ELECTRONIC STRUCTURE AND ELASTIC PROPERTIES OF Sc_5CuIn_3: FIRST PRINCIPLES STUDY

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1. Introduction

Ternary systems of rare earth metals (RE) with transition elements, especially Ni, Co, Cu, and In have been investigated intensively because of existence of numerous compounds with different crystal structures and interesting physical properties.

In recent years, elemental scandium and its alloys have attracted much attention of materials scientists due to their perspective constructional qualities with a suitable combination of such important characteristics as lightness, strength, heat endurance, and corrosion resistance.

Sc–Cu–In system has not been investigated systematically as yet. It should be noted that Sc is a unique rare earth element with empty 4f electron shell and fairly small atomic radius. These features may bring about peculiarities related to crystal structures and physical properties of Sc-based intermetallics. However, influence of Sc additions on the mechanical and related properties of multi-component alloys, has been widely discussed in the literature [1]. So far four compounds Sc_2Cu_2In, $ScCu_2In$, $ScCu_4In$ and Sc_5CuIn_5 have been reported.

In this paper, we report on crystal structure, electronic and elastic properties of the novel ternary Sc_5CuIn_3 compound.

2. Structure and methods of calculation

The novel compound Sc_5CuIn_3 was prepared by arc-melting elemental constituents under argon atmosphere and subsequent annealing at 870 K for 40 days. Its crystal structure was determined from the single-crystal X-ray diffraction data [2]. The compound was established to crystallize with a hexagonal structure of the Hf_5CuSn_3 type (space group $P6_3/mcm$, No. 193, lattice parameters: $a = 8.6089(6)$, $c = 6.2029(6)$ Å, $Z = 2$, $R_1 = 0.0354$, $wR_2 = 0.0853$), closely related to Mn_5Si_3 and Ti_5Ga_4 types.

Figure 1 presents the projection of the unit cell of Sc_5CuIn_3 on the hexagonal ab plane as well as the coordination polyhedra of Sc, Cu and In atoms. Each crystallographic position is fully occupied. The Sc1 atom is surrounded by 11 nearest atoms. Seven of them *viz.* two Cu atoms ($d = 2.729$ Å) and five In atoms ($d = 2.9416$-3.2857 Å), form distorted pentagonal bipyramid and additional four Sc2 atoms ($d = 3.581$ Å) expand such coordination sphere resulting in 11-vertex polyhedron (CN = 11). The nearest neighbors of the Sc2 atoms form a distorted hexagonal prism composed of three In atoms ($d = 3.0872$ Å) and three Sc1 atoms ($d = 3.581$ Å) at each base, capped with two Sc2 atoms ($d = 3.1015$ Å) opposite to those bases (CN = 14). As a result 14-vertex polyhedron is composed around the Sc2 atom. The Cu atom lies at high symmetry 2b Wyckoff position (-3.m) and therefore its coordination polyhedron is a perfect trigonal antiprism (octahedron) (CN = 6) formed by six Sc1 atoms ($d = 2.729$ Å).
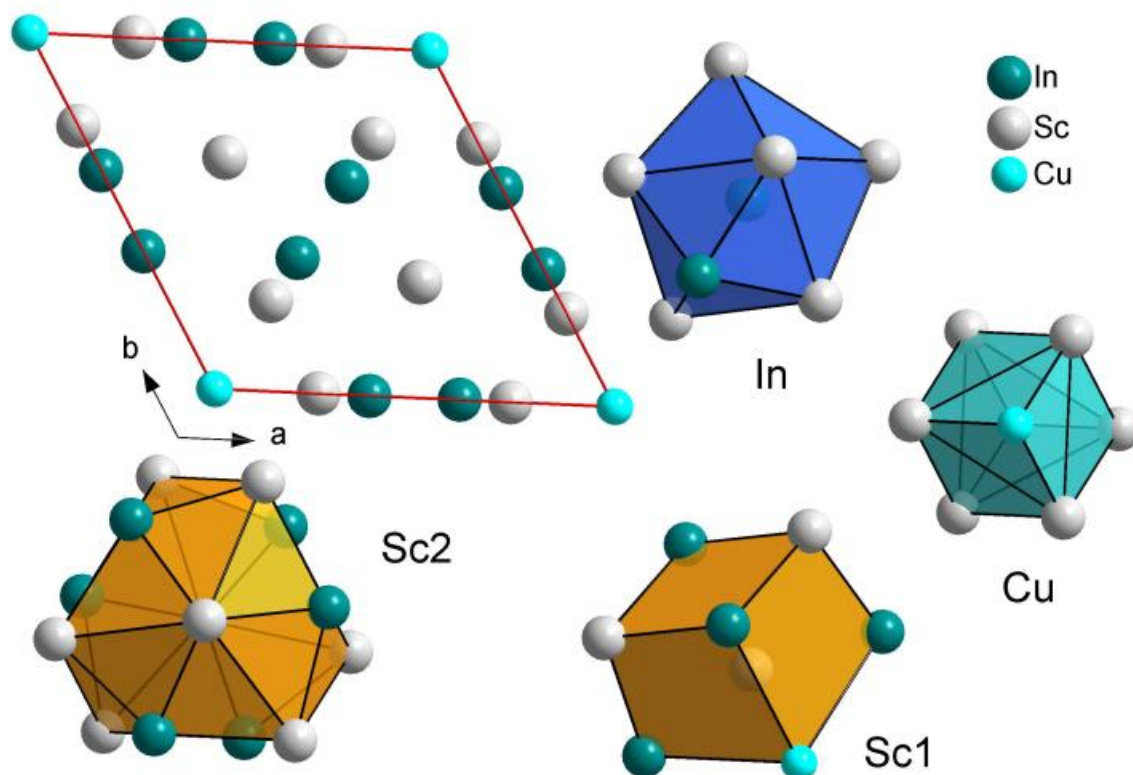

Fig. 1. Projection of the unit cell of Sc_5CuIn_3 on the *ab* plane and the coordination polyhedra of the atoms.

Also, two Cu atoms are located at the larger distance to the central Cu atom (d = 3.1014 Å, $\Delta d = 21.34$ %) and they were not included into the coordination polyhedron. In turn, the In atom are surrounded by nine Sc atoms ($d = 2.9416$-3.2857 Å). Additionally, two In atoms are placed at slightly higher distance ($d = 3.6631$ Å) and expands coordination sphere to 11-vertex polyhedron (CN = 11).

Despite the promising performances of Sc-based compounds in structural and coating application fields, and the intensive investigations to improve its mechanical properties such as toughness, ductility, and high-temperature strength, as well as oxidation resistance, only limited information is available for the structural, electronic, and vibrational properties of Sc–Cu–In compounds.

In this work, we report the lattice structure, electronic structure and mechanical properties of Sc_5CuIn_5 intermetallic compound obtained by first-principles calculations based on density functional theory (DFT). Calculations are performed using the PWscf (Quantum-Espresso) package [3]. The electron-ionic core interaction is represented by the ultrasoft pseudopotentials with valence electron configuration of $3s^2 3p^6 3d^1 4s^2$ for Sc, $3d^{10} 4s^1$ for Cu, $4d^{10} 5s^2 5p^1$ for In. The PBE form of the generalized gradient approximation (GGA) is adopted to describe the exchange correlation interaction. To describe the electronic structures more accurately, we used GGA+U method. Geometrical optimizations were performed using Broyden–Fletcher–Goldfarb–Shanno (BFGS) method. All calculations were spin-polarized.

The k-point meshes for Brillouin zone sampling were constructed using the Monkhorst-Pack scheme [4]; the (6x6x8) k-points mesh was used for all calculations. The lattice-dynamical properties were calculated using the density functional linear response method [5]. The ground state of considered compound was found by minimizing the total energy as a function of the lattice parameters, Birch-Murnaghan equation of states (EOS) was used to fit the total energies as a function of primitive unit cell volume to obtain the bulk modulus and the equilibrium lattice parameter for the investigated system.

The elastic properties play an important role in providing valuable information about the binding characteristic between adjacent atomic planes, they can define how a material undergoes stress deforms and then recovers and returns to its original shape after stress ceases. These properties play an important role in providing valuable information about the structural stability, anisotropic factors, Debye temperature, phonon spectra, and specific heat capacity. All those information are usually defined by the elastic constants C_{ij}. Determining the elastic moduli requires knowledge of the derivative of the energy as a function of the lattice strain. The hexagonal crystals have five independent elastic constants, which are C_{11}, C_{12}, C_{13}, C_{33} and C_{44}; and they can be determined by selectively imposing strains either individually or in combination along specific crystallographic directions. In order to calculate the elastic constants for our material, five independent strains, giving five independent equations for the elastic constants are required. The total energy has been calculated for distortions of ±0.01,

±0.02 and ±0.03 for all the five strains for Sc_5CuIn_5 at 0 GPa. Then the elastic constants C_{ij} can be found from a polynomial fit to the calculated energies.

3. Results and discussion

3.1. Equilibrium lattice determination, elastic properties and mechanical stability

The lattice parameters and internal coordinates of these intermetallic phases have been optimized using the BFGS method and the optimized lattice parameters are displayed in Table 1, along with the experimental data [2]. The calculated structural parameters agree with the corresponding experimental values.

Table 1. Calculated and experimental crystallographic data for Sc_5CuIn_5 intermetallic

	a (Å)	c (Å)	V (Å^3)	c/a	B_0 (GPa)
Experimental [2]	8.6089	6.2029	398.13	0.7205	
Present calculation	8.6880	6.2035	405.516	0.7140	64.47

The optimized structure was used for obtaining the five independent elastic constants C_{ij}. The calculated elastic constants C_{ij} are presented in table 2.

Table 2. Elastic constants (GPa) of Sc_5CuIn_5 according to the GGA+U calculations

Elastic Constants (GPa)	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}
Present calculation	137.2 ± 4.6	33.7 ± 4.7	42.8 ± 2.4	117.6 ± 3.5	38.1 ± 0.2

For a stable hexagonal structure, the five independent elastic constants should satisfy the well-known Born stability criteria:

$$C_{11} > |C_{12}|; \quad 2C_{13}^2 < C_{33}(C_{11} + C_{12}); \quad C_{44} > 0,$$

The calculated elastic constants presented in table 2 are positive and they clearly satisfy the Born stability criteria, suggesting that the Sc_5CuIn_5 structure is mechanically stable.

Then, the theoretical polycrystalline elastic modulus of Sc_5CuIn_5 can be determined by using the two approximation methods, namely the Voigt and the Reuss methods. Voigt assumes the uniform strain throughout a polycrystalline aggregate and Reuss assumes the uniform stress. The bulk modulus B, Young's modulus E, shear

modulus G and Poisson's ratio ν are calculated directly by the Voigt–Reuss–Hill (VRH) method (table 3).

According to the elastic criterions, a material is brittle (ductile) if the B/G ratio is less (greater) than 1.75. In fact the value of B/G is smaller than 1.75 for our crystal (exactly 1.63), hence, our material should behave in a brittle manner. However, this result can be confirmed using the classical criteria of the Cauchy pressure ($C_{12} - C_{44}$), a crystal with a negative Cauchy pressure is brittle; otherwise, it is ductile. The positive value of the Cauchy pressure for Sc_5CuIn_5 (-4.4 GPa) confirm their brittle nature. According to the Frantsevich rule, the critical value of Poisson's ratio that distinguishes between a brittle or ductile material is 1/3. Ductile compounds usually have a Poisson's ratio greater than 0.33.

The Young's modulus is defined as the ratio of stress to strain, and used to provide a measure of the stiffness of a material. The value of the Poisson's ratio is indicative of the degree of directionality of the covalent bonds. This value is small ($v = 0.1$) for covalent materials, whereas for ionic materials a typical value of v is 0.25. The calculated Poisson's ratio is 0.24.

Table 3. The calculated shear modulus (G), bulk modulus (B), Young's modulus (E), and Poisson's ratio (v) of Sc_5CuIn_5, all modulus values are in GPa except v without unity

	Voigt	Reuss	Hill
Bulk modulus	70.07	69.96	70.02
Shear modulus	43.78	42.85	43.32
Lame lambda	40.88	41.39	41.14
Young modulus	108.71	106.76	107.74
Poisson ratio	0.24	0.24	0.24

Is of importance to calculate the elastic anisotropy in the crystals, in order to cover and understand their different mechanical properties. There are several methodologies used to indicate the elastic anisotropy of hexagonal crystals. First, the shear anisotropic factors are used for measuring the degree of anisotropy of atomic bonding in different crystallographic planes. Second, the elastic anisotropy can be described by the universal anisotropy index A_U and by the percentages anisotropy in compression A_{comp} and in shear A_{shear} , respectively. A crystal with $A_U = 0$ is isotropic. The large deviation of A_U from zero suggests a high mechanical anisotropy. The value of universal anisotropy index for our compound is 0.11, suggesting some elastic anisotropy.

We have estimated the average sound velocitity (3202.9 m/s) and Debye temperature (337.4 K) of Sc_5CuIn_5 compound.

Debye temperature θ_D is one of the most important parameter and it determines the thermal characteristics of materials. The Debye temperature can be defined in terms of the mean sound velocity and gives explicit information about lattice vibration. It is the highest temperature that can be achieved due to a single normal vibration. At low temperature the vibrational excitations arise solely from acoustic vibrations. Hence, at this condition θ_D calculated from elastic constants are the same as that determined by the specific heat measurements.

Our calculated elastic and thermal properties could not be compared because measured data are not available in the literature. Hence, the present results should be good theoretical references for future works on Sc-based intermetallics.

3.2. Electronic structure

In this section, the electronic band structure (Fig. 2), the total density of states (TDOS) and partial density of states (PDOS) of Sc_5CuIn_5 intermetallic compound have been calculated with spin polarization, and the results near the Fermi level (E_F) are showed in Fig. 3.
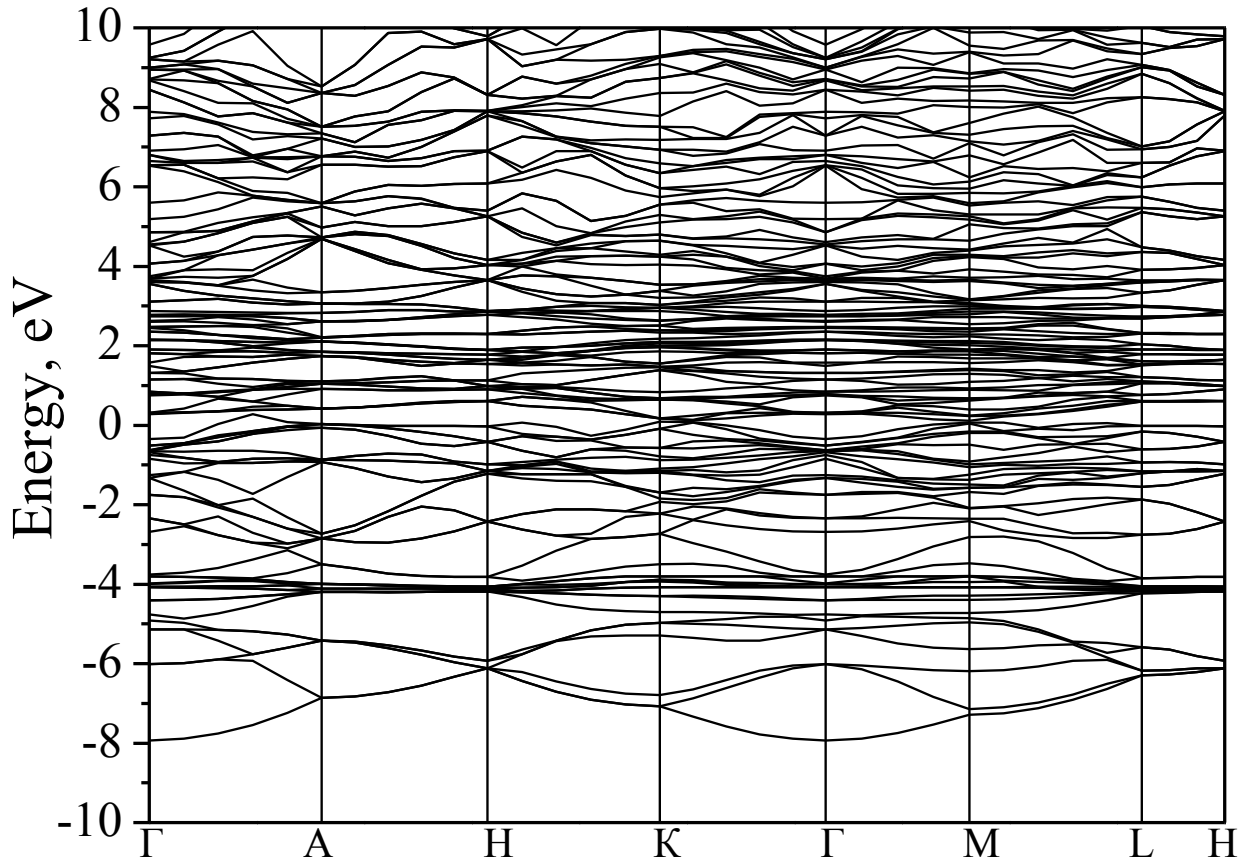

Fig. 2. The electronic band structure for Sc_5CuIn_5 compound along several lines of high symmetry in the Brillouin zone.

The vertical dashed line at the position of 0 eV in each figure represents the corresponding Fermi level.

The spin-polarized electronic band structures has no band gap at the Fermi level, and, hence, Sc_5CuIn_5 is metallic. The bands at the Fermi level are mainly contributed by Sc d-orbitals and by In p-orbitals. The s-states of Cu lying below the Fermi level whereas the Sc d-states are situated above the Fermi level.
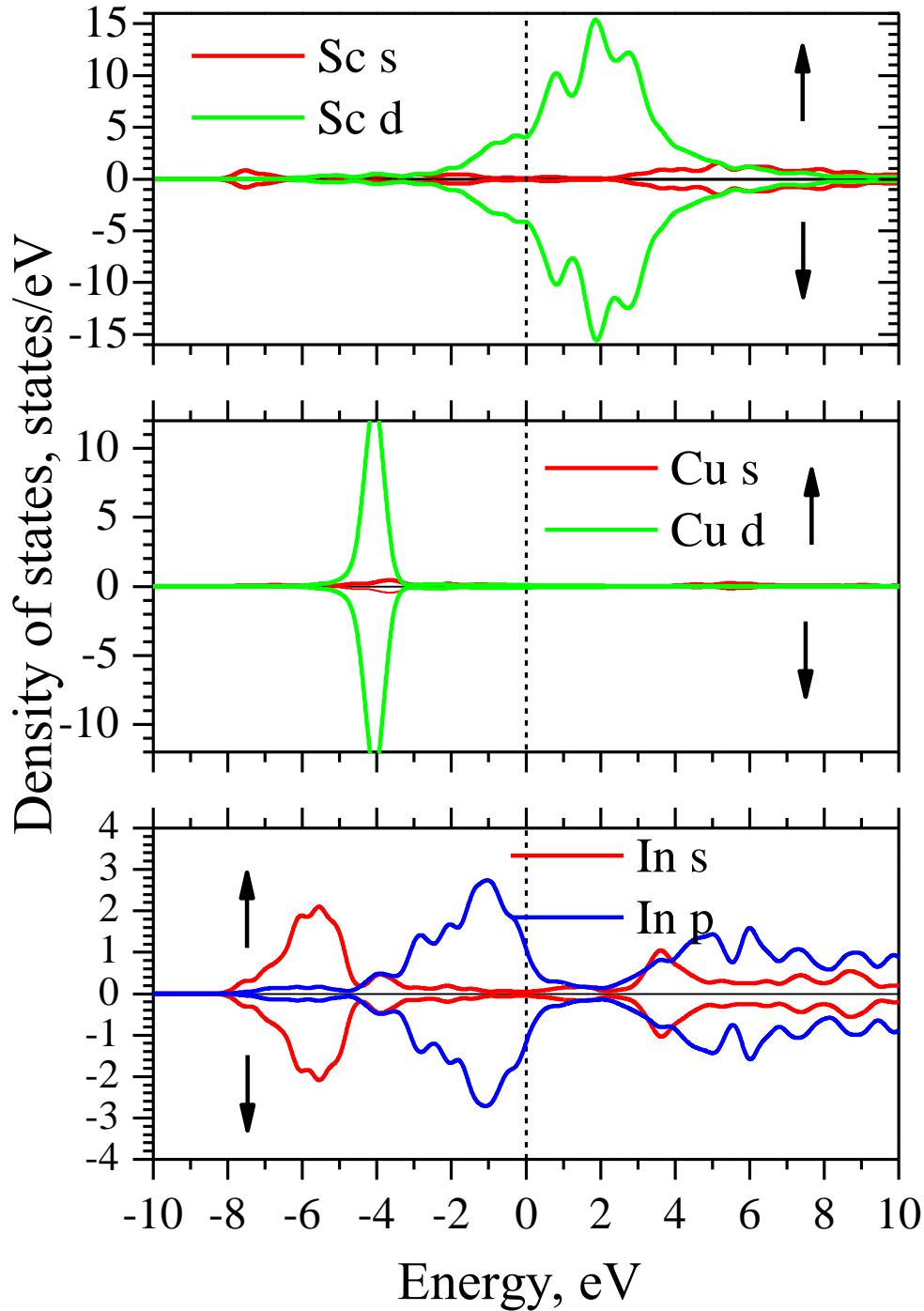

Fig. 3. Calculated partial DOS near Fermi level for Sc_5CuIn_5 compound. The dash lines represent the Fermi level.

Besides, from the TDOS of Sc states (Fig. 4), it can be seen that asymmetry between spin up and down appears near the Fermi level, which can be mainly attributed to the spin polarization of Sc–3d orbitals.
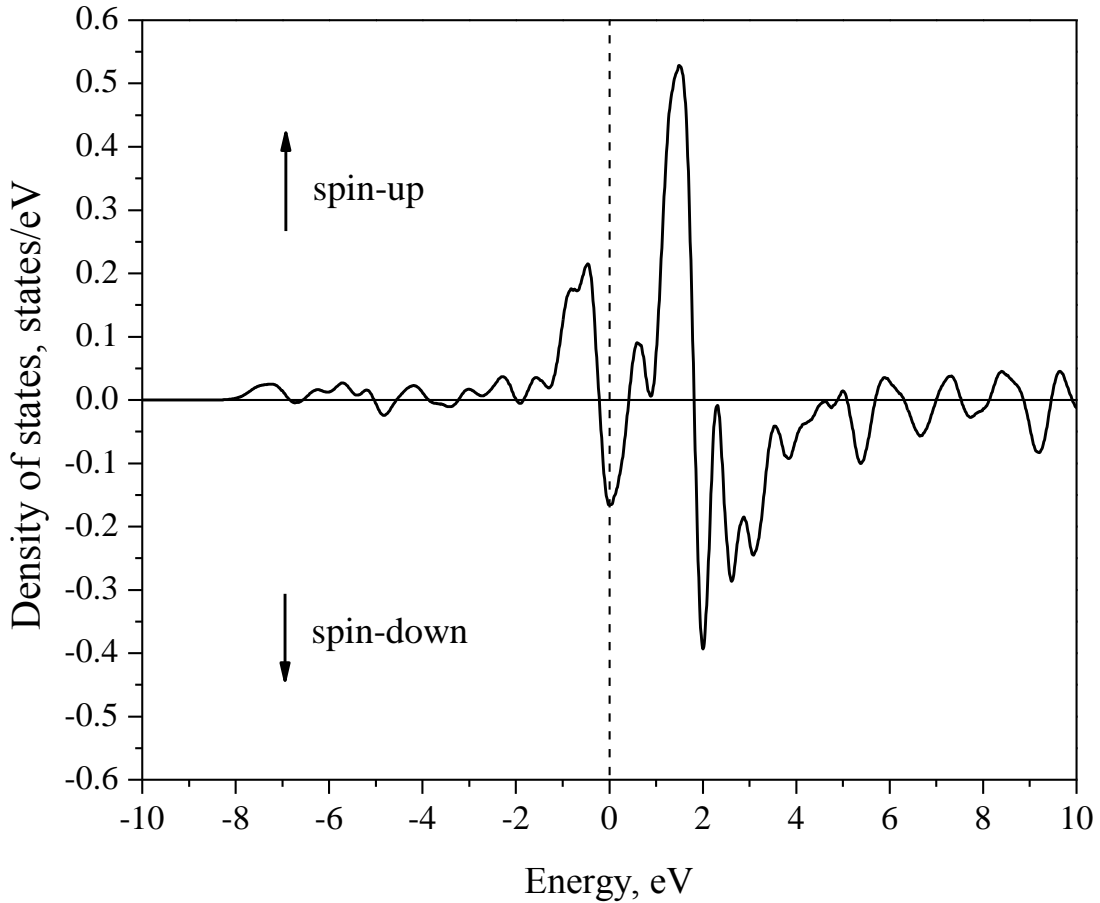

Fig. 4. Difference between spin-up and spin-down TDOS for Sc ions.

This result shows that Sc_5CuIn_5 is magnetic compound. However, from the absolute value of the TDOS shown in Fig. 4, the spin polarization effect is not strong in this compound.

4. Conclusion

In this work, the lattice structures, phase stability, elastic properties, Debye temperatures and electronic properties of the Sc_5CuIn_5 intermetallic compounds have been predicted by first-principles calculations. The calculated lattice parameters are close to the experimental results using the GGA+U for the exchange and correlation potential. Using Voigt–Reuss–Hill approximation, the ideal polycrystalline aggregates bulk modulus, shear modulus, Young's modulus, and Poisson's ratio, are calculated and discussed. The sound velocity and Debye temperature were also calculated for

compound under study. Our simulation results based on the DOS and band structures show that all of the investigated Sc_5CuIn_5 compound is metallic in nature. The asymmetry between spin up and down appears near the Fermi level, which can be mainly attributed to the spin polarization of $Sc-3d$ orbitals.

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