

## A STUDY OF THE $\text{SnO}_2$ AND $\text{CuSb}_2\text{O}_6$ BASED SOLID SOLUTIONS: ELECTRICAL AND MAGNETIC PROPERTIES

O. Scarlat\*, A. C. Payne<sup>a</sup>, S. Mihaiu, G. Aldica<sup>b</sup>, M. Zaharescu

Romanian Academy, Institute of Physical Chemistry "I. G. Murgulescu",  
202 Splaiul Independentei, 77208 Bucharest 6, Romania

<sup>a</sup>1101 University AV Madison, Chemistry Dept., WI 53706, USA

<sup>b</sup>National Institute for Physics of Materials, PO Box MG-7, RO-76900 Bucharest,  
Magurele, Romania

Two types of solid solutions (i. e.  $\text{Sn}_{1-x}\text{Cu}_{x/3}\text{Sb}_{2x/3}\text{O}_2$  and  $\text{Cu}_{1-x}\text{Sb}_{2(1-x)}\text{Sn}_{3x}\text{O}_6$  mixed crystals), have been experimentally evidenced over a large concentration range, in the  $\text{SnO}_2$  -  $\text{CuSb}_2\text{O}_6$  binary system. For these two types of solid solutions, the measured values of the unit cell parameters obey Vegard's rule. The electric and magnetic properties of the  $\text{Sn}_{0.50}\text{Cu}_{0.167}\text{Sb}_{0.33}\text{O}_2$  and  $\text{Cu}_{0.923}\text{Sb}_{1.836}\text{Sn}_{0.231}\text{O}_6$  mixed crystals, with compositions placed at the maximum solid solubility limit, on either side, were evaluated over 77 to 1123 K and 2 to 300 K, respectively.  $\text{Sn}_{0.50}\text{Cu}_{0.167}\text{Sb}_{0.33}\text{O}_2$  sample exhibited semiconducting behaviour, with activation energy  $E_d$  (eV) and Seebeck coefficient ( $\mu\text{V}/\text{grad}$ ) values close to the values reported for metals, while the  $\text{Cu}_{0.923}\text{Sb}_{1.836}\text{Sn}_{0.231}\text{O}_6$  sample can be treated as insulators. Short - range magnetic ordering has been evidenced at about 60 K for the  $\text{CuSb}_2\text{O}_6$  binary compound and  $\text{Cu}_{0.923}\text{Sb}_{1.836}\text{Sn}_{0.231}\text{O}_6$  mixed crystal, with calculated magnetic moments in good agreement with literature data. In contrast, the  $\text{Sn}_{0.50}\text{Cu}_{0.167}\text{Sb}_{0.33}\text{O}_2$  mixed crystal presented only a paramagnetic behaviour.

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### 1. Introduction

Many important applications of the  $\text{SnO}_2$  - based materials as catalytic and gas - sensing devices [1, 2] or as electrodes in glass industry and aluminium electrometallurgy [3], are a result of the donor levels supplementary introduced in the  $\text{SnO}_2$  conduction band by the addition of transitional metal oxides [4]. For instance,  $\text{Sb}_2\text{O}_3$  doping was reported to drastically increase (by four to five orders of magnitude) the electrical conductivity of  $\text{SnO}_2$  [5]. Furthermore, the addition of  $\text{CuO}$  to the  $\text{SnO}_2$  -  $\text{Sb}_2\text{O}_4$  based compositions, developed the formation of dense ceramics,  $\text{SnO}_2$  - based solid solutions respectively, with special metallic conduction [6], due to an enhanced sintering ability.  $\text{CuSb}_2\text{O}_6$  on the other hand, is known to be a paramagnetic binary compound, whose structure belongs to the same  $P4_2/mnm$  space group as  $\text{SnO}_2$ . Due to the presence in the  $\text{CuSb}_2\text{O}_6$  structure of the magnetic  $\text{Cu}^{2+}$  ions, separated from each other by two sheets of  $\text{Sb}^{5+}$  diamagnetic ions, the magnetic cation sublattice of this compound is the same as that of  $\text{K}_2\text{NiF}_4$  structure - a square lattice two - dimensional antiferromagnet [7]. Since by X-ray diffraction only the  $\text{CuSb}_2\text{O}_6$  characteristic peaks have been noticed in the  $\text{CuSb}_2\text{O}_6$  - based solid solutions, previously evidenced to be formed in the  $\text{SnO}_2$  -  $\text{CuSb}_2\text{O}_6$  binary system [8], the ordering of the cations from the  $\text{CuSb}_2\text{O}_6$  matrix presumably keep the base line of the *trirutile* type structure.

The aim of this work consists in evaluating the electric and magnetic properties of the solid solutions previously reported in the  $\text{SnO}_2$  -  $\text{CuSb}_2\text{O}_6$  system [8]. It is worth to mention here that the

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\* Corresponding author: ioana@chimfiz.icf.ro

magnetic behaviour is more sensitive in revealing the degree of cation ordering than X-ray diffraction technique, the latter being of primary importance for the magnetic properties of these  $\text{SnO}_2$  and  $\text{CuSb}_2\text{O}_6$  based solid solutions.

## 2. Experimental

$\text{SnO}_2$  (Merck, Co) and  $\text{CuSb}_2\text{O}_6$  (prepared in our laboratory [8]) were used as starting materials for the preparation, by classical ceramic method [5, 8], of the  $(1-x)$   $\text{SnO}_2 - x$   $\text{CuSb}_2\text{O}_6$  ( $x = 0 \dots 1$ ) studied compositions. Uniaxially pressed pellets (30 MPa,  $\phi = 10$  mm) were thermally treated at 1373 K – 3h (4 grd/min) [6]. For phase determination, a Scintag Automated Diffractometer ( $\text{CuK}\alpha$  radiation -  $\lambda_{\text{K}\alpha 1} = 1.54059 \text{ \AA}$ ), was used over the range of 10 to  $80^\circ 2\theta$ . X-ray step scans ( $0.01^\circ$  step size, 2.5 s counting time) were performed to measure the unit cell parameters.

A direct current bridge was used for electrical resistivity measurements (four points scheme) on the gold - coated pellet [9], in the 77 to 1123 K temperature range. The Seebeck coefficient was measured at room temperature (warm point method, platinum reference).

Magnetization measurements, were performed in a commercial MPMS - SQUID magnetometer, by cooling the sample from room temperature to  $T = 5$  K in zero applied field; then a field of  $H = 200$  Oe was applied, and the variation of magnetization was measured with increasing temperature up to  $T = 300$  K.

## 3. Experimental results

Previous studies have been devoted to the study of the subsolidus phase relationships of the  $\text{SnO}_2 - \text{CuSb}_2\text{O}_6$  pseudobinary system [5, 8]. According to the phase composition, three subsolidus domains were evidenced at 1373 K as follows

$-0 < y \leq 0.25$	$\text{SnO}_2$ ss	described as $\text{Sn}_{1-x}\text{Cu}_{x/3}\text{Sb}_{2x/3}\text{O}_2$
$-0.25 < y < 0.8$	$\text{SnO}_2$ ss + $\text{CuSb}_2\text{O}_6$ ss	
$-0.8 < y \leq 1$	$\text{CuSb}_2\text{O}_6$ ss	described as $\text{Cu}_{1-x}\text{Sb}_{2(1-x)}\text{Sn}_{3x}\text{O}_6$

### 3.1. X - Ray diffraction results

The variation of the unit cell lattice parameters vs. composition for the  $\text{SnO}_2 - \text{CuSb}_2\text{O}_6$  system is presented in Fig. 1. For the tin rich - end members of the series, which crystallise with the *rutile* type lattice, in the composition range of  $P4_2/mnm$  structure, the decreasing of the measured  $a_0$  [ $\text{\AA}$ ] and  $c_0$  [ $\text{\AA}$ ] lattice parameters (Fig. 1) obey Vegard's Rule up to the limit concentration of  $x_{\text{CuSb}_2\text{O}_6} \cong 0.25$ .

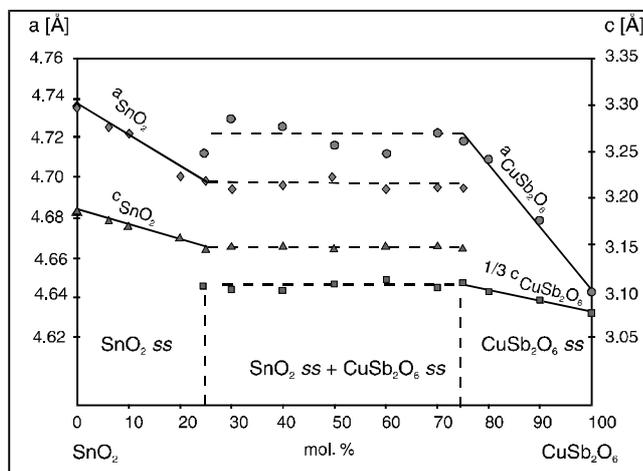


Fig. 1. Lattice parameters vs. composition for the  $\text{SnO}_2 - \text{CuSb}_2\text{O}_6$  binary system.

$$a_0 = 4.736 - 0.0016 \cdot x_{\text{CuSb}_2\text{O}_6} \pm 0.002 \text{ \AA}$$

$$c_0 = 3.1865 - 0.0016 \cdot x_{\text{CuSb}_2\text{O}_6} \pm 0.002 \text{ \AA}$$

Similarly, the solid solubility limit of SnO<sub>2</sub> in CuSb<sub>2</sub>O<sub>6</sub> varied in accordance with Vegard's Rule, up to  $x_{\text{SnO}_2} \leq 0.20$  (see Fig. 1), a concentration range for which the lattice parameters increased with the increasing of SnO<sub>2</sub> content

$$a_0 = 4.679 + 0.0005 \cdot x_{\text{SnO}_2} \pm 0.002 \text{ \AA}$$

$$c_0 = 11.065736 + 0.017544 \cdot x_{\text{SnO}_2} \pm 0.002 \text{ \AA}$$

According to the data presented in Fig. 1, the compositions placed at the maximum solid solubility limit in the base matrix, were purposely selected (see Table 1) for detailed structure - properties investigations. These compositions consist of the *rutile* type SnO<sub>2</sub> lattice for Sn<sub>1-x</sub>Cu<sub>x/3</sub>Sb<sub>2x/3</sub>O<sub>2</sub>, and the *trirutile* type CuSb<sub>2</sub>O<sub>6</sub> lattice for Cu<sub>1-x</sub>Sb<sub>2(1-x)</sub>Sn<sub>3x</sub>O<sub>6</sub> mixed crystals [8].

Table 1. The composition of the studied mixed crystals.

oxide composition (molar ratio)			initial composition (molar ratio)			mixed crystal formula
SnO <sub>2</sub>	Sb <sub>2</sub> O <sub>3</sub>	CuO	SnO <sub>2</sub>	Sb <sub>2</sub> O <sub>4</sub>	CuSb <sub>2</sub> O <sub>6</sub>	
100	-----	-----	100	-----	-----	SnO <sub>2</sub>
60	20	20	75	-----	25	Sn <sub>0.50</sub> Cu <sub>0.167</sub> Sb <sub>0.333</sub> O <sub>2</sub>
11.11	44.44	44.44	20	-----	80	Cu <sub>0.923</sub> Sb <sub>1.836</sub> Sn <sub>0.231</sub> O <sub>6</sub>
-----	50.00	50.00	-----	-----	100	CuSb <sub>2</sub> O <sub>6</sub>

### 3. 2. Electrical properties

The dependence of the electrical conductivity in the form of  $\ln k$  versus  $10^3/T$  in the 77 to 1123 K temperature range was plotted in Fig. 2 only for the SnO<sub>2</sub> -based solid solution, i. e. for Sn<sub>0.50</sub>Cu<sub>0.167</sub>Sb<sub>0.333</sub>O<sub>2</sub> mixed crystal.

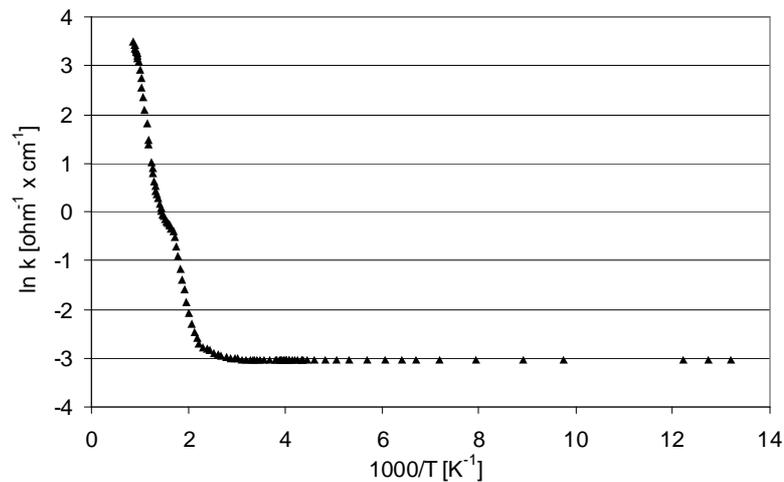


Fig. 2. Arrhenius behaviour for the Sn<sub>0.50</sub>Cu<sub>0.167</sub>Sb<sub>0.333</sub>O<sub>2</sub> mixed crystal.

For the *trirutile* – type solid solution placed to the other end of the solid solubility limit, i. e.  $\text{Cu}_{0.923}\text{Sb}_{1.836}\text{Sn}_{0.231}\text{O}_6$  mixed crystal, it was not possible to measure the electrical conductivity in the present experimental conditions, due to the high resistivity of the selected sample.

The  $\text{Sn}_{0.50}\text{Cu}_{0.167}\text{Sb}_{0.333}\text{O}_2$  solid solution exhibits a typical semiconducting behaviour (Fig. 2). Data presented in Table 2, referring to the measured negative Seebeck coefficient value ( $\mu\text{V}/\text{K}$ ), and to the values for the  $E_d$  (eV) activation energy [calculated considering an Arrhenius – type behaviour, based on  $k = k_0 \cdot \exp(-E_d / k_B T)$ , where  $k_0$  is a constant,  $k_B$  is the Boltzmann constant], are typical for materials with metallic conduction [9].

Table 2. Seebeck coefficient values ( $\mu\text{V}/\text{K}$ ) and activation energy  $E_d$  (eV) for the  $\text{Sn}_{0.50}\text{Cu}_{0.167}\text{Sb}_{0.333}\text{O}_2$  mixed crystal.

Sample	T [K]	$E_d$ (eV)	Seebeck coefficient ( $\mu\text{V} / \text{K}$ )
$\text{Sn}_{0.50}\text{Cu}_{0.167}\text{Sb}_{0.333}\text{O}_2$	234 - 245	0.08	- 54
	490 - 580	0.48	
	840 - 940	0.71	

### 3. 3. Magnetic properties

As discussed in previous section, the obtained electrical properties of the  $\text{SnO}_2$  – based solid solution confirmed the previous results for the tin dioxide – based materials [9]. However, for the second type of solid solutions evidenced in the  $\text{SnO}_2$  –  $\text{CuSb}_2\text{O}_6$  binary system, i. e.  $\text{Cu}_{1-x}\text{Sb}_{2(1-x)}\text{Sn}_{3x}\text{O}_6$  mixed crystals, their magnetic properties were considered to be of primary importance due to the paramagnetic base matrix of the  $\text{CuSb}_2\text{O}_6$  binary compound.

Magnetization data at an applied field of 200 Oe are shown in Fig. 3 – (a) for  $\text{CuSb}_2\text{O}_6$ , evidencing a broad maximum at about 60 K which is indicative of short range magnetic order [7, 10]. This latter maximum is diminished, but still evident in the *trirutile* type solid solution with the  $\text{Cu}_{0.923}\text{Sb}_{1.846}\text{Sn}_{0.231}\text{O}_6$  chemical formula (Fig. 3 - b), while the  $\text{Sn}_{0.50}\text{Cu}_{0.167}\text{Sb}_{0.333}\text{O}_2$  *rutile* type solid solution exhibit only a paramagnetic behaviour (Fig. 3 - c).

The  $1/\chi$  ( $\text{mol}/\text{cm}^3$ ) reciprocal susceptibility of the paramagnetic compound  $\text{CuSb}_2\text{O}_6$  and of the  $\text{Sn}_{0.50}\text{Cu}_{0.167}\text{Sb}_{0.333}\text{O}_2$  and  $\text{Cu}_{0.923}\text{Sb}_{1.846}\text{Sn}_{0.231}\text{O}_6$  mixed crystals, show a linear dependence on temperature (T) (Fig. 3 – a, b, c). All these data were fitted to a Curie-Weiss law [ $\chi^{-1} = C^{-1} (T - \theta)$  where C and  $\theta$  are the Curie and Weiss constants, respectively] over 140 – 300 K interval, after correction for diamagnetism (diamagnetic correction for  $\text{Cu}^{2+} = -12.8 \times 10^{-6}$  [c.g.s. units] ).

The obtained characteristic magnetic parameters [ $\theta$ ,  $\mu_p = 2.84 \sqrt{C_{\text{mol}}}$  = paramagnetic moment, and S = spin quantum number according to the spin only approximation  $\mu_p = g \sqrt{S(S+1)}$  with  $g=2$ ] are listed in Table 3.

Table 3. Evaluated parameters ( $\theta$ ,  $\mu_p$ , 2S) for temperature intervals ( $T_i$  to  $T_f$ ) where Curie - Weiss law is satisfied.

Mixed crystal formula	$T_i - T_f$ (K)	$\theta$ (K)	$\mu_p$ (B.M.)	2S	n
$\text{CuSb}_2\text{O}_6$	140 - 300	- 50.4	2.48	1.67	1
$\text{Cu}_{0.923}\text{Sb}_{1.846}\text{Sn}_{0.231}\text{O}_6$	140 - 300	- 88.7	2.05	1.28	1
$\text{Sn}_{0.50}\text{Cu}_{0.167}\text{Sb}_{0.333}\text{O}_2$	140 - 300	- 75.3	1.63	0.91	1

## 4. Discussion

As previously reported [8] and seen from the variation of the unit cell lattice parameters presented in Fig. 1, the formation mechanism of the  $\text{SnO}_2$  as well as  $\text{CuSb}_2\text{O}_6$  based solid solutions,

evidenced to be formed in the  $\text{SnO}_2$ - $\text{CuSb}_2\text{O}_6$  binary system, takes place by the incorporation of the  $\text{CuSb}_2\text{O}_6$  binary compound into the *rutile* type lattice and of  $\text{SnO}_2$  into the *trirutile* type lattice. However, for both types of mixed crystals, so far there is no clear evidence for the  $\text{Cu}^{(\text{II})}$  and  $\text{Sb}^{(\text{V})}$  cation distribution in the base  $\text{P4}_2/\text{mmm}$  matrix, either *rutile* or *trirutile* type.

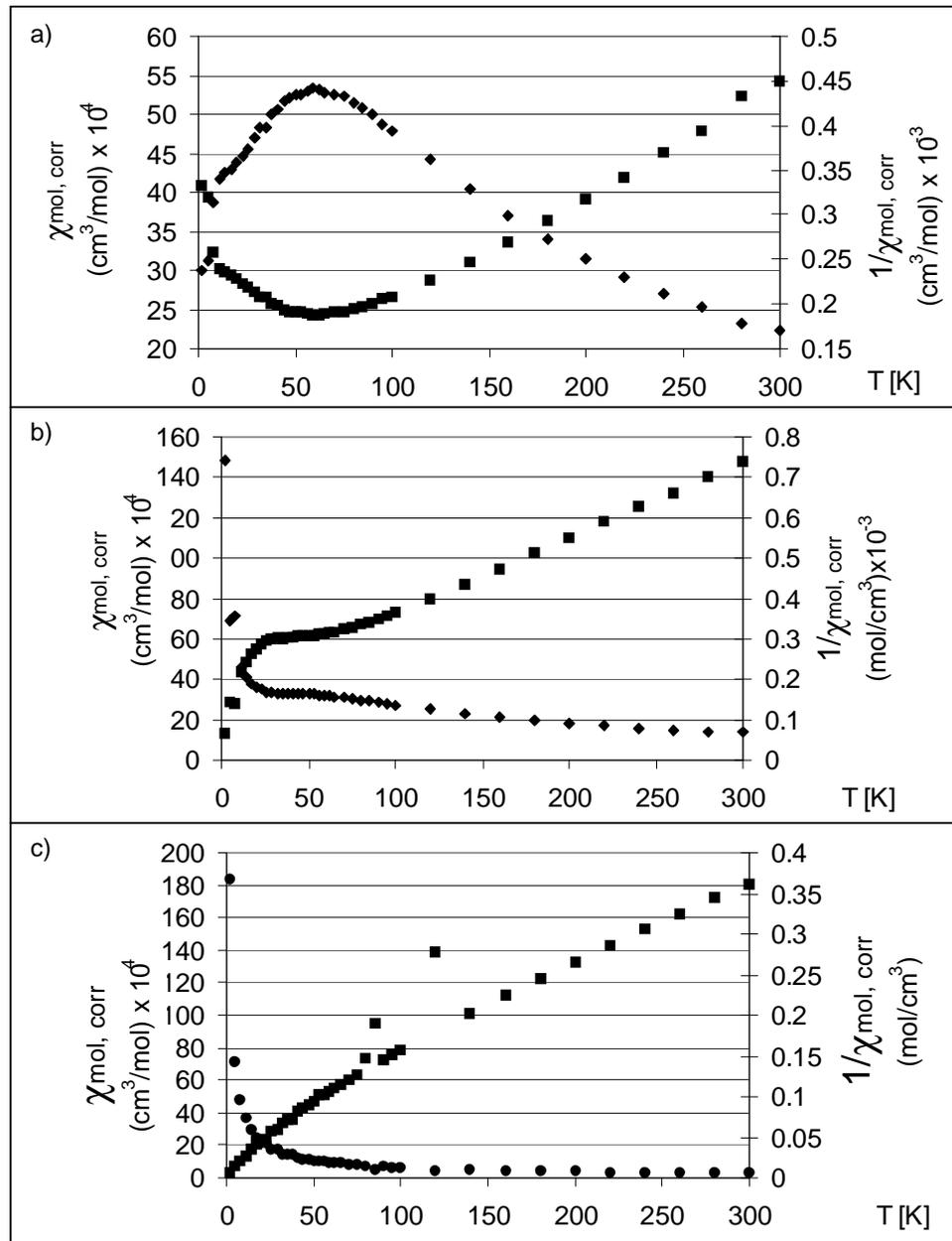


Fig. 3. Magnetic susceptibility and inverse susceptibility data versus temperature for  $\text{CuSb}_2\text{O}_6$  - (a),  $\text{Cu}_{0.923}\text{Sb}_{1.846}\text{Sn}_{0.231}\text{O}_6$  (b) and  $\text{Sn}_{0.50}\text{Cu}_{0.167}\text{Sb}_{0.333}\text{O}_2$  - (c) mixed crystals at an applied field of 200 Oe.

For the  $\text{Sn}_{1-x}\text{Cu}_x\text{Sb}_{2x/3}\text{O}_2$  *rutile* type solid solutions, as seen from the data presented in Fig. 2, the  $\text{Sn}_{0.75}\text{Cu}_{0.083}\text{Sb}_{0.167}\text{O}_2$  composition exhibits a typical semiconducting behaviour. The negative values of the Seebeck coefficient ( $\mu\text{V}/\text{K}$ ) obtained for this sample indicates that electrons are the major charge carriers; i. e. electronic and steps conduction mechanism due to the three reported values

for the  $E_d$  (eV) activation energy (data from Table 2). A higher electron concentration in the *rutile* type lattice is also predicted as a result of the  $Sb^{(V)}$  incorporation in the  $SnO_2$  solid solution [6] and was evidenced by the dark and shiny colour obtained in the studied  $Sn_{0.75}Cu_{0.083}Sb_{0.167}O_2$  sample. The paramagnetic behaviour evidenced for this *rutile* type solid solution (Fig. 3 – c), i. e. the studied  $Sn_{0.75}Cu_{0.083}Sb_{0.167}O_2$  composition, can be therefore regarded only as a result of the positioning of  $Cu^{2+}$  species in the same types of lattice sites as in  $CuSb_2O_6$ , octahedral coordination respectively.

For the  $Cu_{1-x}Sb_{2(1-x)}Sn_{3x}O_6$  *trirutile* type solid solution the magnetic properties obtained for the  $Cu_{0.923}Sb_{1.846}Sn_{0.231}O_6$  composition are consequences of the magnetic order evidenced in the  $CuSb_2O_6$  base lattice. As seen from the data presented in Fig. 3 all the studied samples presented a paramagnetic behaviour. Moreover, the last columns of Table 3 gives the number of unpaired electrons ( $n$ ) predicted from ionic models with completely quenched orbital momenta for the Cu atoms. The discrepancies between these and the “observed” values ( $2S$ ) are no more than one would expect from the simplicity of the used model, and still agree quite well with the reported literature data for the  $Cu^{2+}$  ion [7].

## 5. Conclusions

The electric and magnetic properties of the two types of solid solutions evidenced in the  $SnO_2$  -  $CuSb_2O_6$  system were investigated.

The solid solutions placed in the  $SnO_2$  rich domain, i. e.  $Sn_{0.50}Cu_{0.167}Sb_{0.333}O_2$  mixed crystal, presented semiconducting properties, revealing an increased concentration of the major charge carriers (electrons). In addition, these types of solid solutions evidenced a paramagnetic behaviour.

The  $CuSb_2O_6$  - based solid solutions, i. e.  $Cu_{0.923}Sb_{1.846}Sn_{0.231}O_6$  mixed crystal, presented high resistivity values and also a paramagnetic behaviour. Moreover, for these latter types of solid solutions, as well as for the  $CuSb_2O_6$  base compound, the magnetization data evidenced a broad maximum ( $\approx 60$  K), indicating a short - range magnetic order.

For both types of solid solutions, the values calculated for the spin quantum number ( $S$ ) according to the spin only approximation, confirmed the presence of  $Cu^{2+}$  species in the crystalline structure.

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