom*). All DOSs are obtained for LDA-optimized *P*1 unit cells. Note the larger absolute values of DOS for Ag(II)SeO₄ than for Ag(II)SO₄ (as the selenate anion is larger than the sulfate anion) and the band-gap closure for Ag(II)CrO₄. Fermi levels have been set to zero

High-pressure behavior: evolution of the electronic band gap and phase transitions

The high-pressure behavior of AgSO_4 is of interest due to the possible metallization of this compound [19]. Therefore, we have calculated the dependence of the electronic band gap in Ag(II)SO_4 at the Fermi level, ΔE_F , on external pressure, initially considering the P-1 cell only (Fig. 4).

The dependence of ΔE_F on pressure is unusual. The band gap first rises slightly, reaching its maximum of 0.87 eV at ca. 4 GPa, and then very slowly decreases with pressure down to ca. 0.7 eV at 20 GPa. Such an increase in band gap with pressure is very rare; it has been proposed for MgO and isoelectronic solids based on dielectric susceptibility vs. pressure experiments [20, 21]. It is remarkable that the band gap of AgSO_4 is present at all at 20 GPa, since semiconductors with band gaps that are smaller than 1 eV metallize at modest external pressures. For example, elemental silicon becomes metallic at 13 GPa [22]. The rate of change in ΔE_F for AgSO_4 with pressure is constant in the 6–20 GPa range and as small as -0.01 eV/GPa, leading to an extrapolated metallization pressure of 90 GPa (here we assume that metallization is *not* preceded by a phase transition). The predicted substantial resistance of the semiconducting P-1 phase of AgSO_4 to metallization is unusual and possibly an artefact; the nature of the ΔE_F vs. p behavior should be verified by experiment.

It is conceivable that AgSO_4 may undergo a structural phase transition at lower pressures before it undergoes metallization in the P-1 structure. Thus, we have attempted to predict pressure-induced structural phase transitions of AgSO_4 while taking into account a range of nearly thirty polymorphic types [8, 9, 23]. We then focused on those with LDA-calculated densities larger than that of the experimentally observed P-1 structure (Table 3). It turns out that majority of the polymorphic forms considered have enthalpies close (within the error margin of DFT) to that for the P-1 type in the range of pressures up to 20 GPa (data not shown). It is thus very difficult to reliably estimate the chance of a pressure-induced structural phase transition.

Beyond sulfate: selenate and chromate of Ag(II)

Since S(VI), Cr(VI) and Se(VI) have comparable bond lengths to oxygen (1.50 Å, 1.64 Å and 1.66 Å, respectively), sulfates(VI), chromates(VI) and selenates(VI) are often isostructural. However, the SeO_4^{2-} and CrO_4^{2-} dianions are electronically softer than SO_4^{2-} and are thus easier to oxidize via the Ag(II) cation. Since the electronic band gap of Ag(II)SO_4 has pronounced charge-transfer character, it can be anticipated that the band gaps of Ag(II)SeO_4 and Ag(II)CrO_4 will be smaller than that of Ag(II)SO_4 , due to the easier introduction of holes into the oxide band.

Interestingly, the LDA+U calculated DOS for the as-yet hypothetical Ag(II)SeO_4 in the LDA-optimized P-1 unit cell (Fig. 5) indicates the presence of the band gap at the Fermi level of 0.82 eV, which is identical to that for Ag(II)SO_4 . An analogous calculation for Ag(II)CrO_4 shows that, although the compound should still be ferrimagnetic, the band gap is closed.

Conclusions

We found that the LDA scheme is superior to GGA (PBE and PW91) at reproducing the essential structural, electronic and magnetic properties of AgSO_4 (the inclusion of Hubbard's U being necessary in the latter two cases). This is likely due to a most fortunate cancellation of errors. Given the unique character of its electronic band gap, AgSO_4 falls at the borderline between a Mott insulator and a charge-transfer insulator, and is of interest in view of its possible chemical doping induced or pressure-induced metallization. Our calculations show that AgSO_4 is unusually resistant to pressure-induced metallization, and that its band gap is open up to at least 20 GPa. However, the related compound Ag(II)CrO_4 should be metallic even at ambient pressure, and attempts are now being made in our laboratory to synthesize this compound. In a parallel line of research, we will attempt to measure the electronic band gap at ambient pressure, as well as the metallization pressure of Ag(II)SO_4 .

Acknowledgments The project “Quest for Superconductivity in Crystal-Engineered Higher Fluorides of Silver” is operated by the Foundation for Polish Science's TEAM program, and co-financed by the EU European Regional Development Fund.

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