Electronic structure, bonding character, and thermoelectric properties of semiconducting rhenium silicide with doping

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The electronic structure and thermoelectric properties of $ReSi_{1.75}$ and its doped systems are studied by the first-principles calculation using the full-potential linearized augmented plane-wave method in the local density approximation with self-interaction correction and the semiclassical Boltzmann theory. $ReSi_{1.75}$ shows narrow gap semiconductor behavior with an indirect gap of 0.12 eV and a direct gap of 0.36 eV. The Fermi levels of Al- and Mo-doped systems move into the valence band. The Al-doped compound remains a semiconductor while the gap of Mo-doped compounds becomes small and nearly disappears. The relations between the electronic structure and thermoelectric properties of doped $ReSi_{1.75}$ are analyzed and explained in detail. Our calculations strongly suggest that an excellent thermoelectric performance can be obtained for *p*-doped $ReSi_{1.75}$ along [100] and for *n*-doped $ReSi_{1.75}$ along [001] compared with the undoped compound.

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I. INTRODUCTION

Rhenium silicide ($ReSi_{1.75}$) has attracted considerable attention for its applications in microelectronic and thermoelectric devices.[1,2] $ReSi_{1.75}$ is a narrow-gap semiconductor whose reported experimental values of band gap vary from 0.11 to 0.36 eV.[3–5] In addition to its excellent thermoelectric properties, anisotropic transport behavior was recently observed in experiments, which displayed a *p*-type behavior along [100] and an *n*-type behavior along [001] for single crystals.[6] The specific crystal structure and electronic structure of $ReSi_{1.75}$ are believed to give rise to such unique semiconducting properties. Doping by Mo and Al has been attempted in this compound[7–9] in order to further improve its thermoelectric performance, which is described as the thermoelectric figure of merit $ZT=\sigma S^2 T/\kappa$ (where σ is the electrical conductivity, S is the Seebeck coefficient, κ is the thermal conductivity, and T is the absolute temperature). The substitutions of Mo on the Re site and Al on the Si site both result in increased σ, thus improving ZT.

The electronic structure of $ReSi_{1.75}$ has been calculated by the linear muffin-tin orbital (LMTO) method[10] and the full potential linearized augmented plane wave (FP-LAPW) method,[11] which showed contradictory results of gap and gapless nature, respectively. It is well known that the local density approximation (LDA) in the above methods is not suitable to describe rhenium having highly localized *d* electrons.[12] However, the LDA+U approach can give a better description of such localized states, where the Hubbard parameter U simulates corrections beyond the LDA.[13] With this orbital dependent LDA+U potential, the orbital polarization becomes possible and the failure of LDA in describing the band gap can be removed. It has been shown that the LDA+U theory can be regarded as an approximation to the *GW* theory that is widely used in different forms in order to take into account the quasiparticle effects in semiconductors.[14,15]

In this paper, we calculated the electronic structure of $ReSi_{1.75}$ by first-principles calculation in the framework of LDA+U with self-interaction correlation (LDA+U^{SIC}). Then, the effect of doping elements such as Al and Mo on the electronic structure and the structure stability of $Re_{0.875}Mo_{0.125}Si_{1.75}$ and $ReSi_{1.625}Al_{0.125}$ were investigated and explained in detail. Based on the calculated band structure and the experimental data, the thermoelectric properties of doped $ReSi_{1.75}$ were analyzed using the Boltzmann theory and the rigid band approach.

II. STRUCTURE AND COMPUTATIONAL METHOD

The basic crystal structure of $ReSi_{1.75}$ is triclinic (space group $P1$, $a=0.3138$ nm, $b=0.3120$ nm, $c=0.7670$ nm, $\alpha=89.9°$, and $\beta=\gamma=90°$) due to a slight distortion from tetragonal structure ($C11_b$ type) where the two silicon sites (Si_{III} and Si_{IV}) are partially occupied with a factor of 0.75.[16] In order to take into account an integer number of each type of atom, we constructed a supercell by doubling the lattice along *a* and *b* axes. Thus, there were a total of 8 rhenium and 14 silicon atoms plus 2 empty sphere sites in the supercell. For doping, the preferential sites of Al substitution for Si and Mo substitution for Re were determined by the cohesive energy.

The first-principles calculation was performed by the FP-LAPW method using WIEN2K code.[17] The LDA of Perdew and Wang[18] was applied as the exchange-correlation potential with a cutoff energy of −8.0 Ry. The muffin-tin radii R_{MT} was set to 2.2 a.u. for all atoms and the plane wave cutoff constant $R_{MT}K_{max}$ was set to 8.0. A self-consistent procedure was performed on a grid containing 51 *k* points in the irreducible Brillouin zone (IBZ) until the energy difference was less than 10^{-5} Ry. Since the properties of $ReSi_{1.75}$ are highly sensitive to its structure, it is necessary to fully optimize and relax the crystal beforehand. The relaxation procedures were performed following the damped Newton dynamic schemes for forces acting on the atoms smaller than 10^{-3} Ry/a.u.. For the electronic structure calculation, the LDA+U^{SIC} method was used. An onsite U_{eff} (U-J, where the exchange $J=0$) term of 0.32 Ry (about 4.4 eV) was used to

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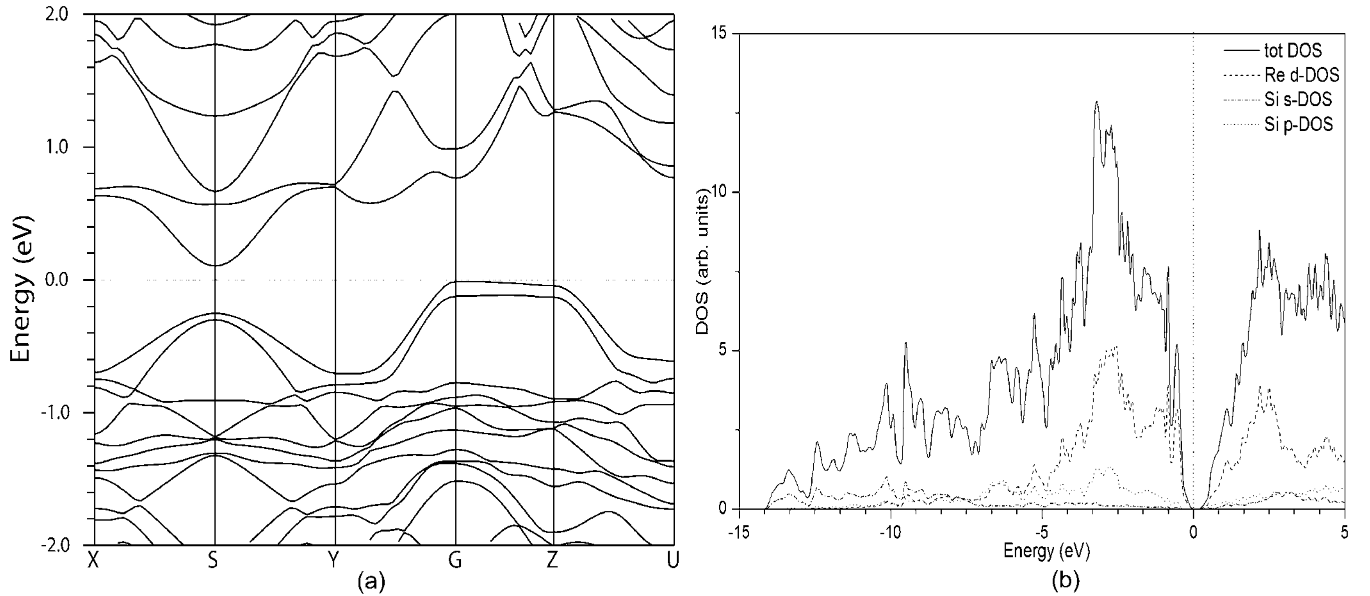

FIG. 1. Band structure (a) and DOS (b) of $ReSi_{1.75}$.

treat the strongly correlated 5*d* electrons of Re.

The thermoelectric properties were calculated from the band structure using the semiclassical Boltzmann theory and the rigid band approach.[19] Under these conditions, the Seebeck coefficient S is expressed as[20,21]

$$S_{ij} = \sum_{\alpha} (\sigma^{-1})_{i\alpha}\nu_{\alpha j}, \quad (1)$$

where

$$\sigma_{ij}(T,\mu) = \frac{1}{\Omega}\int \sigma_{ij}(\varepsilon)\left[-\frac{\partial f_{\mu}(T,\mu)}{\partial \varepsilon}\right]d\varepsilon, \quad (2)$$

$$\nu_{ij}(T,\mu) = \frac{1}{eT\Omega}\int \sigma_{ij}(\varepsilon)(\varepsilon-\mu)\left[-\frac{\partial f_{\mu}(T,\mu)}{\partial \varepsilon}\right]d\varepsilon, \quad (3)$$

and

$$\sigma_{ij}(\varepsilon) = e^2\int d^3\mathbf{k}\,\tau(\mathbf{k})v_i(\mathbf{k})v_j(\mathbf{k})\,\delta[\varepsilon-\varepsilon(\mathbf{k})], \quad (4)$$

where $\varepsilon(\mathbf{k})$ is the band energy, $v_i(\mathbf{k})$ is the band velocity $(\partial\varepsilon(\mathbf{k})/\partial k_i)$, $\tau(\mathbf{k})$ is the relaxation time, μ is the chemical potential, and f_{μ} is the Fermi function. In the above equations, if the bands are fixed and the relaxation time τ is a constant, then we can obtain a quantitative S independent of τ. The electrical conductivity σ can only be calculated with respect to the τ, which is somehow included as a parameter.

For the transport tensors calculation, eigenenergies of 3204 k points on a nonshifted mesh in the IBZ were calculated by the BOLTZTRAP code,[22] which is based on a well tested smoothed Fourier interpolation to obtain an analytical expression of the bands. The original k mesh was interpolated onto a mesh five times as dense as the original.

III. RESULTS AND DISCUSSION

A. Electronic structure and bonding character

After fully optimizing and relaxing, the equilibrium lattice constants of $ReSi_{1.75}$ following the Murnaghan equation of states[23] are found to be $a=0.3119$ nm, $b=0.3102$ nm and $c=0.7624$ nm, which are about 0.6% smaller than the experimental values. Vacancy prefers to occupy the Si_{III} and Si_{IV} sites in the lattice, with the lowest cohesive energy. Tanaka *et al.*[24] recently argued a Si vacancy ordering in the crystal. We constructed several configurations of vacancy sites in the supercell. However, the total energy differences of those configurations were almost negligible (energy differences are less than 0.005 eV/unit cell, consistent with Shaposhnikov's results[11]), indicating little ordering of vacancy on the Si_{III} and Si_{IV} sites. This is somehow reasonable because the vacancy ordering was found in an extended lattice with the space group of *Cm* containing 44 atoms.

Figure 1 shows the calculated band structure and density of states (DOS) of $ReSi_{1.75}$ using the LDA+U method. It is shown that $ReSi_{1.75}$ represents narrow gap semiconductor behavior with an indirect gap of 0.12 eV and a direct gap of 0.36 eV, which are in good consistence with the experimental values[4,16] and the results by LMTO,[10] as well as the results by LAPW after a rigid shift.[11,25] Our orbital composition analysis results reveal that Re *d* states take 77% and 49% of the eigenstates at the valence band maximum and conduction band minimum, respectively. In comparison, all the Si states take 3% and 19% and others are interstitial. Therefore, the Re *d* states and the band structure can be described by the LDA+U method fairly well. The feature of the band structure is peculiar: very flat bands along the ΓZ direction (valence band maximum) and parabolic bands around the S point (conduction band minimum). This peculiar feature may lead to great differences in the effective mass and transport

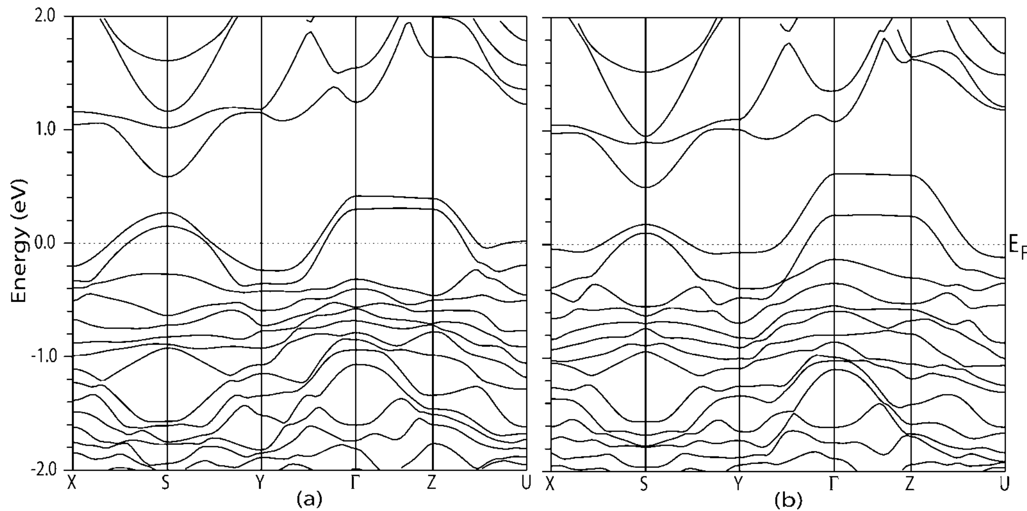

FIG. 2. Band structures of (a) $ReSi_{1.625}Al_{0.125}$ and (b) $Re_{0.875}Mo_{0.125}Si_{1.75}$.

mobility for holes and electrons along the corresponding directions, which is attributed to a large anisotropy of conduction type in $ReSi_{1.75}$. Our calculated effective masses for holes and electrons are $m_h^*=10.60m_0$ and $m_e^*=0.39m_0$ along the [001] direction and $m_h^*=0.24m_0$ and $m_e^*=0.40m_0$ along the [100] direction. From the DOS, it can be found that the valence states of $ReSi_{1.75}$ extend down to 14 eV below the Fermi level. The DOS of $ReSi_{1.75}$ from the bottom up to −8 eV is mainly composed of deep Si s states. From −8 to −1 eV, the hybridized Si p states and Re d states determine the shape of the DOS. From −1 eV to 1 eV, the localized Re d states play a dominant role in this energy range. This is in agreement with the results of the spectra experiment.[4] According to Fig. 1(b), there is a sharp change of the DOS around the Fermi level, indicating that an enhancement of thermoelectric properties may be obtained if the position of the Fermi level can be tuned by doping.[26,27]

According to the crystal structure of $ReSi_{1.75}$, there are four and two inequivalent sites for Si and Re, respectively, in the $C11_b$ lattice. Thus, when Al substitutes for Si or Mo substitutes for Re, there are four or two possible occupations, respectively. Our calculated cohesive energies of different occupations show that when Al takes the Si_{III} sites or Mo takes the Re_I sites, the system has the lowest energy, indicating that the configuration is favorable and can be stable. The feature of the band structures (Fig. 2) of $ReSi_{1.625}Al_{0.125}$ and $Re_{0.875}Mo_{0.125}Si_{1.75}$ is similar to that of $ReSi_{1.75}$, indicating a highly anisotropic transport behavior. Compared to the band structure of $ReSi_{1.75}$ [Fig. 1(a)], the Fermi levels of $ReSi_{1.625}Al_{0.125}$ and $Re_{0.875}Mo_{0.125}Si_{1.75}$ move downward into the valence bands to turn these silicides into a degenerate semiconductor. This can be explained by the electronic configurations of Al and Mo. Both Al and Mo have one valence electron less than Si and Re, respectively, resulting in one more hole, and act as an acceptor in $ReSi_{1.75}$. The downward shift of the Fermi level fairly increases the carrier density and results in an increase of the electrical conductivity. On the other hand, the doping element may enhance the deformation and point defect scattering to the phonons and thus decrease the lattice thermal conductivity. These two factors are both beneficial to the improvement of thermoelectric figure of merit ZT. This is consistent with the experimental observations,[6–9] wherein a considerable increase of ZT has been achieved via doping due to the decreased electrical resistivity and thermal conductivity.

Despite tuning of the Fermi level, the band structures of $ReSi_{1.625}Al_{0.125}$ and $Re_{0.875}Mo_{0.125}Si_{1.75}$ are somewhat different. $ReSi_{1.625}Al_{0.125}$ remains an indirect gap of 0.12 eV between Γ and S points. However, in $Re_{0.875}Mo_{0.125}Si_{1.75}$ the maximum valence band along the ΓZ direction rises due to the hybridization of Mo d states and Re d states and the gap becomes small and nearly disappears. This indicates that Mo

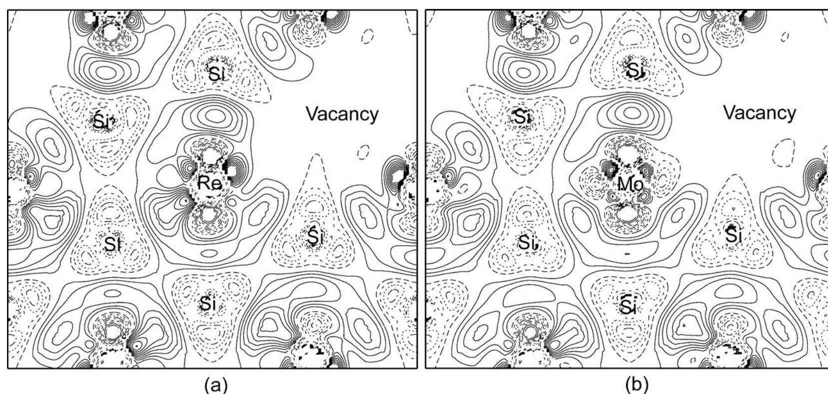

FIG. 3. Valence bonding charge densities for (a) $ReSi_{1.75}$ and (b) $Re_{0.875}Mo_{0.125}Si_{1.75}$ on the (110) plane. The contours range from −0.2 to 0.2 e/Å^3 and increase by 0.2 e/Å^3. The solid (dotted) contours represent contours of increased (decreased) charge.

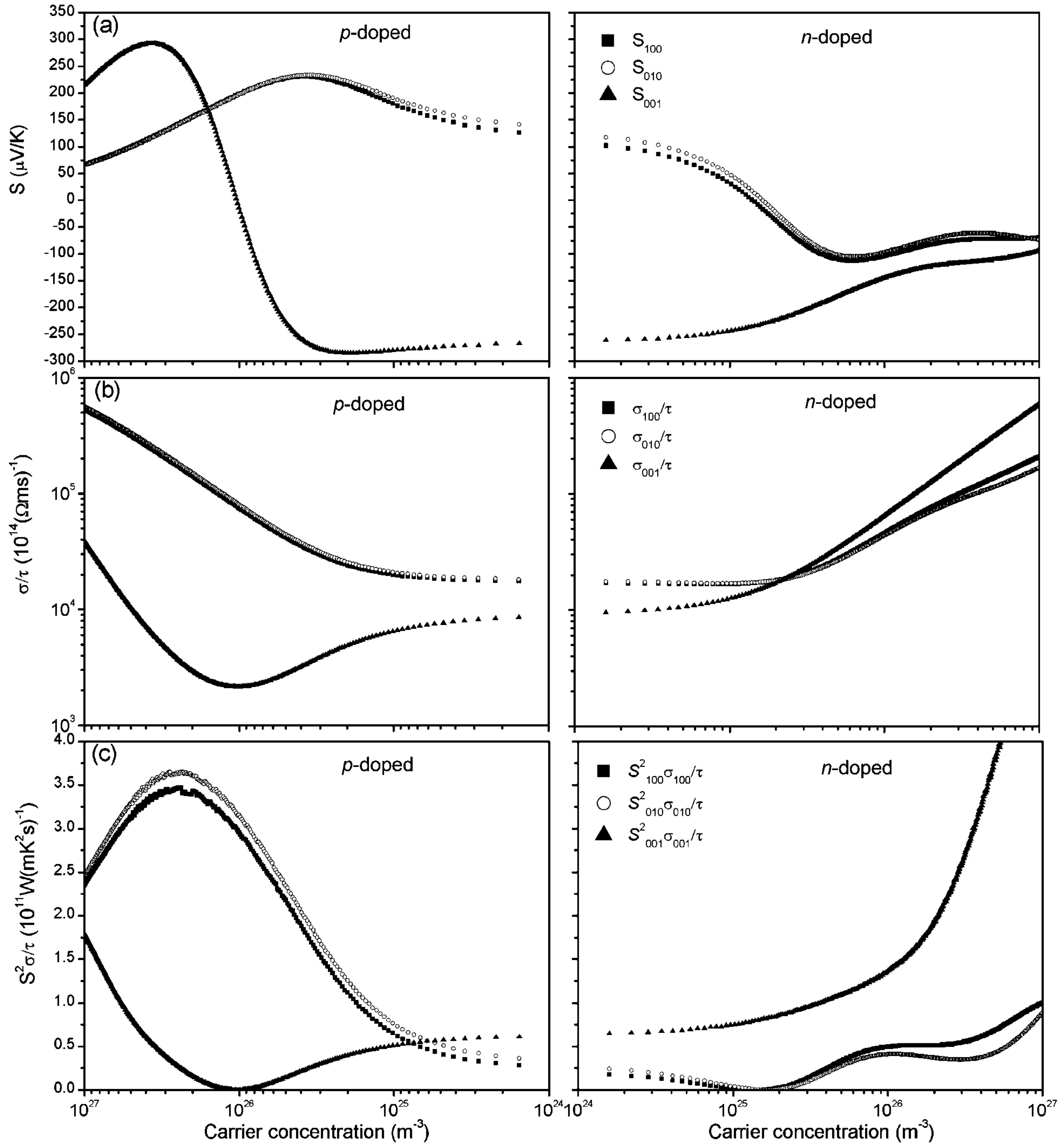

FIG. 4. Thermoelectric properties along different directions calculated from the band structure of $ReSi_{1.75}$ at 600 K as a function of carrier concentration. (a) Seebeck coefficient, (b) electrical conductivities relative to relaxation time σ/τ, and (c) power factor relative to relaxation time $S^2\sigma/\tau$ as a function of doping.

doping has a tendency to change the compound from semiconductor to semimetal, which may be unfavorable for thermoelectric properties. This abnormality can be explained by the bonding character between the metal atoms and silicon atoms. The bonding charge density is defined as the difference between the total charge density in the solid and the superpositions of neutral atomic charge densities at the atom sites. Valence bonding charge densities on the (110) plane show that the Re-Si bond and the Mo-Si bond are covalent (Fig. 3). Compared to the Re-Si bond in Fig. 3(a), the bonding electron density of the Mo-Si bond in Fig. 3(b) slightly decreases, which indicates that the Mo substitution weakens the metal-silicon bond. In Fig. 3(a), the electron density between Re and vacancy bonding increases, indicating that a dangling bond is formed between the Re atom and the Si vacancy. However, the bonding electron density between the Mo atom and the vacancy decreases, thus the dangling bond of Mo disappears. As it has been indicated[10,28] that vacancy is important to the semiconducting properties of $ReSi_{1.75}$, it is believed that the bonding charge transfer between Mo and the vacancy increases the valence states and decreases the band gap after doping.

B. Thermoelectric properties

It has been shown that the band structure of doped $ReSi_{1.75}$ keeps almost the same feature as that of undoped $ReSi_{1.75}$ (the deviation of band structure by Mo doping is negligible in real practice). The rigid band approach can be used to investigate the transport properties by the semiclassical Boltzmann theory. Meanwhile, the relatively accurate band gap we obtained offers a solid basis for such prediction. Figure 4 shows the calculated thermoelectric properties as a function of carrier concentration at 600 K, without consideration of the specific dopant types. The anisotropic transport behavior is well illustrated. The calculated Seebeck coefficients S for binary $ReSi_{1.75}$ are 140 μV/K along [100] and −280 μV/K along [001] direction, respectively, which agree with the experimental values of 146 μV/K and −290 μV/K at 600 K.[8] For p-doped $ReSi_{1.75}$ in the feasible doping ranges (10^{25}–10^{26} m^{-3}), Fig. 4(a) reveals that S keeps a large value and then decreases at a higher doping amount. The maximum S along [100] and [001] are 234 μV/K and −285 μV/K, respectively, which are larger than those observed in Si-Ge alloys[29] and β-$FeSi_2$.[30] However, S decreases with increasing doping amount for n-doped $ReSi_{1.75}$ in Fig. 4(a). It should be noted that in the heavily doped degenerate systems (10^{27} m^{-3}), S_{100} and S_{001} approach to a similar value, showing little anisotropy and are comparable with those of metals. The prediction agrees well with the available experiments. For example, 3% Al-doped $ReSi_{1.75}$ has approximately the same S as that of a binary compound.[7] In contrast, the S of a 2% Ru-doped compound turns out to be very low.[8]

Although it appears that little enhancement of S can be achieved by doping, our above analysis and the calculated results in Fig. 4(b) show that an increase in σ can be achieved. By using the constant relaxation time assumption and the experimental[8] electrical conductivity $\sigma_{100}=6.3\times10^4$ S/m, the relaxation time τ was fitted to be 3.3×10^{-14} s. It should be stressed that under these assumptions, the calculated [001] component (2.31×10^4 S/m) coincides with the experimental value (2.2×10^4 S/m), which underlines the calculation reliability.

Figure 4(b) shows significant increases in σ_{100} in p-doped systems and σ_{001} in n-doped systems as the carrier concentration increases, which is favorable to the thermoelectric performance. However, the σ_{001} in p-doped systems first decreases and then increases with increasing doping amount. These can be explained by the different effective mass of electrons and holes. In semiconductors, the electrical conductivity is expressed as[31]

$$\sigma = nq\mu_n + pq\mu_p = \frac{nq^2\tau_n}{m_e^*} + \frac{pq^2\tau_p}{m_h^*}, \tag{5}$$

where n (p) is the electron (hole) concentration and μ_n (μ_p) is the electron (hole) mobility. Since m_h^* is comparable to m_e^* along [100], σ_{100} increases with increasing carrier concentration (n or p). However, m_h^* is much larger than m_e^* along [001]. When the hole concentration is not so high in p-doped systems, the electron still plays a dominant role and thus σ_{001} decreases. This also explains why σ_{001} increases much faster than σ_{100} in n-doped systems.

Due to the increased σ, the resulting power factor $S^2\sigma$ values [Fig. 4(c)] along [100] for p-doped $ReSi_{1.75}$ and [001] for n-doped $ReSi_{1.75}$ over all the carrier concentrations are found to be significantly larger than that of the undoped compound. If the lattice thermal conductivity is assumed to be independent of doping (actually it may decrease due to the impurity scattering), the figure of merit ZT can be greatly improved. These results indicate a practical way and may act as a guide in optimizing doping for p- and n-type materials in future experiments.

IV. CONCLUSION

We have carried out a theoretical study of the electronic structure, the bonding character and the thermoelectric properties of binary and doped $ReSi_{1.75}$ using FP-LAPW in the LDA+U^{SIC} framework and the semiclassical Boltzmann theory. We find that the LDA+U method is fairly applicable to describe the Re d states and results in a relatively accurate band structure of $ReSi_{1.75}$. The Fermi levels of Al- and Mo-doped systems move into the valence band. The Al-doped compound remains a semiconductor while the gap of Mo-doped compounds becomes small and nearly disappears. The power factors along [100] for p-doped $ReSi_{1.75}$ and [001] for n-doped $ReSi_{1.75}$ over all the carrier concentrations are found to be remarkably larger than that of the undoped compound.

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