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Short communication

Phonon spectra and phonon-dependent properties of $AgSO_4$, an unusual sulfate of divalent silver

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This work is dedicated to Leszek Stolarczyk at his 60th birthday.

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ABSTRACT

Phonon spectra of recently synthesized $Ag(II)SO_4$ have been measured using infrared absorption and Raman scattering spectroscopy, and theoretically predicted using density functional theory calculations. Excellent agreement between experimental and theoretical results with correlation coefficient of 1.05 allowed for full assignment of the experimentally observed vibrational bands, as well as calculation of standard vibrational entropy of $AgSO_4$ (118.2 $J\,mol^{-1}\,K^{-1}$), vibrational heat capacity at constant volume (99.1 $J\,mol^{-1}\,K^{-1}$), zero-point energy (48.3 $kJ\,mol^{-1}$). The experimental cut-off frequency of the phonon spectrum equals 1116 cm^{-1} which translates to the Debye temperature of 1606 K. High frequencies of S–O stretching modes render sulfate connections of Ag(II) attractive precursors of high-T_C superconductors.

1. Introduction

$Ag(II)SO_4$, a recently prepared sulfate of divalent silver [1] shows several anomalous features rendering it unique among all transition metal sulfates: (i) a narrow electronic band gap at the Fermi level (>0.25 eV), (ii) a pronounced free radical character of sulfate anions, (iii) a one-dimensional antiferromagnetism, which persists up to the thermal decomposition of (110 °C), and (iv) an atypical pathway of thermal decomposition via a redox reaction, which yields disulfate of Ag(I). Notably, $AgSO_4$ is dissimilar to sulfates of its lighter and heavier congeners, respectively Cu and Au [2].

Lattice dynamics of $Ag(II)SO_4$ is of immediate interest in context of its possible chemical doping- or pressure-induced metallization [3], and generation of phonon-driven (BCS-type [4]) superconductivity. However, the published infrared absorption spectrum of $AgSO_4$ [1] has not been analyzed in detail. Also, in the course of systematic studies it turned out that the Raman spectrum presented in Electronic Supplementary Material to the original paper [1] originates from an unknown product of photochemical reaction of $AgSO_4$ mixed up with $Ag_2S_2O_7$ (product of thermal decomposition of black $AgSO_4$ in the laser beam, see Section 2). The current combined experimental and theoretical study is aimed at providing correct Raman spectrum, detailed assignment of the vibrational spectra of $Ag(II)SO_4$, and calculating of the phonon-dependent thermodynamic properties.

2. Experimental

$AgSO_4$ has been synthesized according to the published procedure [1]. The compound is dark black and very sensitive to moisture. IR spectra were measured using a Vertex 80V vacuum spectrometer from Bruker. For mid-IR region (500–7500 cm^{-1}) the powdered samples were placed on the surface of AgCl windows, while for far-IR (50–650 cm^{-1}) the samples were placed on polyethylene windows. Raman spectra were recorded using Horiba Jobin Yvon LabRam-HR Raman micro-spectrometer with 632.8 nm He–Ne laser exciting beam. We found that it is necessary to use very low laser power when measuring Raman spectra in the microscope (focused beam) mode for black $AgSO_4$ to prevent thermal decomposition. For $AgSO_4$ we found out that reliable spectra can only be obtained at laser power of 0.17 mW or smaller; at larger powers (such as 1.7 mW used before [1]) the Raman spectrum changes

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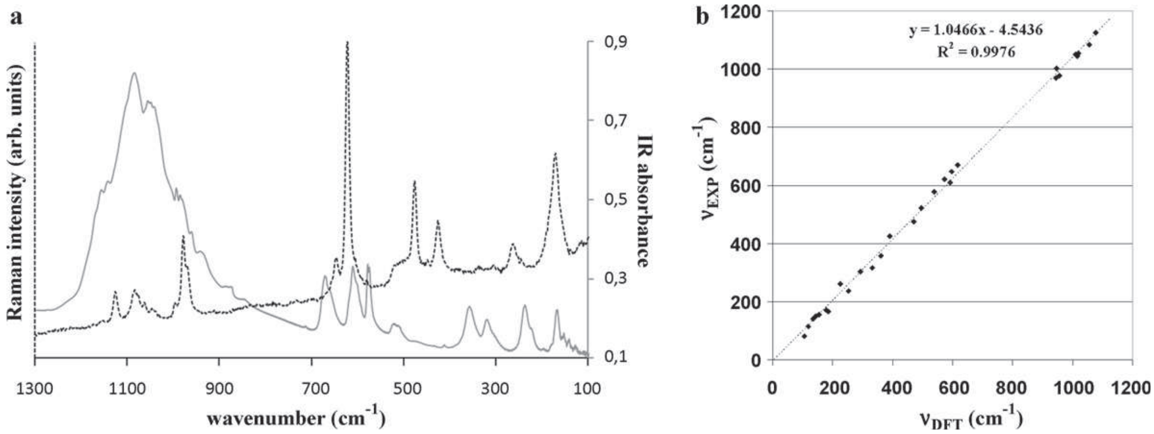

Fig. 1. (a) IR (top) and Raman (bottom; 632.8 nm He–Ne excitation, backscattering geometry) spectrum of Ag(II)SO_4 in 100–1200 cm^{-1} range. (b) Correlation between experimental (IR + Raman) and theoretical (LDA) wavenumbers of vibrational bands of Ag(II)SO_4. Linear regression is shown by dotted line. For numerical values see Table 1.

considerably and it indicates presence of $Ag_2S_2O_7$ as testified by appearance of the 1077 cm^{-1}, 725 cm^{-1} and 325 cm^{-1} bands (recall, disulfate is a product of thermal decomposition of $AgSO_4$). It is unclear to what extent the measured Raman spectrum has a resonance character; photochemistry of $AgSO_4$ will be discussed in detail elsewhere.

3. Computational details

Our spin non-polarized density functional theory (DFT) calculations (within framework of local density approximation, LDA, or generalized gradient approximation, GGA) used projector-augmented wave method (PAW) [5] as implemented in Vienna ab initio simulation package (VASP) [6]. Previously we have found out that LDA proves superior to GGA in reproduction of unit cell parameters of $AgSO_4$ [7] and LDA was our method of choice for calculating phonons, with GGA being used for comparison only (*cf.* SI). Parameters for full geometry optimization were: SCF convergence criterion 10^{-7} eV, forces on atoms <0.02 eV/Å, k-point mesh at ~0.5 $Å^{-1}$, valence electrons were described by plane waves with kinetic energy cutoff of 600 eV providing good convergence of electronic energy. Calculations of phonon dispersion and phonon density of states (DOS) were carried out using PHONON for the $1 \times 2 \times 2$ supercell ($Z = 8$) containing 48 atoms [8]. The Helmann–Feynmann forces, needed for the PHONON calculations, were evaluated in single-point total energy calculations for each atomic displacement (by ±0.03 Å).

4. Results and discussion

Ag(II)SO_4 crystallizes in the centrosymmetric triclinic unit cell containing two formulae units ($Z = 2$). The sulfate anions are severely distorted from tetrahedral symmetry and local symmetry is reduced to C_1. Eight S–O stretching modes, ten O–S–O deformation modes, fifteen Ag–O stretching and lattice modes, and 3 acoustic modes are expected. With the support of DFT calculations we were able to identify all 8 S–O stretching modes, 9 out of 10 O–S–O deformation modes, and 11 out of 15 Ag–O stretching and lattice modes; the remaining very weak IR or Raman bands or shoulders originate from either impurities or combination modes (Table 1).

Mid-infrared (MIR) absorption spectrum of Ag(II)SO_4 (Fig. 1a and Table 1) is predominated by a very strong 'sulfate band' centered at 1084 cm^{-1}. The band is very broad reflecting the fact that there are two interacting sulfate anions in the triclinic P-1 unit cell of this compound [1], and that each of them exhibits four different

Table 1
Experimentally observed (Raman and IR) and DFT-predicted vibrational modes of $AgSO_4$ together with their assignment and symmetry. All wavenumbers ±2 cm^{-1}.

IR	Raman	DFT[a]	Assignment
1156 sh			Impurity or combination mode
1142 sh			Impurity or combination mode
	1125 m	1076	S–O stretch Ag
1084 vs	1083 m[b]	1055	S–O stretch Au
	1063 w		Impurity or combination mode
1055 s		1018	S–O stretch Au
	1045 w	1016	S–O stretch Ag
1050 vs		1010	S–O stretch Au
	997 w		Impurity or combination mode
	978 s	956	S–O stretch Ag
1002 sh		945	S–O stretch Au
993 sh			Impurity or combination mode
985 sh			Impurity or combination mode
	970 s	944	S–O stretch Ag
960 sh			Impurity or combination mode
930 sh			Impurity or combination mode
887 vw			Impurity or combination mode
670 m		616	O–S–O deformation Au
660 sh			Impurity or combination mode
	647 m	596	O–S–O deformation Ag
610 m		590	O–S–O deformation Au
600 sh			Impurity or combination mode
	622 vs	573	O–S–O deformation Ag
578 m		539	O–S–O deformation Au
		537	O–S–O deformation Ag
523 w	520 w[b]	495	O–S–O deformation Au
	503 w		Impurity or combination mode
	476 s	469	O–S–O deformation Ag
		408	O–S–O deformation Au
	425 m	389	O–S–O deformation Ag
358 m		360	Lattice Au
	305 vw	292	Lattice Ag
318 m		332	Lattice Au
237 m		253	Lattice Au
	262 m	224	[AgO_4] stretching and lattice Ag
222 sh			Impurity or combination mode
167 m		185	Lattice Au
	171 s	177	[AgO_4] stretching and lattice Ag
		161	Lattice Ag
157 w		155	Lattice Au
152 w		142	Lattice Au
141 w		134	Lattice Au
	116 w	118	Lattice Ag
	83 m	106	Lattice Ag
		90	Lattice Au
		70	Lattice Au

[a] The IR and Raman intensities were not calculated with DFT.

[b] Mutual exclusion principle applies for centrosymmetric P-1 group but it may be bent due to application of selection rules other than dipole moment-related.

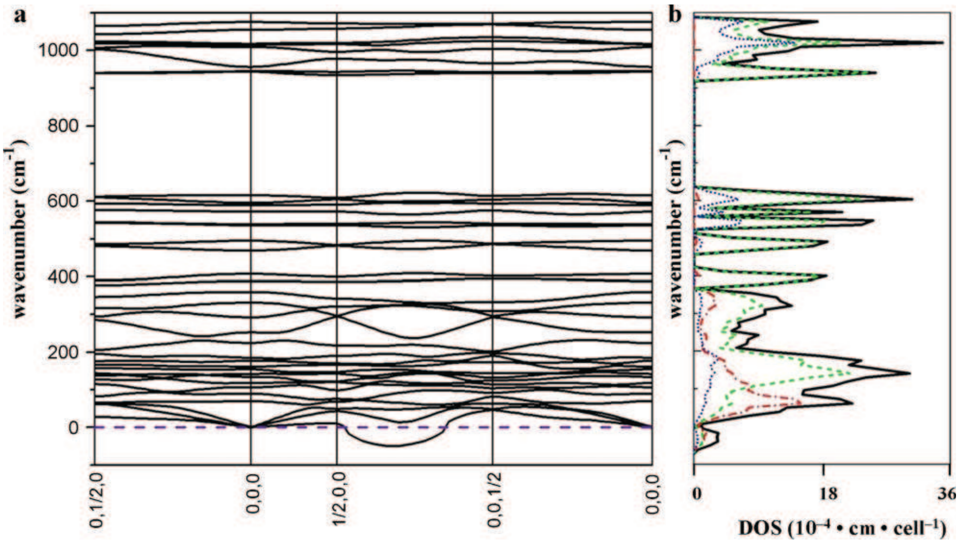

Fig. 2. (a) Phonon band structure and (b) phonon DOS including atomic contributions to DOS, as calculated for Ag(II)SO$_4$ using LDA. Slight softening of the acoustic mode between (1/2 0 0) and (0 0 1/2) is a numerical artifact since following this deformation does not lead to energy improvement. Total DOS – continuous, oxygen – dashed (green), sulfur – dotted (blue), silver – dot-dashed (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

S–O bond lengths ranging from 1.427 Å to 1.503 Å. In the Raman (R) spectrum, the strongest bands assigned to the υ (S–O) stretching modes appear at 970, 978, 1083 and 1125 cm^{-1}. General shape of the vibrational spectra is similar to those for anhydrous PdSO$_4$ [9], and typical for sulfates with all O atoms engaged in chemical bonding to metal cation (*i.e.* without terminal S=O groups). The far-infrared (FIR) spectrum in 50–700 cm^{-1} range contains several bands; analysis of the atomic contributions to the calculated phonons density of states (DOS, see below) allows for unequivocal assignment of the bands appearing in 400–700 cm^{-1} region to the OSO deformation modes, and those appearing in 50–400 cm^{-1} region to various lattice modes with large contribution from Ag atoms.

The LDA calculations of the phonon dispersion and phonon density of states (DOS) (Fig. 2) allow for much better reproduction of phonon frequencies than those performed within GGA scheme (*cf.* SI). The theoretical phonon dispersion consists of eight phonon branches assigned to S–O stretching modes (1076–944 cm^{-1}), ten branches assigned to OSO deformation modes (616–389 cm^{-1}, with predominant contribution from O atoms), fifteen lower-frequency lattice and Ag–O stretching modes (360–155 cm^{-1} with substantial contribution from motion of Ag atoms) and three acoustic branches (~0 cm^{-1}). An excellent agreement between experimental and theoretical LDA results (Fig. 1b and Table 1), described by linear regression: $\upsilon_{\mathrm{exp}} = 1.05\upsilon_{\mathrm{LDA}} + 4.5\ \mathrm{cm}^{-1}$, allows for assignment of nearly all fundamentals. The linear correlation coefficient is slightly larger than unity, which comes from a typical slight underestimation of the strength of chemical bonds (and of associated force constants) within LDA.

Joint experimental and theoretical data enabled us to calculate several important phonon-related properties of AgSO$_4$ (Table 2). The calculated zero-point energy (ZPE) of AgSO$_4$ reaches 48.3 kJ mol^{-1}, standard vibrational entropy, S^0_{vib}, is 118.2 J mol^{-1} K^{-1}, and predicted vibrational heat capacity at constant volume, $C_{\mathrm{v}}^{\mathrm{vib}}$, is 99.1 J mol^{-1} K^{-1} (±1.6%). The phonon calculations allowed us also to derive thermodynamic functions of AgSO$_4$ (*cf.* SI) in the temperature range 0–400 K (400 K being close to the temperature of thermal decomposition of the compound). The comparison between theoretical and experimental values of these properties must await until the experimental estimates are available.

Table 2
The LDA-calculated (theor.) or experimental (exp.) values of selected phonon-dependent physicochemical parameters of AgSO$_4$; all data for T = 298 K.

Symbol	Property	Theor.[a]	Exp.
υ_0	Cut-off frequency of the phonon spectrum	1076 cm^{-1}	1116 cm^{-1}
θ_{D}	Debye temperature	1548 K	1606 K
$C_{\mathrm{v}}^{\mathrm{vib}}$	Vibrational heat capacity at constant volume	99.1 J mol^{-1} K^{-1}	NA[b]
S^0_{vib}	Vibrational entropy at standard conditions	118.2 J mol^{-1} K^{-1}	NA[b]
ZPE	Zero-point energy	+48.3 kJ mol^{-1}	NA[b]

[a] Uncertainty of ~1.6% applies to the LDA data due to weak softening of one of the acoustic phonons outside Γ.
[b] NA = not available.

The experimental cut-off frequency of the phonon spectrum falls at 1116 cm^{-1} (*cf.* LDA value of 1076 cm^{-1}) which is equivalent of a Debye temperature, θ_{D}, of 1606 K (*cf.* LDA value of 1548 K). These values exceed by the factor of nearly 2 the corresponding values measured for oxocuprate superconductors [10]. Provisionally using the predictions of the BCS theory of superconductivity [4] one anticipates that high frequencies of S–O stretching modes render sulfate connections of Ag(II) attractive precursors of high-T$_{\mathrm{C}}$ superconductors; however, metallization of AgSO$_4$ should first be achieved by doping or applying of an external pressure.

5. Conclusions

The first assignment of vibrational (IR and Raman) spectra of Ag(II)SO$_4$ based on the LDA calculations of the phonon spectrum is presented. The assignment covers 27 out of 33 fundamentals (optical phonons). The large cut-off frequency of the phonon spectrum of 1116 cm^{-1}, connected with S–O stretching vibrations, can be translated to an appreciable Debye temperature, θ_D, of 1606 K (both very accurately predicted by phonon calculations done within local density approximation). Substantial value of θ_D suggests that large critical superconducting temperature might be achieved if a small band gap of black $AgSO_4$ semiconductor is closed via chemical doping or by use of external pressure. Such attempts are now conducted in our laboratory.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.vibspec.2011.07.001.

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