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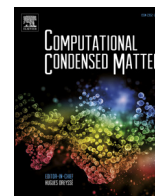
Regular article

Ground state and electronic structures of the series $Li_2Cu_{1-x}S_xSb$ with ($x = 0, 1/8, 2/8, 3/8, 4/8, 5/8, 6/8, 7/8, 1$)

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ABSTRACT

Li_2CuSb is considered as multifunctional material, electrode for high capacity of rechargeable batteries and novel material for second harmonic generation. First principle electronic structure calculations of series $Li_2Cu_{1-x}S_xSb$ (with $x = 0, 1/8, 2/8, 3/8, 4/8, 5/8, 6/8, 7/8, 1$) has been done. New optimized distribution has been introduced for atoms among the allowed positions of the Heusler structure Li_2CuSb. The primary compound Li_2CuSb is a Heusler compound based on one 3d transition metal. The injection of S into Li_2CuSb, instead of Cu, introduces a new aspects about the important role of 3d in the electrical properties of the compound. Theoretical investigation of the effect of atomic positions on the properties of the series is included. These calculations show that moving Li atom from the surface of the unit cell into the inside improves the compound applications in the high capacity of rechargeable batteries. The present calculations are in agreement with the previous theoretical and experimental publications in the increase of capacity [1,2]. Band structure and DOS indicate an increase in the density of states at Fermi level with more dispersion for the occupied states of $Li_2Cu_7S_1Sb$ and $Li_2Cu_1S_7Sb$. As a result, the electronic specific heat coefficient and the conductivity increases.

1. Introduction

Heusler alloys (HA) are a class of materials which may be metals, semiconductors or semimetals and most of them are ferromagnet. Interesting physical properties of Heusler alloys have attracted the attention of physicists for many decades since they were first discovered by Heusler [3]. Heusler compounds belong to a group of ternary intermetallics with the stoichiometric composition X_2YZ, where X, Y and Z occupies the Wyckoff position 8c, 4a and 4b respectively as shown in Fig. 1. Crystallographic structure of these alloys can be constructed from an arrangement of four interpenetrating FCC sublattices. Such sublattices are shifted towards body diagonal and the chemical disorder within these sublattices causes drastic changes in the physical properties [4,5]. Heusler compounds are spatially arranged according to regularity in three simple structures that are $L2_1$, B2 and A2 [6,7]. In the $L2_1$-structure type, the fully ordered HA, the four sublattices are occupied by X, Y, X, and Z atoms. Obviously, $L2_1$-structure type is hard to be obtained because there is a variety of possible disorder [8]. CsCl structure-type or B2 is attained when X atoms remain ordered and full

disorder occurs only between Y and Z sites. If disorder occurs between one X site and either Y or Z sites, the atomic arrangement may lead to a $DO_3(Fe_3Al)$ structure. Finally an A2 structure is formed when random order occurs between all X, Y and Z sites.

The wide variety of possible compositions of the Heusler compounds allows one to easily produce materials with desired physical properties. The easiest way to compose new materials is by the exchange of one or more of the elements X, Y, and Z. This is widely used in experimental and theoretical fields [9–16]. For example in metals, two mutually exclusive types of effects tend to slow down the flow of electrons and reduce electrical conductivity. These two effects are structural transition or the changes in the electronic structure due to doping and other effect are the blocking of electrons by other electrons.

The Li_2CuSb Heusler compound is presently under intensive investigation because of its applications. Such applications are: electrode for high capacity rechargeable batteries, materials for second harmonic generation and solarcell [1,17–19]. In particular, the Li_2CuSb Full-Heusler compound is classified as semiconductor material [17]. Additionally, D. Kieven et al. issued 0.8 eV band gap for LiCuS in their calculations in Ref [20]. This semiconductor behavior of Li_2CuSb and LiCuS reinforces the idea of injecting Li_2CuSb by S with respect to Cu or Sb. This may introduce new

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Fig. 1. Structure of Heusler compound.

Table 1
Optimized structural parameters for Li_2CuSb and the positions, according to the arrangement of the formula in the first column, are (0.25 0.25 0.25), (0.0 0.0 0.0), (0.5 0.0 0.0) and (0.75 0.75 0.75) with space group number 216 (F-43m).

Formula	Lattice constant Å	Volume Å^3	Energy	Pro
CuLiLiSb	6.3448	430.96	−16,307.5067	Conductor
LiCuSbLi	6.3448	430.92	−16,307.5065	Conductor
LiLiCuSb	6.3406	430.07	−16,307.528	Semiconductor
LiSbLiCu	6.3405	430.03	−16,307.528	Semiconductor
SbCuLiLi	6.3417	430.09	−16,307.528	Semiconductor
LiCuLiSb	6.3413	430.21	**−16,307.5297**	Semiconductor
LiLiSbCu	6.3413	430.23	**−16,307.5297**	Semiconductor
LiSbCuLi	6.344	430.89	−16,307.5065	Conductor
CuSbLiLi	6.341	430.23	**−16,307.5296**	Semiconductor
SbLiLiCu	6.344	430.8	−16,307.5067	Conductor

Table 2
Optimized structural parameters for Li_2CuSb and the positions, according to the arrangement of the formula in the first column, are (0.25 0.25 0.25), (0.0 0.0 0.0), (0.5 0.5 0.5) and (0.75 0.75 0.75) with space group number 216 (F-43m).

Formula	Lattice constant Å	Volume Å^3	Energy	Pro
CuLiLiSb	6.342	430.30	−16307.5166	Semiconductor
LiCuSbLi	6.346	431.22	−16307.5188	Semiconductor
LiLiCuSb	6.347	431.44	−16307.4787	Conductor
LiSbLiCu	6.341	430.11	**−16307.5301**	Semiconductor
SbCuLiLi	6.345	431.02	−16307.5067	Conductor
LiCuLiSb	6.342	430.33	−16307.5165	Semiconductor
LiLiSbCu	6.345	431.05	−16307.4937	Conductor
LiSbCuLi	6.342	430.37	**−16307.5301**	Semiconductor
CuSbLiLi	6.345	431.05	−16307.5067	Conductor
SbLiLiCu	6.342	430.30	**−16307.5302**	Semiconductor

Table 3
Optimized structural parameters for Li_2CuSb, and the positions according to the arrangement of the formula in the first column is (0.25 0.25 0.25), (0.75 0.75 0.75), (0.0 0.0 0.0), (0.5 0.5 0.5) and with space group number 255 (Fm-3m).

Formula	Lattice constant Å	Volume Å^3	Energy	Pro
Li$_2$SbCu	6.3446	430.875	−16307.5066	Conductor
Li$_2$CuSb	6.3472	431.422	−16307.4917	Conductor

aspects about the produced alloys. The study of the series $Li_2Cu_{1-x}S_xSb$ (with $x = 0, 1/8, 2/8, 3/8, 4/8, 5/8, 6/8, 7/8, 1$) is rare. This makes the series attractive for comparative investigations. Hence, the aim of the study is to draw a clear picture for the electronic structure of $Li_2Cu_{1-x}S_xSb$ compounds through first-principles density functional calculations. The density functional theory has been proven to be one of the accurate methods for calculating the ground state properties of the solid [21−27].

2. Supercell calculation

The atoms Li, Li, Cu and Sb have been distributed among the allowed positions and spatial arrangement using all possible configurations as shown in Tables 1−3. According to the Wyckoff positions for space group 216 (F-43m), only two different groups of the atom positions for the formula X$_2$YZ are available. The first group is (0.25 0.25 0.25), (0.0 0.0 0.0), (0.5 0.0 0.0) and (0.75 0.75 0.75) as in Table 1. The second group is (0.25 0.25 0.25), (0.0 0.0 0.0), (0.5 0.5 0.5) and (0.75 0.75 0.75) as in Table 2. Additionally the second group of positions has been calculated with space group 225 (Fm-3m) as in Table 3. The energy and lattice parameter have been calculated through the energy minimization per formula unit for each distribution of the compound Li_2CuSb as shown in the first column of Tables 1−3. In this process the atoms may change their positions but can be brought to equilibrium by monitoring the forces acting on them.

From Tables 1 and 2, the structural minimization results in: i) the most stable structure for Li_2CuSb compound may be one of the distributions LiCuLiSb, LiLiSbCu, CuSbLiLi, LiSbLiCu, LiSbCuLi or SbLiLiCu. The most stable arrangement is SbLiLiCu as indicated by boldface in the energy column. Thus the spatial arrangement or space group for Li_2CuSb compound should be 216. ii) Semiconductor behavior is associated with the most stable structures as shown in the 4th and the 5th columns in Tables 1 and 2. iii) The calculated lattice parameter for the most stable compound SbLiLiCu is 6.342 Å as indicated in Table 2. According to the available experimental data, the calculated lattice parameter for Li_2CuSb is likely the same as the experimental value [18,19].

From now on, the calculations will be based on space group 216, lattice parameter 6.342 Å and arrangement SbLiLiCu will be in

positions (0.25 0.25 0.25), (0.0 0.0 0.0), (0.5 0.5 0.5) and (0.75 0.75 0.75) respectively.

A $2 \times 2 \times 2$ cubic supercell has been performed for SbLiLiCu. Then, the alloy compounds have been formed by replacing S atom with Cu in the supercell according to the required ratio in the series $Li_2Cu_{1-x}S_xSb$, where $x = 0, 1/8, 2/8, \ldots, 1$. Such $S \rightarrow Cu$ replacement may reduce the symmetry as shown in the 4th column of Table 4. It should be noticed that, all the structures initially have cubic structure and S.G. 216. After that, the symmetry calculations of the

Table 4
Optimized structural parameters for $Li_2Cu_{1-x}S_xSb$.

Calculated formula	x	Calculated lattice parameters	Space group
Li$_2$CuSb	0	$a = 6.341$ Å	216 F-43m
Li$_{16}$Cu$_7$SSb$_8$	0.125	$a = 6.43$ Å	216 F-43m
Li$_8$Cu$_3$SSb$_4$	0.25	$a = 6.514$ Å	215 P-43m
Li$_{16}$Cu$_5$S$_3$Sb$_8$	0.375	$a = 4.097$ Å	119 I-4m2
		$c = 8.508$ Å	
Li$_4$CuSSb$_2$	0.5	$a = 4.007$ Å	115 P-4m2
		$c = 9.175$ Å	
Li$_{16}$Cu$_3$S$_5$Sb$_8$	0.625	$a = 4.01$ Å	119 I-4m2
		$c = 9.392$ Å	
Li$_8$CuS$_3$Sb$_4$	0.75	$a = 6.754$ Å	215 P-43m
Li$_{16}$CuS$_7$Sb$_8$	0.875	$a = 6.798$ Å	216 F-43m
Li$_2$SSb	1.0	$a = 6.843$ Å	216 F-43m
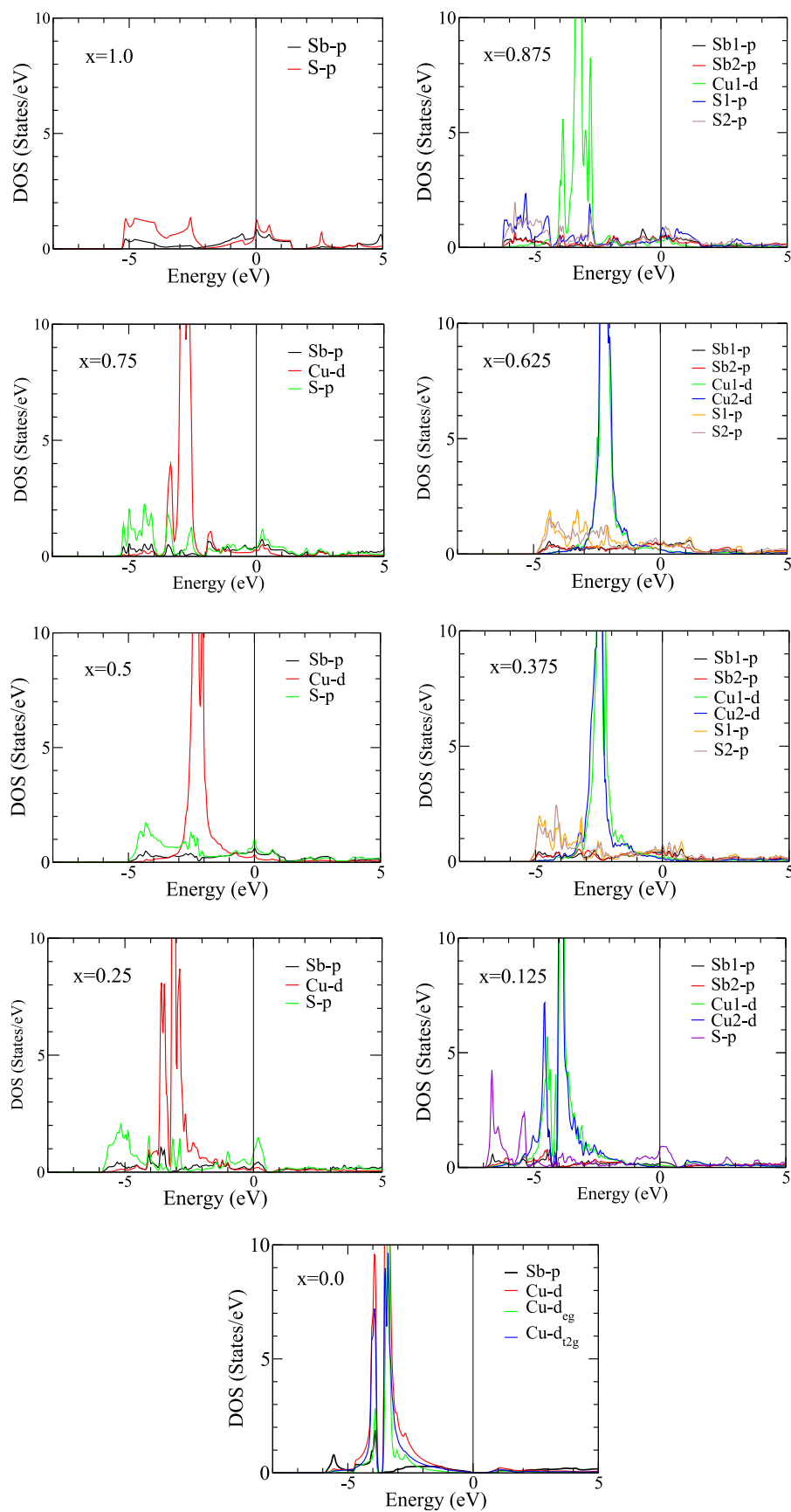
Fig. 2. *l* Resolved DOS for Cu-3d and p-orbital of main group element of the series Li$_2$Cu$_{1-x}$S$_x$Sb.

formed supper cell have been done as implemented in Wien2k code [28]. These symmetry calculations produce the required alloys and geometries (space groups) of the studied series as shown in Table 4. The structural relaxation has been performed again for each produced alloy using the full potential linearized augmented plane wave method (FLAPW). The calculated lattice parameters for the pure and alloys are in Table 4. Structure transition from cubic to tetragonal has been observed for $x = 3/8, 4/8, 5/8$ as shown in Table 4.

The self-consistent band structure calculations have been carried out using the scalar-relativistic FLAPW provided by Blaha et al. as implemented in Wien2k code [28]. The exchange-correlation functional has been taken within the generalized gradient approximation (GGA) in the parameterization of E. Engel and S. H. Vosko [29]. In self-consistent calculations the k-mesh has been generated by specifying 10^4 as the number of k-points in the whole Brillouin zone (BZ). All muffin-tin radii R_{MT} have been set to ensure that the spheres nearly touch one another and minimize the interstitial space. The energy threshold between the core and the valence states has been set to -81.634 eV. The cut of parameter $R_{MT} \times k_{max} = 7$ has been used for the number of plane waves to achieve the convergence for the basis of the wave function. The expansion of the partial wave functions has been set to $\ell = 10$ inside the muffin tin atomic spheres. The charge density has been expanded according to Fourier up to $G = 12$. The energy and charge convergence criterion have been set to 10^{-5} Ry and 10^{-4} electron respectively.

3. Results and analysis

The first-principles calculations have been performed to evaluate the most stable structure for the position distribution possibilities of the compound Li_2CuSb as shown in Tables 1–3. Table 3 indicates that Li_2CuSb is conductor with space symmetry 255 (Fm-3m). But, it is well known experimentally that the Li_2CuSb compound has semiconducting properties [17,30]. Therefore, Li_2CuSb should be described by space group 216 instead of 255. Tables 1 and 2 show that Li_2CuSb is swinging between semiconductor and conductor as long as the Li atom moves from the surface of the crystal to the inside. Obviously, by comparing the energies per formula unit in Tables 1–3, the most stable state for Li_2CuSb compound is semiconductor with energy -16307.5302 Ry as shown with bold line in Table 2. From now on, the arrangement SbLiLiCu and the positions of its atoms, as the most stable compound, will be taken as the base to study the series $Li_2Cu_{1-x}S_xSb$ ($x = 0, 1/8, 2/8, 3/8, 4/8, 5/8, 6/8, 7/8, 1$). The $Li_2Cu_{1-x}S_xSb$ compounds, with the half-Heusler structure, will be studied by using FPLAPW calculations. The crystal structures and the calculated parameters for the series are summarized in Table 4.

Regarding the l-resolved density of states (PDOS) for $Li_2Cu_{1-x}S_xSb$ in Fig. 2 which compares the densities of states near the Fermi energy (E_f) for Cu-3d and the p-orbital of the main group element. The energy scale is referenced to the Fermi energy which taken as the top of the valence band. Conductive behavior has been observed for all concentrations except only for one compound with $x = 1.0$. This compound has indirect gap 0.6 eV. The density of states near the Fermi energy shows a strongly covalent bonding in the sublattice between Cu-3d and p-orbital of main group element. The concentrations with $x = 1/8$ and $7/8$ showed a greater tendency to covalent bonding. Where, covalent bond is formed between some states from S-3p and Cu-3d with a little share from Sb-5p as shown for concentrations $x = 0.875, 0.75$ and 0.25. Hence, the localization behavior has been mostly observed for Sb atom than S. It has been observed a higher Cu-3d splitting for $x = 0.875$ and 0.125 than other concentrations.

To sum up, replacing d-orbital of Cu by the lighter p-orbital of atom S, shown in Fig. 2, destroys the semiconductor properties of the binary compound. Where, injecting the S atom instead of Cu produces a decrease in symmetry which in turn produces new energies for the occupied states. These occupied states will be in different energy from binary compound states, with regard to symmetry. For example, S atom in Fig. 2 for concentrations $x = 0.875, 0.625, 0.375$, and 0.125, has two different symmetry positions in the unit cell. Each one of these two positions has different surrounding group of the nearest neighbors. These two different groups of nearest neighbors should produce different potential or different states for the p-orbital of the same type of atom named S1-p and S2-p in Fig. 2. Some of these states acquire energy higher than the Fermi energy which in turn leads to the conductive behavior. This behavior has been observed also for Cu and Sb as shown in Fig. 2.

Typical Heusler binding energy gap is located at about -5.4 eV for all concentrations but at about -6.2 for the two tetragonal phases $Li_{16}Cu_5S_3Sb_8$ and $Li_{16}Cu_3S_5Sb_8$. Binding energy gap separates the low lying s bands from bands of predominantly d character. These low lying s bands emerge mainly from the main group element. This gap is about 3.2 eV for all concentrations except $Li_{16}Cu_3S_5Sb_8$ and $Li_{16}Cu_5S_3Sb_8$ which have small gap of about 2 eV.

The band structure in the direction of the pure ($x = 0, 1$) and the doped ($x = 1/8, 2/8, 3/8, 4/8, 5/8, 6/8, 7/8$) compounds has been calculated but not displayed here. Electronic structure shows that the Fermi surfaces and band structures of these phases are qualitatively rather similar. In particular, the pure compounds show small compensating electron and hole at Fermi surfaces. However, high densities of occupied states for alloys specially for $Li_{16}Cu_7SSb_8$ and $Li_{16}CuS_7Sb_8$ have been observed as shown in Fig. 3 as predicted before in Ref. [2]. The two phases $Li_{16}Cu_7SSb_8$ and $Li_{16}CuS_7Sb_8$, with less periodicity, have increases in the occupied states around Fermi level. Such increases in electronic states are due to the increasing of band width for both the valence and conduction bands of Cu-3d states as shown in Fig. 2 for $x = 0.125$ and 0.875. Accordingly, the increases in the allowed states at Fermi level refer to the improved conductive or the n-type behavior for concentrations $x = 0.125$ and 0.875 in Fig. 3.

The tetragonal compound Li_4CuSSb_2 with equal ratio of Cu and S, and higher symmetry than other alloys, has a less number of occupied states near Fermi level per convention unit cell than the other two tetragonal compounds in Table 4. Such rarity in the occupied states will decrease the number of basis for the wave function around Fermi level as shown in Fig. 2 for $x = 0.5$. Similarly, for $Li_8Cu_3SSb_4$, Li_4CuSSb_2 and $Li_8CuS_3Sb_4$ the number of occupied states present less condensation around Fermi level than
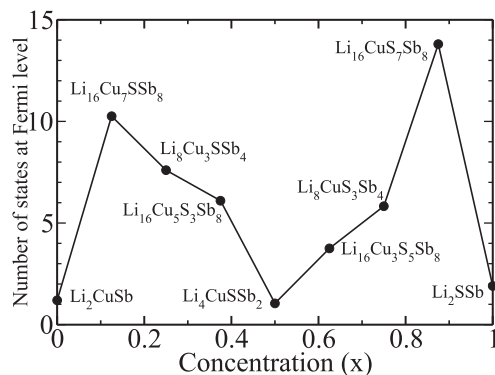

Fig. 3. Number of occupied states per formula unit at Fermi level as a function of the concentration of sulfur ($\times$) for the series $Li_2Cu_{1-x}S_xSb$.

$Li_{16}Cu_5S_3Sb_8$ and $Li_{16}Cu_3S_5Sb_8$ as shown in Fig. 3.

The pure compounds Li_2CuSb and Li_2SSb with high ordering and symmetry display a rarer occupied states at Fermi level than the other studied compounds.

In summary, Fig. 3 introduces a clear picture for the discussion of band structure, where the figure indicates the relation between the concentration x and the number of occupied states at the Fermi level. Such number of occupied states indicates the conductivity of the compound. Accordingly, the conductivity increases for $Li_{16}Cu_7SSb_8$ and $Li_{16}CuS_7Sb_8$ and nearly the same as the three higher symmetry compounds Li_2CuSb, Li_4CuSSb_2 and Li_2SSb. In conclusion, the injecting of Li_2CuSb by S instead of Cu or injecting of Li_2SSb by Cu with respect to S improves the conductive properties of the studied compounds. Such improvement for conductive properties occurs at small injecting ratio of S or Cu.

4. Conclusion

The Heusler compound Li_2CuSb has been fully optimized by FLAPW with GGA for exchange correlation. This optimization shows that the most stable structure for Li_2CuSb has space group 216, lattice parameter 6.342 Å and arrangement SbLiLiCu with positions (0.25 0.25 0.25), (0.0 0.0 0.0), (0.5 0.5 0.5) and (0.75 0.75 0.75) respectively. Semiconductor behavior has been obtained for Li_2CuSb with direct band gap 0.6 eV. Electronic structure calculations, for the substitutional series $Li_2Cu_{1-x}S_xSb$ with ($x = 0, 1/8, 2/8, 3/8, 4/8, 5/8, 6/8, 7/8, 1$), displays a conductive behavior for the series except $x = 1.0$. The calculations indicate that any site disorder, resulted from the doping by S atom, destroys the semiconducting properties of the parent compound Li_2CuSb and increases the conductivity of the alloys. The electrical properties of the studied series have been introduced briefly in Fig. 3. To sum up, the addition of S-3p states shifts the Cu-3d states toward the Fermi energy. This indicates precisely the effect of the Cu-3d and S-3p on the conductivity of the studied series.

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