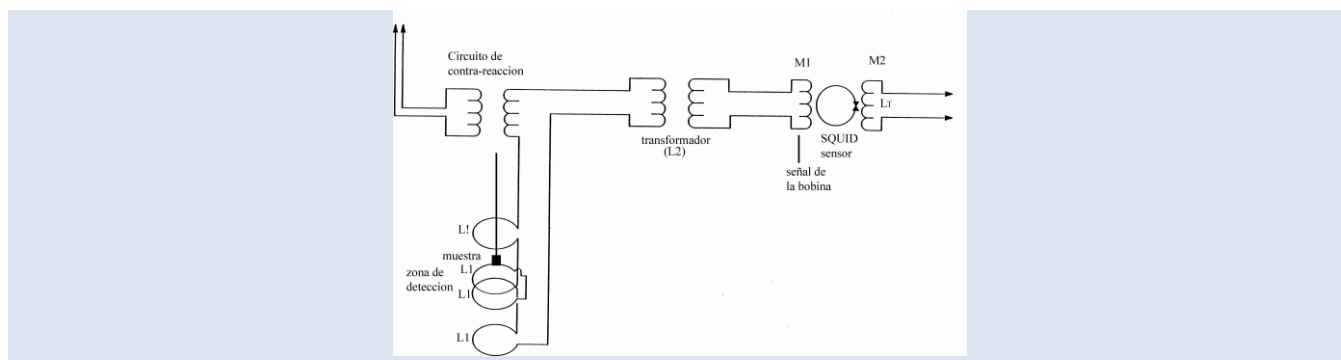


MAGNETIC SUSCEPTIBILITY FOR THE  $\text{Cu}_2\text{-II-IV-S}_4$  (II=Mn, Fe; IV=Si, Ge or Sn)  
COMPOUNDS: EXCHANGE INTERACTION PARAMETERS

M. Quintero<sup>1</sup>, E. Quintero<sup>1</sup>, E. Moreno<sup>1</sup>, P. Grima-Gallardo<sup>1,2\*</sup>, J. Marquina<sup>3</sup>, S. Alvarez<sup>1,3</sup>, C. Rincón<sup>1</sup>, D. Rivero<sup>1</sup>, M. Morocoima<sup>1</sup>, J. A. Henao<sup>4</sup>, M. A. Macías<sup>4</sup>, J. M. Briceño<sup>5</sup>, N. Rodríguez<sup>5,6</sup>

1: Centro de Estudios de Semiconductores (CES), Departamento de Física, Facultad de Ciencias, Universidad de los Andes, Mérida 5101, Venezuela. 2: Centro Nacional de Tecnología Óptica (CNTO), Centro de Investigaciones de Astronomía (CIDA), Mérida 5101, Venezuela. 3: Centro de Estudios Avanzados en Óptica (CEAO), Departamento de Física, Facultad de Ciencias, Universidad de los Andes, Mérida 5101, Venezuela. 4: Grupo de investigación en Química Estructural (GIQUE), Facultad de Ciencias, Escuela de Química, Universidad Industrial de Santander, Apartado aéreo 678, Bucaramanga, Colombia. 5: Laboratorio de Análisis Químico y Estructural de Materiales, Departamento de Física, Universidad de Los Andes, Mérida 5101, Venezuela. 6: Departamento de Ciencias, Área de Física, Núcleo Bolívar, Universidad de Oriente, Venezuela.

\*e-mail: peg@ula.ve



## ABSTRACT

Measurements of magnetic susceptibility  $\chi$  as a function of temperature (from 2 to 300 K) were made on polycrystalline samples of the compounds  $\text{Cu}_2\text{MnSiS}_4$ ,  $\text{Cu}_2\text{MnGeS}_4$ ,  $\text{Cu}_2\text{MnSnS}_4$ ,  $\text{Cu}_2\text{FeSiS}_4$  and  $\text{Cu}_2\text{FeGeS}_4$ . From the  $1/\chi$  versus T curves, it was concluded that the samples were antiferromagnetic. These curves were also used to determine values of the Néel temperature  $T_N$  and the Curie-Weiss temperature  $\theta$  for each compound. When the values of  $T_N$  and  $\theta$  are plotted against its molecular weight W, it was found that the compounds containing Mn lie on the same straight line, while those with Fe lie on a different one. For each compound, an analysis was carried out in terms of the simple mean-field theory and using the virtual transition model of Geertsma *et al.* for exchange interaction, and values of exchange interaction parameters were determined from the measured  $T_N$  and  $\theta$  data.

**Keywords:** magnetic semiconductor compound; magnetic properties; magnetic exchange interaction.

## SUSCEPTIBILIDAD MAGNÉTICA DE LOS COMPUESTOS $\text{Cu}_2\text{-II-IV-S}_4$ (II=MN, FE; IV=SI, GE O SN). PARÁMETROS DE LA INTERACCIÓN DE INTERCAMBIO

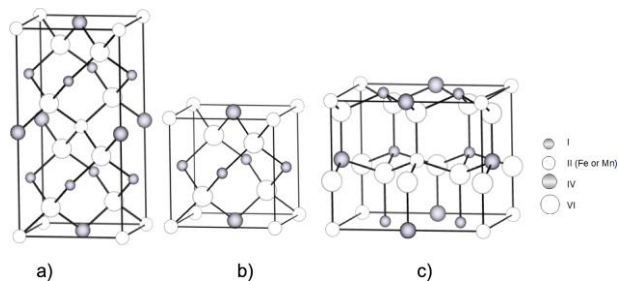
## RESUMEN

Se realizaron medidas de la susceptibilidad magnética  $\chi$  en función de la temperatura (2 a 300K) sobre muestras policristalinas de los compuestos  $\text{Cu}_2\text{MnSiS}_4$ ,  $\text{Cu}_2\text{MnGeS}_4$ ,  $\text{Cu}_2\text{MnSnS}_4$ ,  $\text{Cu}_2\text{FeSiS}_4$  y  $\text{Cu}_2\text{FeGeS}_4$ . De las curvas  $1/\chi$  versus T, se concluye que las muestras fueron antiferromagnéticas. Estas curvas fueron también usadas para determinar los valores de la temperaturas de Néel  $T_N$  y de Curie-Weiss  $\theta$  para cada uno de los compuestos. Cuando se grafican los valores de  $T_N$  y  $\theta$  en función del peso molecular W, se encuentra que tanto los compuestos que contienen Mn como Fe muestran una dependencia lineal, pero con diferentes pendientes. Para cada compuesto, fue llevado a cabo un análisis en términos de la teoría de campo medio y el modelo de transición virtual de Geertsma *et al.* para la interacción de intercambio permitiendo la determinación de los valores de los parámetros de interacción a partir de los valores medidos de  $T_N$  y  $\theta$ .

**Palabras clave:** compuestos semiconductores magnéticos; propiedades magnéticas; interacción magnética de intercambio.

## 1. INTRODUCTION

Quaternary magnetic semiconducting compounds of the  $I_2-II-IV-VI_4$  type, where  $II = Mn, Fe$  or  $Co$ ,  $IV = Si, Ge, Sn$  or  $Pb$  and  $VI = S, Se$  or  $Te$ , are of great interest because of their large magneto-optical effects which are observed due to the presence of paramagnetic ions [1-2]. As has been reported [2-4], most of these compounds showed either the tetrahedral tetragonal stannite ( $I\bar{4}2m$ ) structure based on zinc-blende, and an orthorhombic superstructure derived from wurtzite (known as wurtz-stannite,  $Pmn2_1$ ). It has been found recently that, at room temperature,  $Cu_2FeSnS_4$  has a tetragonal crystal structure with space group  $P\bar{4}$  [5]. All these structures are shown in figure 1.



**Figure 1.** a) Tetragonal stannite  $I\bar{4}2m$ , b) pseudo-cubic  $P\bar{4}$  and c) orthorhombic wurtz-stannite  $Pmn2_1$  structures.

Results on the lattice parameter values and differential thermal analysis DTA for these materials have been reported lately in Ref. [6]. In a previous work [7], the magnetic behavior of some  $I_2-Mn-IV-Se_4$  compounds has been published. However, the available information related to the magnetic behavior of  $I_2-(Mn,Fe)-IV-S_4$  materials is very scarce. Hence, measurements of magnetic susceptibility  $\chi$  as a function of temperature  $T$  in the range between 2 and 300 K have been carried out on the  $Cu_2MnSiS_4$ ,  $Cu_2MnGeS_4$ ,  $Cu_2MnSnS_4$ ,  $Cu_2FeSiS_4$  and  $Cu_2FeGeS_4$  compounds. The magnetic results thus obtained were correlated with the details of the crystal structure to give values for the exchange interaction parameters for these compounds.

## 2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUES

The samples were produced by the melt and anneal technique. In each case, highly pure components (copper 99.98 %, manganese 99.97 %, iron 99.9 %, cobalt 99.99 %, silicon 99.999%, germanium 99.999%, tin 99.999 %, sulphur 99.997 % and/or selenium 99.9997 %) of 1 g sample were sealed under vacuum ( $\approx 10^{-5}$  Torr) in a small quartz ampoule, and then the components were heated up to 200 °C and kept for about 1-2 h, then the temperature was raised to 500 °C using a rate of 40 K/h, and held at this temperature for 14 hours. After, the samples were heated from 500 °C to 800 °C at a rate of 30 K/h and kept at this temperature for another 14 hours. Then it was raised to 1150 °C at 60 K/h, and the components were melted together at this temperature. The furnace temperature was brought slowly (4 K/h) down to 600 °C, and the samples were annealed at this temperature for 1 month. Then, the samples were slowly cooled to room temperature using a rate of about 2 K/h. Magnetic susceptibility measurements as a function of  $T$  from 2 to 300 K were made using a Quantum Design MPMS-5 SQUID magnetometer with an external magnetic field of  $1 \times 10^{-2}$  T. Resulting  $1/\chi$  versus  $T$  curves were analyzed to give various magnetic parameters, as discussed below.

## 3. RESULTS AND DISCUSSION

### 3.1 Magnetic Results

Measurements of zero-field cooling (zfc) (heating curve) and field cooling (fc) (cooling curve) magnetic susceptibility were made on the samples and typical obtained  $1/\chi$  vs  $T$  curves are shown in figs. 2a and 2b for  $Cu_2MnSnS_4$  and  $Cu_2FeSiS_4$  respectively.

The rest of the sample showed similar curves. It can be seen from these figures that, for each compound, the  $1/\chi$  vs  $T$  plot is linear at higher temperatures and the extrapolation of this line to  $1/\chi=0$  gives a negative value of the Curie-Weiss  $\theta$  indicating that these compounds are antiferromagnetic AF. It is also seen from these figures that, in each case, the susceptibility run under zero field cooling (zfc) is identical to the one obtained under field cooling (fc) condition, so that spin-glass behavior is ruled out here. Hence, almost ideal collinear antiferromagnetism is present for each compound. The Néel temperature  $T_N$  values for the materials

can be obtained from the maximum peaks shown in the inset of figs. 2a and 2b.

For antiferromagnetic behavior, the variation of  $1/\chi$  with  $T$  above the  $T_N$  is given by the relation [9],

$$1/\chi = (T-\theta)/C \quad (1)$$

where  $C$  the Curie constant and its theoretical value of  $C$  is given by [9]

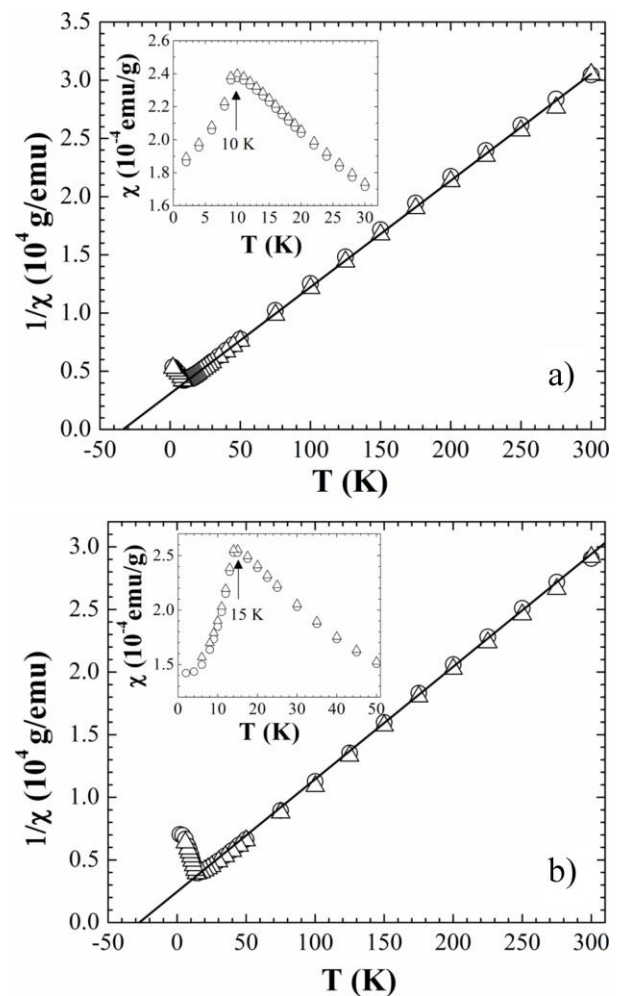
$$C = N_A g^2 \mu_B^2 J(J+1)/3K_B W \quad (2)$$

$N_A$  being the Avogadro number,  $\mu_B$  the Bohr magneton and  $W$  the molecular weight of the compound. Thus, the  $1/\chi$  vs  $T$  experimental data were fitted to eq. (1) and the resulting values of the magnetic parameter  $C$  and  $\theta$  as well as values for  $T_N$  are listed in table 1, together with the lattice parameter values reported in earlier works for  $\text{Cu}_2\text{FeSnS}_4$  [5],  $\text{Cu}_2\text{FeGeSe}_4$  [8],  $\text{Cu}_2\text{MnSnSe}_4$  [10],  $\text{Cu}_2\text{MnGeSe}_4$  [11], and  $\text{Cu}_2\text{FeSnSe}_4$  [11]. The variations of  $\theta$  and  $T_N$  as a function of  $W$  of the material are shown in figs. 3a and 3b respectively.

As expected, it is observed from table 1 that for the Mn samples the experimental values of  $C_E$  are, close to the theoretical values of  $C_T$  obtained from eq. (2) using  $J=S=5/2$ ,  $L=0$  and  $g=2$  for the  $\text{Mn}^{2+}$  ion. While for  $\text{Cu}_2\text{FeSiS}_4$ ,  $\text{Cu}_2\text{FeGeS}_4$  and  $\text{Cu}_2\text{FeSnS}_4$  it is found that the value of  $C_E$  is close to the one obtained for  $C_T$  when the spin-only values ( $J=S=2$ ,  $L=0$  and  $g=2$ ) are used in eq. (2) for the  $\text{Fe}^{2+}$  ion. This result would be due to the presence of crystal field effects and/or magnetic anisotropy which are responsible for the quenching of the orbital moment ( $L=0$ ) in these samples. However, for  $\text{Cu}_2\text{FeGeSe}_4$  and  $\text{Cu}_2\text{FeSnSe}_4$ , it is found that  $C_E \approx C_T$  when  $L=S=2$ ,  $J=4$  and  $g=1.5$  are used in eq. (2) for  $\text{Fe}^{2+}$ . This result would indicate that  $\text{Fe}^{2+}$  ions exhibit an orbital contribution to the magnetic moment which is also feasible in other materials involving  $\text{Fe}^{2+}$ .

It can be seen from fig. 3a that independent of the crystal structure of the sample, the values of  $\theta$  for the Mn and Fe lay on different straight lines. It is also seen for the Mn samples that the variation of  $\theta$  vs  $W$  is very small, i.e.  $\theta \approx (-26 \pm 3)$  K, while for the Fe materials the absolute values of  $\theta$  increase linearly as  $W$  is increased. These results would indicate that the values of  $\theta$  for the Mn are not

influence by the presence of diamagnetic cations contrary to that observed in the Fe samples. With regard to the variation of  $T_N$  with  $W$  it is seen from fig. 3b that the values of  $T_N$  for the Mn and most of the Fe materials lay on nearly parallel straight lines. It is also observed that  $\text{Cu}_2\text{FeSnS}_4$  has a very large  $T_N$  value compared with the rest of the compounds. This would suggest that another straight line would exist for  $\text{P}\bar{4}$  compounds. This behavior would be due to the smallest size of the pseudo-cubic  $\text{P}\bar{4}$  structure, resulting in the highest magnetic interaction between the nearest magnetic neighbors.



**Figure 2.** Typical curves of the reciprocal of susceptibility  $1/\chi$  against temperature  $T$  for a)  $\text{Cu}_2\text{MnSnS}_4$  and b)  $\text{Cu}_2\text{FeSiS}_4$ . Zero field cooling zfc: open circles, field cooling fc: open triangles. The Curie–Weiss behavior is represented by the solid line. Inset: temperature dependence of the magnetic susceptibility  $\chi$  for a)  $\text{Cu}_2\text{MnSnS}_4$  and b)  $\text{Cu}_2\text{FeSiS}_4$  showing the Néel temperature  $T_N$ .

**Table 1.** Parameter values for antiferromagnetic Cu<sub>2</sub>-II-IV-S<sub>4</sub>(Se<sub>4</sub>) quaternary compounds. Experimental values of *a*, *b* and *c* taken from Ref. [7]. T<sub>N</sub> and θ are the resulting Neel and Curie-Weiss temperatures. Resulting values of α and -I<sub>0</sub>/k and -J<sub>1</sub>/k obtained with u=2.

N°	Compounds	parameters	<i>W</i>	T <sub>N</sub>	θ <sub>a</sub>	C <sub>T</sub> (x10 <sup>-3</sup> )	C <sub>E</sub> (x10 <sup>-3</sup> )	Ref.	α	-I <sub>0</sub> /k	-J <sub>1</sub> /k	
	Space group	(nm)	(g/mol)	(K)	(K)	(emu.g/K)	(emu.g/K)		(nm <sup>-1</sup> )	(Knm <sup>2</sup> )	(K)	
1	Cu <sub>2</sub> MnSiS <sub>4</sub> Pmn2 <sub>1</sub>	a=0.7536 b=0.6442 c=0.6187	338.38	8	-29	12.9	11.5	Our	L=0 J=S=5/2	3.34	0.78	0.46
2	Cu <sub>2</sub> MnGeS <sub>4</sub> Pmn2 <sub>1</sub>	a=0.7616 b=0.6513 c=0.6230	382.93	9	-20	11.4	11.4	Our	L=0 J=S=5/2	6.43	4.22	0.46
3	Cu <sub>2</sub> MnSnS <sub>4</sub> I42m	a=0.5518 c=1.0807	429.00	10	-32	10.2	10.8	Our	L=0 J=S=5/2	3.74	1.31	0.55
4	Cu <sub>2</sub> FeSiS <sub>4</sub> Pmn2 <sub>1</sub>	a=0.7421 b=0.6417 c=0.6141	339.28	15	-27	8.85	11.1	Our	L=0 J=S=2	8.88	31.37	1.05
5	Cu <sub>2</sub> FeGeS <sub>4</sub> I42m	a=0.5336 c=1.0522	383.84	17	-48	7.8	8.0	Our	L=0 J=S=2	4.45	4.02	1.31
6	Cu <sub>2</sub> FeSnS <sub>4</sub> P4̄	a=0.5433 c=0.5410	429.91	38	-74	7.0	7.11	[6]	L=0 J=S=2	5.09	9.97	2.17
7	Cu <sub>2</sub> MnGeSe <sub>4</sub> Pmn2 <sub>1</sub>	a=0.7996 b=0.6857 c=0.6572	570.51	10	-22	7.668	7.60	[12]	L=0 J=S=5/2	6.16	5.29	0.51
8	Cu <sub>2</sub> MnSnSe <sub>4</sub> I42m	a=0.5766 c=1.1368	616.58	16	-25	7.09	6.60	[11]	L=0 J=S=5/2	9.57	59.99	0.72
9	Cu <sub>2</sub> FeGeSe <sub>4</sub> I42m	a=0.5601 c=1.1056	571.42	20	-162	9.84	9.77	[9]	L=S=2 J=4	1.07	1.08	1.88
10	Cu <sub>2</sub> FeSnSe <sub>4</sub> I42m	a=0.5705 c=1.1271	617.49	19	-200	9.11	10.00	[11]	L=S=2 J=4	0.56	0.78	1.75

### 3.2 Exchange Interaction Results

Another point of interest here is to discuss the exchange interaction parameters J<sub>i</sub> in the present compounds. The mean field theory gives the following equations for θ and T<sub>N</sub> [9]:

$$\theta = 2J(J+1) \sum m_i J_i / 3k \quad (3)$$

$$T_N = 2J(J+1) \sum \eta_i m_i J_i / 3k \quad (4)$$

where the summation is over sets of equidistant magnetic neighbors from a chosen magnetic atom, *m<sub>i</sub>*, and *J<sub>i</sub>* being the number and exchange interaction for the *i*-th set, *J* being the total angular moment and *η<sub>i</sub>* being +1 for antiparallel and -1 for parallel spin. It was suggested in earlier work carried out on the Mn-III<sub>2</sub>-VI<sub>4</sub> compounds [12] that a possible mechanism that explains the magnetic interaction between magnetic ions is the one proposed by Geertsma and Haas [13], based on the work of Concalves da Silva and Falicov [14]. This exchange interaction involves virtual transitions between the p-valence band and a band of d states

arising from the magnetic ions, and the exchange parameter *J<sub>i</sub>* can be taken to vary with distance *r<sub>i</sub>* as

$$J_i = I_0 \exp(-\alpha r_i) / r_i^u \quad (5)$$

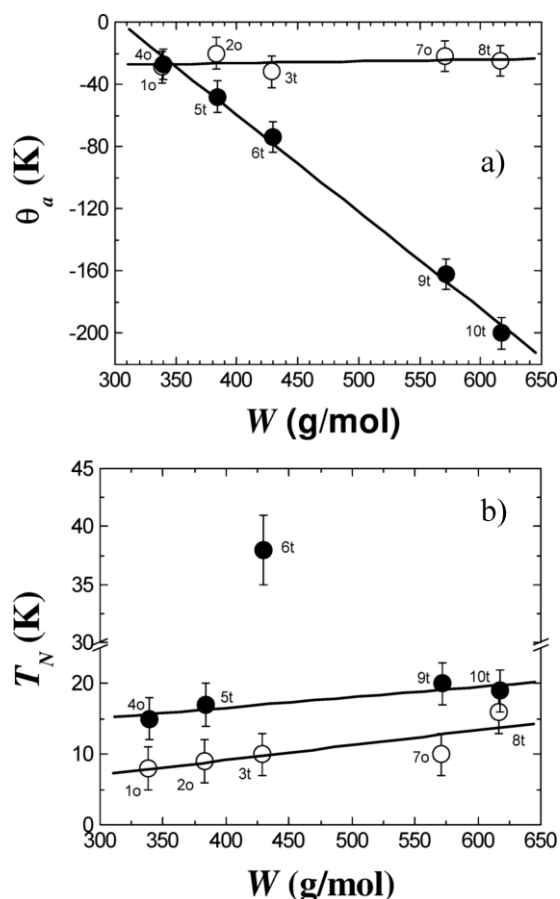
where α depends on the effective mass of the valence band and the energy difference involved in the virtual transition. It has been shown that in the case of the Mn-III<sub>2</sub>-VI<sub>4</sub> compounds [12] good results are obtained with u=2. If u=2 is used in the analysis, then, substituting eq. (5) into (3) and (4) one obtains

$$\theta / T_N = [\sum m_i \exp(-\alpha r_i) / r_i^2] / [\sum \eta_i m_i \exp(-\alpha r_i) / r_i^2] \quad (6)$$

and the value of I<sub>0</sub>/k can be determined from the following relation,

$$I_0/k = 3\theta / [2J(J+1) \sum m_i \exp(-\alpha r_i) / r_i^2] \quad (7)$$





**Figure 3.** a) Dependence of the Curie-Weiss temperature  $\theta$  with  $W$ . Open circles: compounds containing Mn; close circles: compounds containing Fe. The solid lines are to guide the eyes. b) Dependence of the Néel temperature  $T_N$  with  $W$ . Open circles: compounds containing Mn; close circles: compounds containing Fe. The solid lines are to guide the eyes.

It is seen that, in order to use equations (6) and (7) to calculate  $\alpha$  and  $I_0$ , and so  $J_i(r_i)$ , it is necessary to know the configuration of the magnetic ions in the crystal structure as well as the orientation of the spins below the temperature  $T_N$  in the material. The magnetic structures for the materials are shown in figure 4, where for clarity only the magnetic cations are shown, and the value of  $i$  for equidistant magnetic cation position is also indicated. Choosing an origin on a magnetic atom site, the distances  $r_i$  between magnetic atoms is given by

$$r_i = [(u_i a/2)^2 + (v_i a/2)^2 + (w_i c/4)^2]^{1/2} \text{ for } \overline{I4}2m, \quad (8)$$

$$r_i = [(u_i a)^2 + (v_i a)^2 + (w_i c)^2]^{1/2} \text{ for } P\overline{4}, \quad (9)$$

$$r_i = [(u_i a/2)^2 + (v_i b/3)^2 + (w_i c/2)^2]^{1/2} \text{ for } Pmn2_1 \quad (10)$$

where  $a$ ,  $b$  and  $c$  are the lattice parameters,  $u_i$ ,  $v_i$  and  $w_i$  are integers. It can be assumed for ideal antiferromagnetic materials that the total spin system can be treated as two interpenetrating sublattices that have no resultant interaction between them.

Then, considering the structures shown in fig. 4 and using the values for the lattice parameter  $a$ ,  $b$  and  $c$  listed in table 1, values of  $m_i$  and  $\eta_i$  were determined for a range of magnetic neighbors ( $u_i, v_i, w_i$ ). The obtained data are given in table 2 for stannite  $\overline{I4}2m$ , for tetragonal pseudo cubic  $P\overline{4}$  and for wurtzstannite  $Pmn2_1$  materials. Thus, using the resulting values given in table 2 together with the experimental values of  $a$ ,  $b$ ,  $c$ ,  $\theta$  and  $T_N$  listed in table 1, values of  $\alpha$  and  $I_0$  were determined from equations (6) and (7), and the resulting values are given in table 1. It was found that for each compound the obtained values of  $J_i$  fall very rapidly with distance  $r_i$ , and  $J_1$  is about 2 and 5 times higher than  $J_2$  and  $J_3$  respectively.

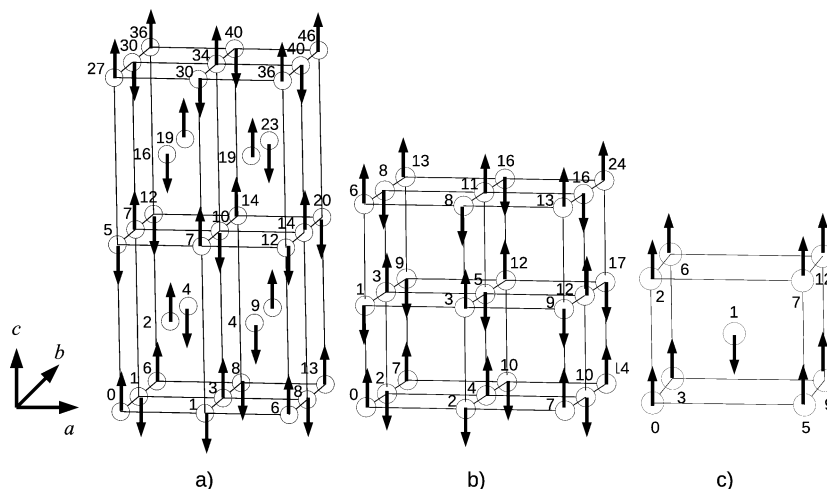
Figures 5a and 5b illustrate the resulting  $\alpha$  vs  $T_N/\theta$  and  $(I_0/k)$  vs  $T_N/\theta$  curves respectively. It is seen from fig. 5a that the calculated values of  $\alpha$  for the Mn as well as for the Fe compounds lay on the same straight line. The exception being the sample  $Cu_2FeSnS_4$ , for which as indicated above, because the smallest volume gives the highest value of  $T_N$ , which yields the lowest value of  $\alpha$  compared with the rest of the compounds. It is observed in fig. 5b that, similar to fig. 5a, the values of  $(I_0/k)$  for the Mn as well as for the Fe compounds lay on the line.

The resulting values of  $-J_1/k$  versus  $W$  for the compounds are shown in fig. 6, where it is seen that the compounds with Mn lay on a different line than the one with Fe. Also, it is seen from this figure that the absolute values of  $-J_1/k$  for the Fe-compounds are higher than the ones for the Mn-compounds; this result is consistent with the values of  $\theta$  shown in fig. 3a. It is found that the values for the exchange constants for the present compounds are small compared to the nearest neighbor  $J_1/k$  in disordered II-VI magnetic semiconductor alloys, typically

$J_1/k \approx -10$  K [15, 16]. Also, it is to be mentioned that, the values of  $\theta$  given in fig. 3a are much smaller than those reported for the disordered zinc-blende  $\text{II}_{1-x}\text{Mn}_x\text{VI}$  spin glass-like magnetic materials [17]. For the disordered zinc-blende superexchange of the type Mn-VI-Mn or Fe-VI-Fe has been found to be the dominant mechanism responsible for the magnetic interaction between nearest magnetic ions [17, 18]. This would not be the case here, since for the present ordered compounds [19] each VI anion is surrounded by two Cu, one IV and one Mn or Fe, and in this case the magnetic superexchange pathways are of the type Mn-Se....Se-Mn and/or Fe-Se....Se-Fe, and contrary to the disordered

materials, no magnetic contact of the type Mn-VI-Mn or Fe-VI-Fe occurs in the ordered compounds.

The smaller values of  $\theta$  for the ordered compounds would be due to the lack of superexchange of the type Mn-VI-Mn and that the closest magnetic neighbors are separated by the lattice parameter  $a$ , while for cubic zinc-blende structure the closest magnetic neighbors are separated by  $(2^{1/2}a)$ . Furthermore, there are fewer neighbors connected by  $J_1, J_2$  and  $J_3$  ( $m_1=4, m_2=8, m_3=4$ , i.e. 16 magnetic atoms for ordered compounds compare to  $m_1=8, m_2=6, m_3=24$ , i.e. 38 atoms for zinc-blende materials).



**Figure 4.** Magnetic unit cells showing the magnetic moments (arrows) for a) stannite  $\bar{I}42m$ , with dimensions  $2a, 2b, 2c$ , b) pseudo-cubic  $P\bar{4}$  with dimensions  $2a, 2b, 2c$  and c) wurtz-stannite  $Pmn2_1$  with dimensions  $a, b, c$  structures. The numbers indicate the equidistant neighbors to magnetic ion from origin atom (zero) to  $i$ th atom in the cell. The diamagnetic ions are not shown.

**Table 2.** Values of  $i, u, v, w, m_i$  and  $\eta$  for stannite  $\bar{I}42m$ , pseudo-cubic  $P\bar{4}$  and wurtz-stannite  $Pmn2_1$   $\text{Cu}_2\text{-II-IV-S}_4(\text{Se}_4)$  antiferromagnetic compounds.

$i$	$u$	$v$	$w$	$m_i$	$\eta$	$u$	$v$	$w$	$m_i$	$\eta$	$u$	$v$	$w$	$m_i$	$\eta$
$\bar{I}42m$						$P\bar{4}$					$Pmn2_1$				
1	2	0	0	4	1	0	0	1	2	1	1	1	1	4	1
2	1	1	2	8	0	1	0	0	4	1	0	0	2	2	-1
3	2	2	0	4	-1	1	0	1	8	-1	0	3	0	2	-1
4	3	1	2	16	0	1	1	0	4	-1	1	-2	-1	4	1
5	0	0	4	2	1	1	1	1	8	1	2	0	0	2	-1
6	4	0	0	4	-1	0	0	2	2	-1	0	3	2	4	-1
7	2	0	4	8	-1	2	0	0	4	-1	2	0	2	4	-1
8	4	2	0	8	1	1	0	2	8	1	-1	4	1	4	1

Table 2. Cont.

<i>i</i>	<i>u</i>	<i>v</i>	<i>w</i>	<i>mi</i>	$\eta$	<i>u</i>	<i>v</i>	<i>w</i>	<i>mi</i>	$\eta$	<i>u</i>	<i>v</i>	<i>w</i>	<i>mi</i>	$\eta$
$\bar{I}42m$						$P\bar{4}$					$Pmn2_1$				
9	3	3	2	8	0	2	0	1	8	1	2	3	0	4	-1
10	2	2	4	8	1	2	1	0	8	1	-1	1	3	4	1
11	5	1	2	16	0	1	1	2	8	-1	1	-2	3	4	1
12	4	0	4	8	1	2	1	1	16	-1	2	3	2	8	-1
13	4	4	0	4	-1	2	0	2	8	-1	1	-5	1	4	1
14	4	2	4	16	-1	2	2	0	4	-1	-3	1	1	4	1
15	6	0	0	4	1	0	0	3	2	1	0	0	4	2	-1

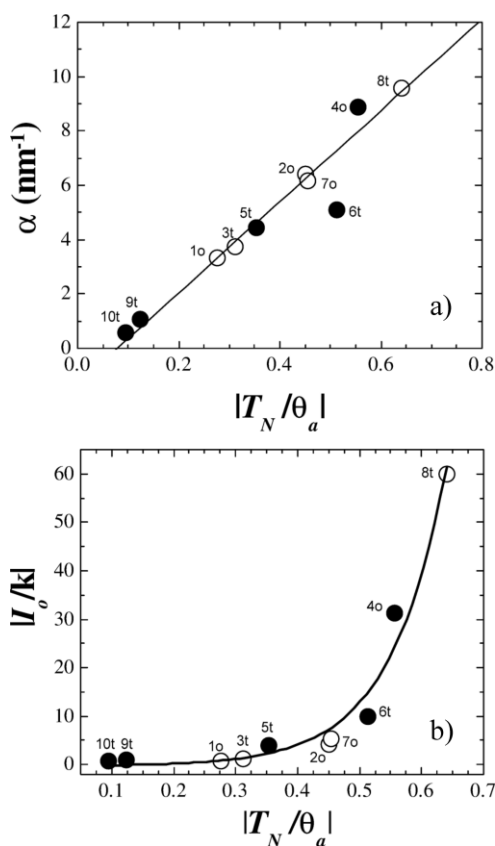


Figure 5. a) Calculated values of  $\alpha$  as a function of the absolute value of  $T_N/\theta$ . Open circles: compounds containing Mn; close circles: compounds containing Fe; t: tetragonal; o: orthorhombic. The solid lines is a linear fit given by  $\alpha = 0.078 + 0.059 (T_N/\theta)$ . b) Calculated values of  $I_0/k$  factor as a function of the absolute value of  $T_N/\theta$ . Open circles: compounds containing Mn; close circles: compounds containing Fe; t: tetragonal; o: orthorhombic. The solid lines are to guide the eyes.

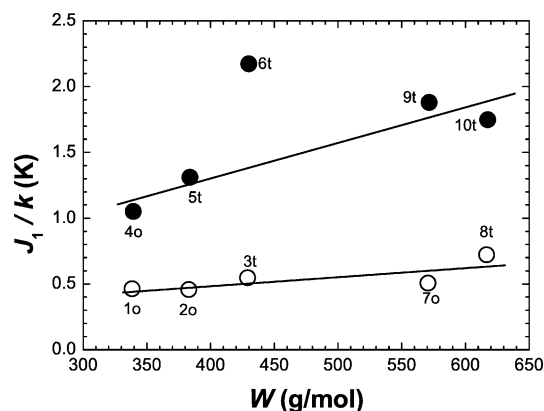


Figure 6. Dependence of the absolute value of first nearest neighbor exchange interaction  $J_1/k$  with  $W$ . Open circles: compounds containing Mn; close circles: compounds containing Fe; t: tetragonal; o: orthorhombic.

#### 4. CONCLUSIONS

The curves of the reciprocal of the magnetic susceptibility  $1/\chi$  against temperature in the range 2-300 K showed that the magnetic behavior of  $Cu_2MnGeS_4$ ,  $Cu_2MnSnS_4$ ,  $Cu_2FeSiS_4$ ,  $Cu_2FeGeS_4$  and  $Cu_2MnSiS_4$  compound is antiferromagnetic. It was observed that, independent of the crystal structure of the sample, the curves of  $\theta$  vs  $W$  and/or  $T_N$  vs  $W$  for the Mn and/or Fe materials, in each case, lay on different straight lines.

Using the crystal structure and lattice parameter values together with the  $T_N$  and  $\theta$  experimental data, values of  $\alpha$  and  $I_0/k$  were estimated for each compound. Hence, value for any  $J_i$ , i.e., for any  $i$ -th set of neighbors, could be estimated. The values of the first nearest neighbor  $J_1/k$  for the compounds

containing Mn were found to be smaller than those containing Fe. Also, it was found that independent of the crystal structure of the sample, the dependence of  $\alpha$  against the absolute values of  $T_N/\theta$  for the Mn and Fe lay on a same line, except for  $\text{Cu}_2\text{FeSnS}_4$  for the reason given above. The exchange interaction values for the present compounds were found to be smaller than those obtained in II-VI disordered magnetic semiconductor alloys.

## 5. ACKNOWLEDGEMENT

This work was partially supported by the Consejo de desarrollo Científico, Humanístico, Tecnológico y de las Artes de la Universidad de Los Andes (CDCHT-ULA) (Projects No. C-1740-11-05-AA and No. C-1885-14-05-B).

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