A first-principles study of a new ternary silicide superconductor Li$_2$IrSi$_3$†

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Abstract. Ab initio calculations were carried out on the structural, elastic, and electronic properties of a newly synthesized ternary silicide superconductor, Li$_2$IrSi$_3$. The obtained lattice parameters show sound agreement with the experimental values, indicating the reliability of the present study. The rigid structure of Li$_2$IrSi$_3$ is due to the strong covalent Ir-Si and Si-Si bonding. The new compound is mechanically stable, brittle and elastically anisotropic. The relatively low value of the Poisson’s ratio for Li$_2$IrSi$_3$ is indicative of its high degree of directional covalent bonding.

Keywords: Li$_2$IrSi$_3$; Density functional theory; Elastic properties; Electronic features

1. Introduction

A covalent bond occurs easily between transition metals and silicon due to their comparable electronegativity. To realize the high temperature phonon mediated superconductivity, the covalent character plays a vital role. Superconductive nature of transition metal silicides has already been identified. For example, the V$_3$Si exhibits superconducting transition at a temperature of 17 K [1]. Moreover, the tunability of the chemical potential due to the change of the transition metals can render an extra channel in the design of the ideal electronic structure [2]. Consequently, the search for new superconductors in the systems of doped covalent metals has received considerable attention. In recent, Hirai et al. have synthesized a new ternary transition metal silicide Li$_2$IrSi$_3$ using the conventional solid state reaction procedure [2]. The new compound crystallizes in the hexagonal space group P6$_3$/mmc (No. 194) and exhibits weak-coupling phonon-mediated superconducting transition below 3.7 K. The crystal structure of Li$_2$IrSi$_3$ consists of Si triangles linked by Ir atoms, forming a three-dimensional network of covalent bonds. The ant-prisms IrSi$_6$ stacked along the c-axis are linked by Si triangles.

Simultaneously, polycrystalline samples of Li$_2$IrSi$_3$ were prepared by Pyon et al. [3] using the arc-melting method, and the space group of Li$_2$IrSi$_3$ was identified as noncentrometric trigonal P3$_1$c (No. 159). Based on the measurements of resistivity and magnetization, they confirm that Li$_2$IrSi$_3$ is a type-II superconductor with $T_c = 3.8$ K. They described the crystalline structure of Li$_2$IrSi$_3$ as a silicon atomic

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planner kagome network with Li and Ir located at unequal distances between the kagome layers, which gives rise to a polar structure along the c-axis.

In the present study, we aim to explore the elastic properties, bonding nature and electronic features of a newly synthesized silicide superconductor using first-principles density functional theory (DFT). The paper is arranged as follows: The computational method is described in section 2. In section 3, the obtained results are discussed in detail. Concluding remarks are presented in section 4.

2. Computational Procedures

The DFT-based plane-wave pseudopotential first principle [4,5] was applied to complete the present study with the Cambridge Serial Total Energy Package (CASTEP) code [6]. Perdew-Burke-Ernzerhof Generalized Gradient approximation (PBE-GGA) [7] was used to solve the Kohn-Sham equations for the exchange-correlation energy. To model the electron-ion interactions the Vanderbilt-type ultrasoft pseudopotentials [8] were used. A plane-wave cutoff energy of 500 eV was chosen throughout the present investigations to limit the number of plane waves in expansion. The Broyden-Fletcher-Goldfarb-Shanno (BFGS) minimization technique [9] was employed to relax the crystal structure completely. A k-point mesh of $15 \times 15 \times 8$-grid within Monkhorst–Pack scheme [10] is used to integrate over the first Brillouin zone. For self-consistent field convergence, the tolerances for total energy, maximum force, maximum stress, and maximum atomic displacement were set to less than $5 \times 10^{-6}$ eV per atom, 0.01 eV/Å, 0.02 GPa, and $5 \times 10^{-4}$ Å, respectively.

The elastic properties were calculated using the finite strain theory [11] embodied in the CASTEP code, which provides the elastic constant as a proportionality coefficient linking the functional strain to the calculated stress, $\sigma_i = C_{ij}\varepsilon_j$. Using the Voigt-Reuss-Hill approximation [12-14] the polycrystalline bulk modulus $B$ and shear modulus $G$ were calculated from $\sigma_i = C_{ij}\varepsilon_j$. The Young’s modulus $Y$, Poisson’s ratio $\nu$, and shear anisotropy factor $A$ were estimated using the equations $Y = (9GB)/(3B + G)$, $\nu = (3B - 2G)/(6B + 2G)$, and $A = 4C_{44}/(C_{11} + C_{33} - 2C_{13})$, respectively.

In the present investigation, spin-orbit coupling (SOC) was not taken into account, although the new compound contains heavy transition metal Ir with 5$d$ orbital. The inclusion of SOC has only a minor effect on structural and elastic properties. For instance, there is little or no change of structural properties of transition metal based MAX phases, like $M_2AlC$ ($M = Ti, V$, and Cr) and $Mo_2AC$ ($A = Al, Si, P, Ga, Ge, As, and In$) when SOC is included in the calculations [15, 16].

3. Results and discussion

3.1. Structural properties

Crystallization of Li$_2$IrSi$_3$ occurs in hexagonal space group $P6_3/mmc$ (194). Its unit cell contains 12 atoms and two formula units. The fully relaxed structure obtained by optimizing the geometry in respect of lattice constants and internal atomic positions is shown in Fig. 1. The Li atoms in the optimized cell takes position at the 4$f$ Wyckoff site with fractional coordinates ($1/3, 2/3, 0.55889$). The Si atoms are situated at the 6$h$ Wyckoff site with the atomic positions (0.34291, 0.17145, 3/4). Ir atoms occupy the fractional coordinates (0, 0, 0) at the 2$a$ Wyckoff site. The structural parameters of Li$_2$IrSi$_3$ obtained in this study are listed in Table 1 together with the obtainable experimental results. It is evident from Table 1 that the theoretical values show fair agreement to the experimental values, indicating the reliability of the present investigations.

3.2. Elastic properties

Elastic properties, calculated at zero pressure and temperature, are listed in Table 2. There is no experimental or theoretical data on elastic properties of Li$_2$IrSi$_3$ for comparison. Remarkably, some of the elastic parameters of the Li$_2$IrSi$_3$ match quite well with the results obtained for a MAX phase, Ti$_2$CdC [17]. The elastic parameters of Ti$_2$CdC are also listed in the Table 2 for comparison. All mechanically stable hexagonal phases must obey the conditions known as Born criteria [18]: $C_{11} > 0$, $C_{12} > 0$, $C_{44} > 0$, $C_{11} - C_{12} > 0$, $C_{13} > 0$, $C_{44} > 0$, $C_{11} + C_{12} + 2C_{13} > 0$, and $C_{66} > 0$. Some of the elastic parameters with the values obtained in this study are given in Table 2. It is evident that the obtained results match fairly well with the results obtained for Ti$_2$CdC [17].
Figure 1. The optimized unit cell of hexagonal silicide superconductor Li$_2$IrSi$_3$.

Table 1. Lattice constants $a$ and $c$, internal parameter $z$, hexagonal ratio $c/a$, unit cell volume $V$, and bulk modulus $B$ with its pressure derivative $B'$ for Li$_2$IrSi$_3$.

| Properties                  | Symbol (unit) | Expt. [2]   | Present Calc. | Deviation (%) |
|-----------------------------|--------------|-------------|---------------|---------------|
| Lattice constant $a$        | $a$ (Å)      | 5.01762     | 5.00690       | 0.21          |
| Lattice constant $c$        | $c$ (Å)      | 7.84022     | 7.86548       | 0.32          |
| Internal parameter $z$      | $z$          | 0.56039     | 0.55889       | 0.27          |
| Unit cell volume $c/a$      | $c/a$        | 1.56254     | 1.57093       | 0.54          |
| Hexagonal ratio $V$ (Å$^3$) | $V$          | 170.944     | 170.763       | 0.11          |
| Bulk modulus $B$ (GPa)      | $B$          | –           | 115.899       | –             |
| Pressure derivative of $B$  | $B'$         | –           | 4.24085       | –             |

$C_{11} - C_{12} > 0$, $C_{44} > 0$ and $(C_{11} + C_{12})C_{33} > 2C_{13}^2$. The calculated elastic constants of Li$_2$IrSi$_3$ fully satisfy the aforesaid conditions. Consequently, Li$_2$IrSi$_3$ is mechanically stable.

The comparative small values of $C_{12}$ and $C_{13}$ indicate the brittle nature of Li$_2$IrSi$_3$ [19]. The Pugh’s criterion [20] and the Frantsevich rule [21] also justify this prediction. In accordance with Pugh’s criterion, a material should behave in brittle manner if it has Pugh’s ratio $G/B > 0.5$, otherwise it should behave in ductile manner. The Frantsevich rule suggests the Poisson’s ratio $\nu \sim 0.33$ as the threshold value that separates the brittle materials from ductile ones. The mechanical property of a material will be dominated by brittleness if its Poisson ratio $\nu$ is less than 0.33, if $\nu$ is larger than 0.33, the mechanical property of the material will show the ductile nature. It is evident from Table 2 that the compound Li$_2$IrSi$_3$ is as brittle in nature as the Ti$_2$CdC, which is the general trend of the MAX phases [17, 22-24]. The comparative small value of $\nu$ for Li$_2$IrSi$_3$ is an indication of its high degree of directional covalency.

As there is a difference between $C_{11}$ and $C_{33}$, Li$_2$IrSi$_3$ will show anisotropy in its elastic properties. Elastic anisotropy of a crystal results in different features of bonding in different directions. Basically all known crystals are elastically anisotropic. A precise description of anisotropic behavior is important as it has involvement in engineering science and crystal physics and it relates to the possibility of the presence of microcracks inside the crystal. The shear anisotropy factor associated with the $\{100\}$ shear
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planes situated within the (011) and (010) directions is defined as \( A = \frac{4C_{44}}{(C_{11} + C_{33} - 2C_{13})} \). The factor \( A = 1 \) for an isotropic crystal, while elastically anisotropic crystal possesses any value smaller or greater than unity that measures the elastic anisotropy level in the crystal. The calculated value of \( A \) is listed in Table 2, which deviates only a little bit from unity, implying that the in-plane and out-of-plane inter-atomic interactions differ only slightly. For the hexagonal crystal, another anisotropic factor defined by the ratio between the linear compressibility coefficients along the \( c \)- and \( a \)-axis is useful to quantify the anisotropy level in crystals: \( k_c/k_a = (C_{11} + C_{12} - 2C_{13})/(C_{33} - C_{13}) \). The calculated value of this factor is listed in Table 2. The obtained value of 0.66 indicates that the compression along the \( c \)-axis is less than along the \( a \)-axis. The new compound has comparatively low shear modulus, which is indicative of its low coefficient of friction and good machinability.

The ratio of the bulk modulus \( B \) to shear elastic constant \( C_{44} \) is used to measure the plasticity [25]. Large values of \( B/C_{44} \) are associated with the excellent dry lubricating property of materials. The values of \( (C_{11} - C_{12}) \) and Young’s modulus \( Y \) can also estimate the plasticity of materials [26]. \( \text{Li}_2\text{IrSi}_3 \) has better plasticity due to its smaller values of \( (C_{11} - C_{12}) \) and \( Y \). The Debye temperature \( \Theta_D \) was calculated to be 488 K. The value of \( \Theta_D \) determined using the phonon contribution to the low temperature specific heat derived from experimental data is 486 K [2]. The present value of \( \Theta_D \) very close to its experimental value, indicating the reliability of the present calculations.

### 3.3. Electronic properties

The band structure of \( \text{Li}_2\text{IrSi}_3 \) is calculated with optimized lattice parameters along the high symmetry directions in the first Brillouin zone and shown in Fig. 2a. The Fermi level, \( E_F \) of \( \text{Li}_2\text{IrSi}_3 \) is located just below the highest point of the Valence band. The occupied valence bands extend broadly from \(-12.3 \text{ eV} \) to Fermi level \( E_F \). The valence bands cross the Fermi level and make the system conducting.

The total and partial energy density of states (DOS) are calculated for \( \text{Li}_2\text{IrSi}_3 \) and shown in Fig. 2b. The total DOS at the Fermi level \( N(E_F) \) has a large value of 3.2 states per eV per unit cell, which shows fair agreement with the literature value of 2.9 states per eV per unit cell [2]. The DOS at \( E_F \) is mainly due to the states of Ir 5d and Si 3p. The finite value of DOS at \( E_F \) confirms the metallic conductivity of \( \text{Li}_2\text{IrSi}_3 \). The wide valence band is composed of several distinct peaks. The lowest-lying valence band with two peak structures situated between \(-12.3 \) and \(-7.5 \text{ eV} \) is due to the hybridization of 3s and 3p states of Si. The next peak structure of total DOS, located between \(-7.5 \) and \(-5.8 \text{ eV} \), mainly originates from the Si 3s, 3p and Ir 5d states. The second highest peak, located between \(-5.8 \) and \(-3.3 \text{ eV} \), is mainly composed of Si 3p and Ir 5d states.

The highest peak located in the range of \(-3.3 \) to \(-1.3 \text{ eV} \) arises from the strong hybridization of the Si 3s, 3p with Ir 5d states. \( \text{Li} \) 2s has little contribution to the highest peak. The sharp peak just below the Fermi level arises due to the hybridization of the Si 3p and Ir 5d states. Covalent interactions occur between the constituting atoms across the entire valence band due to the fact that the states degenerate with respect to both angular momentum and lattice site. It is expected that the hybridization between 3s and 3p of Si in the lowest energy region results in the formation of covalent Si-Si bond, which forms a

| Single crystal elastic properties | Polycrystalline elastic properties |
|----------------------------------|----------------------------------|
| \( C_{11} \) (GPa)              | \( B \) (GPa)  | \( C_{11} \) (GPa)              | \( B \) (GPa)  |
| \( C_{12} \) (GPa)              | \( G \) (GPa)  | \( C_{13} \) (GPa)              | \( Y \) (GPa)  |
| \( C_{33} \) (GPa)              | \( G/B \)     | \( C_{44} \) (GPa)              | \( \nu \)      |
| \( C_{66} \) (GPa)              | \( A \)       |                               |                |
three-dimensional rigid network as a whole [2]. Moreover, a rather strong hybridization of Si 3p with Ir 5d states in the region of the Fermi level plays the key role in the formation of the covalent Ir-Si bond to crystallize the rigid structure of Li$_2$IrSi$_3$. Further, some ionic character can be expected among the constituent atoms due to their difference in electronegativity. Therefore, the bonding character of Li$_2$IrSi$_3$ can be described as a mixture of metallic, covalent and ionic.

4. Conclusions
In summary, the present study was accomplished with DFT to investigate the structural, elastic, and electronic properties of a silicide superconductor, Li$_2$IrSi$_3$. The fair agreement of theoretical lattice constants to the experimental values indicates the reliability of the present study. The strong covalent Ir-Si and Si-Si bonding lead to form the rigid structure of Li$_2$IrSi$_3$. The new compound Li$_2$IrSi$_3$ possesses mechanical stability, brittleness and anisotropy in elasticity. Li$_2$IrSi$_3$ is characterized with the high degree of directional covalent bonding although the bonding nature of Li$_2$IrSi$_3$ is a mixture of metallic, covalent and ionic.

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