Electronic structure and transport properties of SrAl$_2$Si$_2$: Effect of yttrium substitution

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1. Introduction

Silicides with transition metals and/or alkaline rare earth as one of the main constituents have attracted considerable attention because of a variety of physical properties from thermoelectricity to superconductivity [1,2]. For examples, iso-electronic and iso-structural compounds CaAlSi$_2$ [3–5] and SrAlSi$_2$ [2] exhibit superconductivity at 7.8 K and 5.4 K, respectively, whereas CoSi and FeSi [1] are known to exhibit a large thermoelectric power factor ($S^2/\rho$). Recently, semimetals or semiconducting compounds with pseudogaps at the Fermi level ($E_F$) density of states (DOS) are being dealt with renewed interest not only as a result of the fascinating electronic properties but also due to a potential thermoelectric application they possess [6]. The absolute value of Seebeck coefficient in ordinary metals at a given temperature is inversely proportional to the DOS, $N(E)$ and directly proportional to its energy derivative, $dN(E)/dE$ [7]. In that case, the presence of a pseudogap at the Fermi level located in steeply varying DOS, a small shift in $E_F$ could set off a large variation in $S$ and other physical properties. Besides, hybridization induced pseudogaps or hollows in the DOS around the $E_F$ are ubiquitous in many ordered binary and ternary aluminides and silicides which results in exotic transport properties [8]. A well-studied silicide of this type is CaAl$_2$Si$_2$, a semimetal arising from a slight overlap of one conduction band and two valence bands, with the Fermi level located at the valley of the density of states. Hall coefficient of CaAl$_2$Si$_2$ exhibit sign reversal at around 150 K, indicative of a change of dominant carrier with temperature whereas $\rho(T)$ is found to be dominated at low-$T$ by intrinsically metallic nature, while at high temperatures, $\rho(T)$ is attributed to a thermally activated increase in density of hole carriers [9]. The observed phenomena in the transport properties of CaAl$_2$Si$_2$ have been attributed to the semimetallic response, based on both experimental observations and electronic structure calculations [5].

The titled compound SrAl$_2$Si$_2$ crystallizes in a La$_2$O$_3$-type layered trigonal structure (space group:$P3m1$), where Al and Si atoms are arranged in chemically ordered double-corrugated hexagonal layers and Si atoms are intercalated between them. A recent study of the transport properties of an SrAl$_2$Si$_2$ single crystal revealed intrinsic semiconducting-like behavior over the temperature range $300 \text{ K} \leq T \leq 1200 \text{ K}$ [10]. However, it was found that at low temperatures SrAl$_2$Si$_2$ exhibits a positive temperature coefficient of resistivity up to 120 K after which $\rho(T)$ shows a broad peak followed by a negative temperature coefficient $\rho(T)$ up to 300 K. These observations indicate that SrAl$_2$Si$_2$ presumably has a pseudogap at the Fermi level DOS instead of a real semiconducting...
energy gap, which may make it a suitable candidate for thermoelectric applications. However, a relative low figure of merit, $ZT = \frac{S^2T}{\rho \kappa}$ on the order of 0.035 is thus realized at room temperature for SrAl2Si2. We have previously reported that a room-temperature ZT value of about 0.4 is achieved in the (Sr1-xYx)Si2 system, which is an order of magnitude larger than that of stoichiometric SrSi2 [11]. Such a finding suggests that the Y substitution onto the Sr sites would cause a significant modification on the electronic band structure of these Sr-contained silicides, which in turn leads to a considerable influence on their thermoelectric properties. In this study, to ascertain the effect of Y substitution on physical properties of SrAl2Si2, electrical resistivity, thermal conductivity, and Seebeck coefficient measurements were performed on well-characterized polycrystalline Sr1-xYxAl2Si2 samples, with x varying from 0 to 0.2, over the temperature range 10K $\leq T \leq$ 300 K. We have also performed the first principle electronic band structure calculation using density functional theory, focusing on the features around the Fermi level. Theoretical results indicate that the Y substitution has an effect of reducing the hole pockets in the vicinity of the Fermi level, being consistent with the experimental results.

2. Experimental methods

Polycrystalline Sr1-xYxAl2Si2 alloys were prepared by arc-melting the appropriate proportion of elements Sr (99.99%), Y (99.99%), Al (99.99%), and Si (99.99%) under an inert atmosphere of argon. These alloys were melted several times to improve the homogeneity. The structure of the alloys was examined by powder X-ray diffraction measurement using conventional Cu-Kα radiation in the diffraction angular range, 2θ, from 10° $\leq 2\theta \leq$ 80°. Electrical resistivity measurements were performed by standard four-probe method from 10 K to 300 K. Thermal conductivity and Seebeck coefficient measurements were performed simultaneously in a close-cycle helium refrigerator by the heat pulse technique. Samples were cut into a rectangular parallelepiped shape of typical size of 1.5 $\times$ 1.5 $\times$ 5 mm³. Very thin differential thermocouple junctions were fixed at the two ends of the sample using thermal epoxy. To measure the Seebeck emf, thin copper leads were placed on the sample very near to the thermocouple junctions using silver paste. One end of sample was mounted on a copper block and a small chip resistor was fixed at the other end of the sample, which serves as a heater. The temperature difference was controlled to be less than 1 K to minimize the heat loss through radiation, and the sample space is maintained in a good vacuum (10⁻³ torr) during experiments. All data were recorded with a slow warming rate of about 20 K/h. The further details of the measurement techniques can be found elsewhere [12,13].

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 displays the X-ray diffraction (XRD) patterns collected on the powder specimens using Cu Kα radiations at room temperature in the Bragg-Brevenno geometry in the range of 2θ from 10° to 80°. The XRD patterns are indexed according to trigonal La₃O₅-type structure [3] as shown in Fig. 1. The more detailed XRD analysis using Rietveld method confirmed the space group, $P3m1$ (No. 164) (same as that of CaSi₅Al₂) with the values of lattice parameters as $a = 4.1842$ Å and $c = 7.442$ Å for SrAl2Si2. These parameters are similar to that of the reported values [10]. Rietveld refinement also revealed a presence of small impurity SrAlSi phase with AlB₂-type structure with P6/mmm (No.191) space group, however the volume fraction of the SrAlSi phase is negligible and hence presumably does not affect the physical properties of the major SrAl2Si2 phase. It is evident from Fig. 1(a) that all the samples with Y-substitution contain a tiny amount of SrAlSi phase except sample x = 0.05 which has single SrAl2Si2 phase and do not exhibit Bragg peaks corresponding to minority SrAlSi phase. As shown in Fig. 1(a), above x = 0.10, the intensity of (101) reflection of SrAlSi phase decreases drastically whereas the intensity corresponds to (102) plane of YAl2Si2 increases. Both the lattice parameters a and c decrease almost linearly with increase in yttrium concentration, as shown in Fig. 1(b), as a consequence of the larger atomic radius Sr (2.15 Å) atoms being replaced with the smaller atomic radius Y (1.81 Å) atoms following the Vegard's law. It also confirms that, as intended, Y atoms occupy Sr sites for the compositional range investigated in the present study. The substitution of yttrium of 20 at.% results in a lattice contraction of about 1.4%, which is equivalent to inducing a positive chemical pressure in SrAl2Si2.

3.2. Electrical resistivity

Fig. 2a displays the temperature dependence of resistivity of Sr1-xYxAl2Si2 alloys over the temperature range 10K $\leq T \leq$ 300 K. For the stoichiometric compound SrAl2Si2, $\rho(T)$ increases monotonically as the temperature is reduced from 300 K then develops a broad hump around 120 K and then decreases smoothly with further reducing temperature. The relative large magnitude and the high-temperature variation of the electrical resistivity are reminiscent of a semimetal
with a pseudogap in the DOS at $E_F$ [14–17]. The appearance of the broad peak in $\rho(T)$ at around 120 K suggests that two competing mechanisms govern the electrical transport in the ternary silicide SrAl$_2$Si$_2$. For temperatures $T \leq 120$ K, we observe a positive temperature coefficient of resistivity (TCR), suggesting that $\rho(T)$ is dominated by intrinsically metallic nature. For $T > 120$ K, the negative TCR indicates that thermally activated behavior is dominant due to an increase in the density of hole carriers across the pseudogap. The activation energy required for the charge carriers is estimated using equation $\rho(T) = \rho_0 - \Delta / T$ where $\Delta$ is the energy gap in the density of states. The small value of $\Delta \sim 0.04$ eV suggests that the density of states of SrAl$_2$Si$_2$ exhibits a pseudogap rather than a real energy gap. Such a result is consistent with our band structure calculations which will be presented in the later section.

Substitution of yttrium for strontium results in a dramatic reduction on the electrical resistivity of SrAl$_2$Si$_2$. As shown in Fig. 2(a), in contrast to the semimetall-like behavior in SrAl$_2$Si$_2$, $\rho(T)$ exhibits a metallic-like behavior in Sr$_{1-x}$Y$_x$Al$_2$Si$_2$. After a significant reduction in residual resistivity (RR) for $x = 0.05$ as compared to SrAl$_2$Si$_2$, further decrease in RR occurs almost linearly with Y concentration (see the inset in Fig. 2(a)). Such a decrease is attributed to increase in charge carriers and DOS at the Fermi level due to the modification of band structure with Y substitution. For $x = 0.05$, $\rho(T)$ roughly follows a $T^x$ dependence at low temperatures ($T < 40$ K) and becomes linear at high temperatures ($T > 200$ K). It is noted that this linear dependence in $\rho$ extends over a wide temperature range as the $Y$ substitution increases. To have a quantitative viewpoint of the measured results, the $\rho(T)$ data for metallic Sr$_{1-x}$Y$_x$Al$_2$Si$_2$ alloys were analyzed by using Bloch Grüneisen relation:

$$\rho = \rho_0 + a_r (T/\theta_D)^{\frac{1}{2}} \int_0^{\theta_D/T} \frac{x^2 dz}{(e^x - 1)(1 - e^{-x})}$$

(1)

where $x = \omega/\kappa T$, $\rho_0$, $\theta_D$, and $a_r$ are residual resistivity, Debye temperature, and a constant of proportionality (a measure of the strength of electron-phonon interaction) respectively. As shown in Fig. 2(a), Bloch Grüneisen relation (solid lines) describes the $\rho(T)$ of Sr$_{1-x}$Y$_x$Al$_2$Si$_2$ alloys quite well over the measured temperature range. The $a_r$ and the Debye temperature, $\theta_D$, obtained from the fits are listed in Table 1. It is clearly seen from Fig. 2(b) that both $a_r$ and $\theta_D$ decrease almost linearly starting from $x = 0.05$, implying that the $Y$ substitution not only sets off a systematic modification on the electronic band structure but also the phonon spectrum for the SrAl$_2$Si$_2$ system. It is noted that the extrapolated $\theta_D$ for SrAl$_2$Si$_2$ is 224 K ($x = 0$, see the left vertical axis of Fig. 2(b), quiet close to the value of isostructural compound CaAl$_2$Si$_2$ [5]). These obtained Debye temperatures will be used for the analysis of thermal conductivity data in Section 4.

3.3. Seebeck coefficient

The temperature dependence of Seebeck coefficient, $S(T)$ for Sr$_{1-x}$Y$_x$Al$_2$Si$_2$ are illustrated in Fig. 3. The negative sign of Seebeck coefficient for all samples over the measured temperature range indicates that predominant charge carriers for the thermoelectric transport are electrons. However, the large magnitude and nonlinear temperature variation of $S(T)$ observed in the stoichiometric compound SrAl$_2$Si$_2$ is strikingly different from the Y substituted alloys. The T-dependent $S$ in SrAl$_2$Si$_2$ exhibits a broad minimum with an absolute value of about 100 $\mu V/K$ near 130 K, and then attains a positive slope at high temperatures. The upturn of $S$ in SrAl$_2$Si$_2$ at high temperatures is attributed to the contribution of thermally excited positive carriers across the pseudogap [11,14]. The change in the slope for $S$ at around 130 K suggests the existence of lighter electron and heavier hole pockets in the band structure of SrAl$_2$Si$_2$. However, the electrons become heavier and thus dominate the $S(T)$ at high temperatures. Such a scenario appears to be consistent with our band structure calculations of SrAl$_2$Si$_2$, where the Fermi surface consists of one electron pockets centered at the M point and two hole pockets centered at the $\Gamma$ point. Within the two-band model, it allows us to consider a contribution from a semi-conducting like holes in addition to a metallic term as a possible explanation for the observed exotic thermoelectric transport behavior in SrAl$_2$Si$_2$. It should be pointed out that these interpretations are consistent with the observations in the isostructural compound CaAl$_2$Si$_2$ [14] and the high-temperature result obtained from a single crystal of SrAl$_2$Si$_2$ [10].

For the Y substituted samples, on the other hand, the hump feature in $S(T)$ is absent and the magnitude of $S$ is drastically reduced, similar to that of the resistivity results. For $x = 0.05$, the magnitude of $S$ at room temperature reduces to almost half of SrAl$_2$Si$_2$ and tends to decrease further with increasing $x$. A shoulder-like feature at around 50 K is noticed in the Sr$_{1-x}$Y$_x$Al$_2$Si$_2$

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Residual resistivity, $\rho_0$ ((\mu\Omega) cm)</th>
<th>$a_r$ ((\mu\Omega) cm)</th>
<th>$\theta_D$ (K)</th>
<th>$E_F$ (eV)</th>
</tr>
</thead>
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<tr>
<td>x = 0</td>
<td>1670</td>
<td>0.66</td>
<td>224</td>
<td>0.071</td>
</tr>
<tr>
<td>x = 0.05</td>
<td>138.68</td>
<td>0.474</td>
<td>214.8</td>
<td>0.183</td>
</tr>
<tr>
<td>x = 0.1</td>
<td>114.23</td>
<td>0.32651</td>
<td>202.3</td>
<td>0.235</td>
</tr>
<tr>
<td>x = 0.15</td>
<td>89.4</td>
<td>0.195</td>
<td>189.1</td>
<td>0.230</td>
</tr>
<tr>
<td>x = 0.2</td>
<td>45.66</td>
<td>0.195</td>
<td>182.3</td>
<td>0.271</td>
</tr>
</tbody>
</table>
alloys, presumably due to contribution from phonon-drag effect. Above 150 K, each magnitude of $S(T)$ increases almost linearly with increasing temperature, reminiscent of typical metals. For ordinary metals, the Seebeck coefficient is expected to be linear in temperature and can be associated with Mott’s formula $S = (\pi^2 k_B^2 / 2eE_F) T$, assuming a one-band model with an energy-independent relaxation time. Here, $E_F$ is the Fermi energy and $k_B$ is the Boltzmann constant. However, the measured $S(T)$ curves for Sr$_{1-x}$Y$_x$Al$_2$Si$_2$ alloys also consists of contribution from interaction between electrons and inhomogeneous distribution of phonons (so called the phonon-drag effect) at low temperatures. To account for this behavior and to separate the linear diffusive contribution from total $S(T)$, we have analyzed the $S(T)$ data with an empirical power law

$$S(T) = AT + BT^3$$  \hspace{1cm} (2)

The first term in Eq. (2) represents the electronic diffusive contribution whereas the second term sets an upper bound to contribution from electron-phonon normal processes to total $S(T)$ [18]. Thus, the linear portion of $S/T$ vs. $T^2$ plots shown in the inset of Fig. 3 exhibits the temperature range over which Eq. (2) is valid. The calculated values of $E_F$, via relation $A = \pi^2 k_B^2 / 2eE_F$ are given in Table 1. It is evident that the Fermi energy for Sr$_{1-x}$Y$_x$Al$_2$Si$_2$ increases with increasing Y concentration. This behavior is presumably attributed to the band filling effect as yttrium has one more electron in its valence shell compared to strontium. It is important to note that values of $E_F$ for Y substituted samples are in the range of 0.2–0.3 eV, which is an order of magnitude smaller than that of typical metals. However, the above analysis is not applicable for SrAl$_2$Si$_2$ due to the non-linear temperature dependence in $S(T)$. However, for the sake of comparison such an analysis for SrAl$_2$Si$_2$ is also performed and displayed in the inset of Fig. 3. The obtained Fermi energy for SrAl$_2$Si$_2$ is about 0.071 eV, much lower than those of the Y substituted alloys. Hence, it is evident that the substitution of Y with respect to Sr induces a semimetal-to-metal like transformation in SrAl$_2$Si$_2$ due to electron-doping effect, and this result is in good agreement with the theoretical calculations presented in the last section.

### 3.4. Thermal conductivity

Fig. 4 displays the measured total thermal conductivity, $\kappa(T)$ for Sr$_{1-x}$Y$_x$Al$_2$Si$_2$ over the temperature range of $10K \leq T \leq 300$ K. The low temperature $\kappa(T)$ exhibits similar behavior for all alloys where a sharp rise is followed by a broad maximum/peak around 40 K and then gradually decreases with increasing temperature. The low-$T$ peak in $\kappa(T)$ is commonly seen in solids due to the reduction of thermal scattering at low temperatures. The maximum in $\kappa(T)$ occurs when the phonon mean free path is comparable to crystal site distance. It is worthwhile addressing that the temperature at which maximum in $\kappa(T)$ occurs and value of $\kappa(T)$ do not exhibit any systematic dependence on Y concentration, suggesting that substitution of yttrium at the Sr sites may result in defects in the alloy system. The room temperature value of $\kappa \sim 13$ W/m-K is found for SrAl$_2$Si$_2$ and the value increases to $\sim 27$ W/m-K for $x = 0.20$. The total thermal conductivity for ordinary metals or semimetals is generally expressed as a sum of electronic and lattice terms. The electronic thermal conductivity, $\kappa_e$ can be estimated by the Wiedemann-Franz law: $\kappa_e = L_0 T$ where $\rho$ is the dc electrical resistivity and the Lorentz number $L_0$ attains the Sommerfelds value of $2.45 \times 10^{-8}$ WQ/K$^2$ under the assumption that inelastic electron scattering processes are absent. As illustrated in Fig. 4, the solid lines represent the calculated electronic thermal conductivity, $\kappa_e$ for Sr$_{1-x}$Y$_x$Al$_2$Si$_2$ alloys using Wiedemann-Franz law. For the stoichiometric compound, $\kappa_e$ is estimated to be at least an order of magnitude lower than the total thermal conductivity over the entire temperature range, indicating that the dominant contribution to $\kappa$ is from the lattice phonons rather than the charge carriers in SrAl$_2$Si$_2$. In Y-substituted samples although, $\kappa_e$ is only 10% of $\kappa$ at low temperatures below 150 K. In contrast with SrAl$_2$Si$_2$, at higher temperatures, $\kappa_e$ has considerable contribution to $\kappa_T$ as illustrated in Fig. 4. For $x = 0.2$ at 300 K, $\kappa_e$ is almost 25% of $\kappa_T$. This enhancement in electronic thermal conductivity at high temperatures is closely related to the bipolar diffusion effects frequently employed to discuss the $\kappa(T)$ of semimetals and narrow-gap semiconductors.
[16]. Such an argument has been successfully applied to the discussion in many Al-based complex metallic alloys such as Al–Re–Si and Al–Mn–Si that possess a pseudogap in the density of states at the Fermi level [19].

The lattice part of thermal conductivity, $k_L$, is estimated by subtracting electronic part from total measured conductivity and displayed in Fig. 5. In order to ascertain the effect of Y substitution on phonon scattering in the Sr$_{1-x}$Y$_x$Al$_2$Si$_2$ system, the lattice thermal conductivity, $k_L$, is analyzed using Debye’s formula:

$$k_L = \frac{k_B}{2\pi c^2} \left(\frac{k_B T}{h}\right)^3 \int_0^{\theta_T / T} \frac{\chi^4 e^x}{\tau_p^{-1} (e^x - 1)^4} dx$$

where $x = h\omega / k_B T$ is a dimensionless quantity, $\omega$ is the phonon frequency, $h$ is the reduced Planck constant, $k_B$ is the Boltzmann constant, $\theta_T$ is the Debye temperature, $v$ is the average phonon velocity, and $\tau_p^{-1}$ is the phonon scattering relaxation rate and is given by Eq. (4):

$$\tau_p^{-1} = \frac{v}{L} + A_0 A + B_0 v^2 T e^{-\theta_T / 3T}$$

where $v$, $L$ and $\omega$ represent phonon velocity, grain size and phonon frequency, respectively. Thus the phonon scattering rate consists of three terms. The first term is a measure of scattering from grain boundaries which is a dominant contribution to $k_L$ at low temperatures. The second term is a measure of point-defect scattering that has a strong influence on the shape and position of the phonon peak occurring in the intermediate temperature regime. The third term represents the phonon–phonon scattering due to Umklapp processes which is important at high temperatures. Using the values of $\theta_T$ obtained by fitting the Bloch Grüneisen relation to the dc electrical resistivity data and determining the phonon velocity $v$ by using $v = \theta_T (k_B h / (8\pi^2 n)^{1/3})$ with the carrier density $n$, $k_L$ can be satisfactorily described by Eq. (3) for $T < 120$ K (solid lines in Fig. 5). We have attempted to include the electron-phonon interaction in the calculations, but such an effort led no significant improvement to the overall fit. We thus conclude that the electron-phonon scattering has minor influence on the lattice thermal conductivity in Sr$_{1-x}$Y$_x$Al$_2$Si$_2$ alloys. It is also noticed that the fitting curves deviate from the data points at high temperatures. The discrepancy may arise from radiation losses during the measurements, temperature dependence of the Lorentz number and errors in the determination of Debye temperatures.

All fitting parameters are tabulated in Table 2. It is clear that the grain size $L$ decreases with the increase in Y substitution with the exception the composition of $x = 0.05$. The Umklapp coefficient $B$ scatters around these samples, presumably due to errors in the Debye temperatures and the carrier density $n$. It should be noted that even though the Debye temperature is an important factor for the Umklapp scattering rate, it only affects the fitting results at high temperatures. According to the model proposed by Klemens, the prefactor $A$ of the second term in Eq. (4) increases with the amount of point defects in the low defect level [20]. Although, for the present system the parameter $A$ is found to be roughly increases however, without a systematic variation with Y-substitution level. These results indicate that Y substitution in SrAl$_2$Si$_2$ may introduce other lattice imperfections such as dislocations and twins rather than point defects for the thermal conductivity reduction at lower temperatures.

### 3.5. Electronic band structure calculations

In order to gain a more insight of the semimetal-to-metal like transformation of Y-doped SrAl$_2$Si$_2$, we have performed first-principles calculations within the framework of density functional theory (DFT) [21] with Vienna ab initio simulation package (VASP) [22]. The exchange-correlation potential is described by the generalized gradient approximation (GGA) proposed by Perdew, Burke and Ernzerhof [23]. The interaction between ions and valence electrons is described by the projector augmented-wave (PAW) method [24]. The Kohn-Sham wave functions were solved by plane-wave basis with energy cutoff of 306.7 eV. The Brillouin zone (BZ) integration is constructed by the Monkhorst-Pack k-point sampling scheme including gamma point [25]. The primitive unit cell of SrAl$_2$Si$_2$ is a hexagonal cell with space group symmetry of P6$_3$M1. The calculated bulk lattice constants ($a = 4.20$ Å, $c = 7.43$ Å), which is obtained with fully optimized lattice and atomic positions with k point set of $24 \times 24 \times 8$ are in good agreement with the experimental values ($a = 4.18$ Å, $c = 7.44$ Å).

To simulate the Y-doped system (Sr$_{1-x}$Y$_x$Al$_2$Si$_2$), a large supercell containing $3 \times 3 \times 2$ primitive unit cells is chosen and the Y concentration of $x = 0.05$, 0.11, 0.165 are simulated by replacing Sr atoms with one, two, and three Y atoms, respectively. All the atomic structures are fully optimized (with $k$ point set of $4 \times 4 \times 4$) until the forces on the ions are less than 0.02 eV/Å. The density of states of the fully relaxed structures is calculated with a denser $k$ point sampling of $8 \times 8 \times 8$. It should be mentioned here that we have calculated all possible configurations for substitution of Sr atoms with Y atoms. The energy differences between these configurations are small, and the band structure and density of state are also very similar. The band structure and density of state of Sr$_{1-x}$Y$_x$Al$_2$Si$_2$ are taken from the most stable configurations (the lowest energy configuration) with c,3v symmetry.

### Table 2
Electronic thermal conductivity at 300 K, and fitting parameters of lattice thermal conductivity determined from Eqs. (3) and (4).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\kappa_e$ (W/m-K)</th>
<th>$L$ (µm)</th>
<th>$A$ ($10^{-43}$ s$^3$)</th>
<th>$B$ ($10^{-18}$ s K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 0$</td>
<td>0.44379</td>
<td>11.2</td>
<td>10.3</td>
<td>1.47</td>
</tr>
<tr>
<td>$x = 0.05$</td>
<td>2.26426</td>
<td>39.03</td>
<td>31.6</td>
<td>0.57</td>
</tr>
<tr>
<td>$x = 0.10$</td>
<td>2.9626</td>
<td>9.42</td>
<td>16.3</td>
<td>1.01</td>
</tr>
<tr>
<td>$x = 0.15$</td>
<td>3.99518</td>
<td>6.59</td>
<td>10.9</td>
<td>1.18</td>
</tr>
<tr>
<td>$x = 0.20$</td>
<td>6.96272</td>
<td>5.2</td>
<td>19.5</td>
<td>0.46</td>
</tr>
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</table>
To investigate the effect of Y doping on SrAl2Si2, the band structure along the high symmetry directions (for the 3 x 3 x 2 supercell) of Sr1-xYxAl2Si2 are illustrated in Fig. 6. It is seen in Fig. 6(a) that there are four distinct bands near the Fermi energy and SrAl2Si2 can be classified a semimetal with both n-type and p-type carriers. The cyan and red bands provide n-type carriers, the blue and green bands provide p-type carriers. With one Y atom replaces a Sr atom in the supercell (x = 0.055), the hole pocket of the green band disappeared in Fig. 6(b), and the red band shifts down to increase n-type carriers. Furthermore, in

![Graph showing band structure](image)

**Fig. 6.** Electronic Band structure (with a 3 x 3 x 2 supercell) of Sr1-xYxAl2Si2 for (a) x = 0, (b) x = 0.055, (c) x = 0.11, and (d) x = 0.165, respectively. The four energy bands near the Fermi level are identified as four different colors. The increase of Y concentration leads to the reduction of the hole states and enhancement of the electron states.

![Projected density of states](image)

**Fig. 7.** The projected density of states for Sr1-xYxAl2Si2 with Sr + Y and Si atom summations on the left and right panels, respectively. The DOSs of Al near Fermi level is negligible, therefore its contribution is not shown in the figure. An upward shift of the Fermi level is clearly seen upon Y substitution in Sr1-xYxAl2Si2 alloys.
Fig. 6(c), the hole pockets almost disappeared and most of the carriers belong to n-type. Finally, in Fig. 6(d), the hole pockets completely eliminated and the material becomes metallic. This trend can also be found from the projected density of states (DOS).

As shown in Fig. 7, the Fermi energy is pushed upward as the increasing of Y concentration and thus diminishes the hole state (from Si) and increases the electron state (from Y and Sr). Thus, the Fermi energy shifts upward and makes the material more metallic. The shift of the Fermi energy (as referred to SrAl2Si2) estimated in our calculations are 0.1, 0.2, and 0.3 eV for Sr0.945Y0.055Al2Si2, Sr0.89Y0.11Al2Si2, Sr0.835Y0.165Al2Si2, respectively. These results are in good agreement in the analysis of $S(T)$ and $\rho(T)$ data which concludes that SrAl2Si2 is a semimetal with pseudogap in the density of states at the Fermi level with low carrier density. Substitution of Y at the Sr sites results in a semimetal to metal-like transformation due to an increase in DOS at Fermi level and electron carriers.

4. Conclusions

In summary, we have investigated the effect of the Y substitution on the transport properties and electronic band structures of Sr1-xYxAl2Si2 alloys with $x = 0.0$ to 0.2. The experimental results and theoretical calculations concurrently suggest that the stoichiometric compound SrAl2Si2 is a low carrier density semimetal with a pseudogap in the density of states at the Fermi level. The substitution of smaller Y atoms onto the Sr sites causes a lattice contraction in the alloy system, resulting in a significant shift of Fermi energy and the modification of electron and hole pockets near band edges, as revealed from ab initio calculations. A semimetal to metal-like transformation with Y substitution is thus observed. The variation in both $S(T)$ and $\rho(T)$ with changes in composition can be understood by the modification of the density of states at the Fermi level as a consequence of pseudogap narrowing. The analysis of lattice thermal conductivity revealed that Y substitution in SrAl2Si2 may introduce lattice imperfections such dislocations and twins rather than point defects to the alloy system.

The conclusion made in this study provides a concise understanding of the evolution of band structures in Sr1-xYxAl2Si2 via lattice contraction and electron doping.

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