Electronic structure of superconducting compounds h-ZrRuX (X=P,As,Si)

Izumi Hase*
Electrotechnical Laboratory, Tsukuba 305-8568, Japan
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The electronic energy-band structures of ordered Fe_2P-type intermetallic superconducting compounds ZrRuX (X=P,As,Si) have been calculated by the full-potential linearized augmented plane-wave method within the local-density approximation. The calculated density of states at the Fermi level $D(E_F)$ is very close to the experiment. An increase of about 4% in the of Ru-Ru distance in ZrRuP causes a 20% increase in $D(E_F)$, which demonstrates the importance of the Ru-Ru distance in the electronic structure of ZrRuX. This is reflected in the electronic structure of ZrRuAs. The calculated $D(E_F)$ of ZrRuSi is about one-half that of ZrRuP.

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I. INTRODUCTION

Several phosphide or arsenide intermetallic compounds have been studied since the discovery of superconductivity in ZrRuP.[1] Now a variety of compounds $TT'X$ (T=Ti,Zr,Hf,Mo; T'=Ni,Ru,Os; X=Si,Ge,P,As)[2–9] has been found. Some of these compounds are superconducting above 10 K, and the highest T_c is ~16 K in MoRuP.[9] Three different structural types are known for these compounds, namely, the Fe_2P-type hexagonal structure (h-$TT'X$), the Co_2P-type orthorhombic structure (o-$TT'X$), and the TiFeSi-type orthorhombic structure (o'-$TT'X$). In spite of the rather high T_c for an intermetallic compound, the observed specific heat shows that the density of states at the Fermi level $D(E_F)$ of h-ZrRuP is not so high, i.e., only about 0.74 states/eV atom.[10]

An electronic band-calculation study using the extended Hückel tight-binding method for h-ZrRuP, o-ZrRuP, and h-ZrRuSi has been performed by Seo *et al.*[11] They obtained a considerably smaller value for $D(E_F)$, i.e., 0.21 states/eV atom for h-ZrRuP. In this paper, we show that the full-potential augmented plane-wave (FLAPW) approach gives leads to $D(E_F)$ of 0.79 states/eV atom, and also gives somewhat different Fermi surfaces. In this paper we focused on the superconducting compounds having the hexagonal structure h-ZrRuX (X=P,As,Si), in order to compare the electronic structures in this series. All these three compounds have a T_c of 12–13 K.

The crystal structure of h-ZrRuX is shown in Fig. 1. We specify the atomic positions for the h-ZrRuX (X=P,As,Si) compounds in Table I. In this structure, the $[Zr_3X(1)]$ and $[Ru_3X(2)_2]$ layers are alternately stacked along the c axis. In the $[Zr_3X(1)]$ layer, each $Zr_3X(1)$ triangle cluster is isolated from others. In the $[Ru_3X(2)_2]$ layer, the three Ru atoms form a Ru_3 triangle cluster, and the $X(2)_2$ form a honeycomb network. However, the in-plane $X(2)$-$X(2)$ distance is 3.85 Å, whereas the in-plane Ru-$X(2)$ distance is 2.53 Å (both for ZrRuP), and thus the in-plane bonding is not so strong. In fact, the interlayer Ru-$X(1)$ bond length is 2.42 Å in ZrRuP, which is longer than the above Ru-$P(2)$ bond length. In spite of the layered structure, it is difficult to predict the dimensionality of the electronic properties due to the strong interlayer interaction.

This paper is organized as follows. The method of calculation is described in Sec. II. We present the results of the energy-band structure, the density of states, and Fermi surfaces, and provide some discussion in Sec. III. Finally, conclusions are given in Sec. IV.

II. METHOD OF CALCULATION

The scheme we used in these calculations is the standard FLAPW method. The present energy-band calculation was performed using the computer code KANSAI94. For handling the space group we used the code TSPACE.[13] For the exchange-correlation potential we adopted the local-density approximation (LDA), in accordance with Gunnarson and Lundqvist.[14] The space group, lattice constants, fractional atomic coordinates, and other parameters of h-ZrRuX used in the calculation are presented in Table I. At each self-

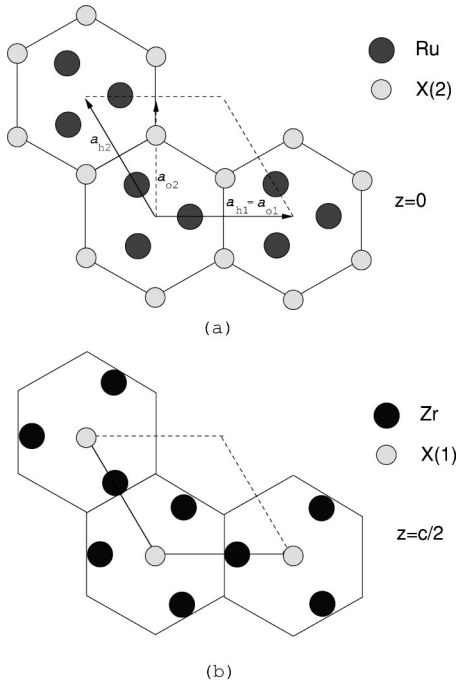

FIG. 1. Crystal structure of h-ZrRuX in the ab plane with (a) $z=0$ and (b) $z=c/2$. Each Ru atom in (a) forms a Ru_3 triangle.

TABLE I. Crystal structure and parameters of *h*-ZrRu*X* compounds used in the calculation.

Crystal structure: Ordered Fe_2P structure				
Space group:	223 D_{3h}^3 $P\bar{6}2m$			
		ZrRuP[a]	ZrRuAs[b]	ZrRuSi[c]
Lattice constants		$a=6.459$ Å	$a=6.586$ Å	$a=6.6838$ Å
		$c=3.778$ Å	$c=3.891$ Å	$c=3.6717$ Å
Zr	$3g$ site	$x=0.585$	$x=0.584$	$x=0.580$
Ru	$3f$ site	$x=0.235$	$x=0.245$	$x=0.248$
$X(1)$	$1b$ site			
$X(2)$	$2c$ site			

[a]Reference 1.
[b]Reference 2.
[c]Reference 12.

consistent step, the core states are reconstructed from the potential (relaxed core). The calculations of these core states and the valence states are carried out by the scalar-relativistic scheme.[15] We took the muffin-tin (MT) sphere radii of each atom as $0.19a$ for Zr and Ru, and $0.165a$ for *X*, where *a* denotes the lattice parameter; see Table I.

Inside the MT spheres, the wave functions were expanded in terms of spherical harmonics with the angular momentum $l \leqslant 7$. For the charge densities and potential the angular momentum expansion $l \leqslant 4$ was used. The basis functions with the wave vector $|\mathbf{k}+\mathbf{G}| < K_{\max}=6.42(2\pi/a)$, where **k** is a wave vector in the Brillouin zone and **G** is a reciprocal-lattice vector used, resulted in about 900 basis LAPW's. The self-consistent potentials are calculated at 15 **k** points in the irreducible Brillouin zone [(IBZ) $\frac{1}{24}$th of the BZ]. As for ZrRuP, we used 40 **k** points in the same IBZ to get further convergence of the potential in order to discuss the detail of the bands. The difference between the eigenenergies of these two potentials is of the order of 1 mRy, and the obtained

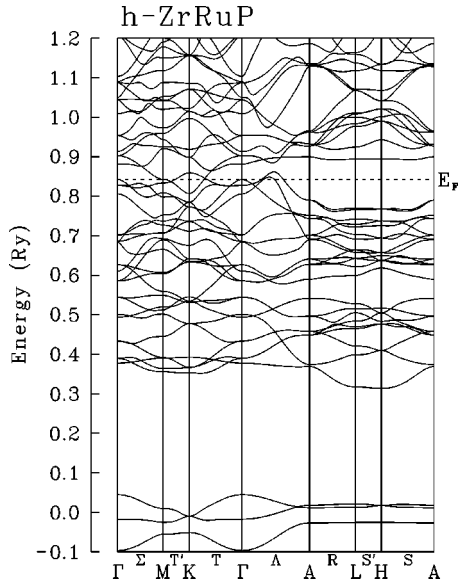

FIG. 2. Energy-band structure of *h*-ZrRuP. The Fermi energy is denoted by E_F.

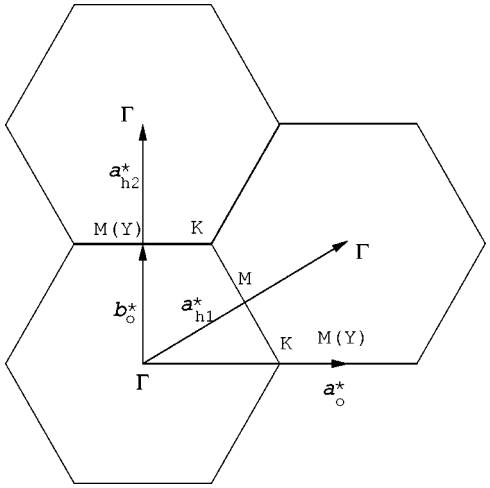

FIG. 3. Reciprocal lattice vectors and the notation of the **k** points on the $k_z=0$ plane of *h*-ZrRuP. The $\mathbf{a}^*h1$ and $\mathbf{a}^*h2$ are the usual hexagonal reciprocal lattice vectors. The $\mathbf{a}^*o$ and $\mathbf{b}^*o$ are the body-centered orthorhombic (bco) reciprocal lattice vectors. For these two basis sets, the first Brillouin zone is identical (both are hexagons). The notations are for hexagonal lattice, except for the (*Y*) point which means the $Y(0,1,0)$ and (1, 0, 0) point of the bco lattice.

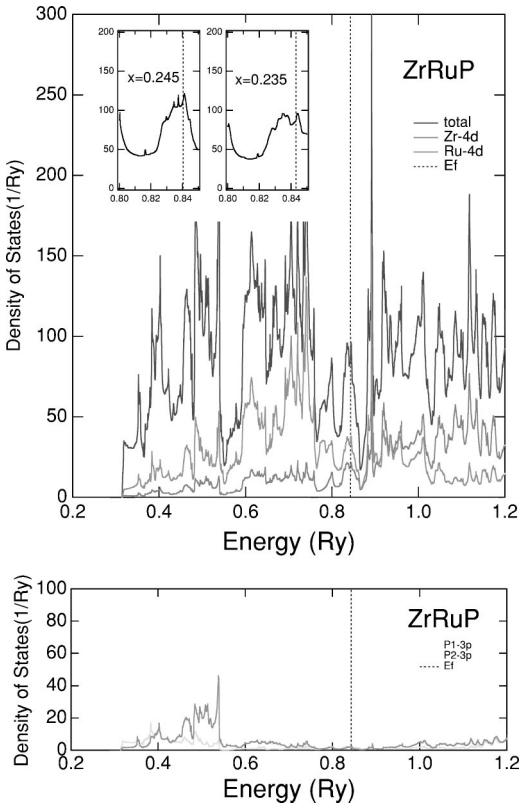

FIG. 4. Calculated density of states (DOS) curve for *h*-ZrRuP (in states per Rydberg and per unit cell containing three ZrRuP). The inset shows the blowup of the DOS curve around E_F for $x=0.235$ (left panel), and for $x=0.245$ (right panel).

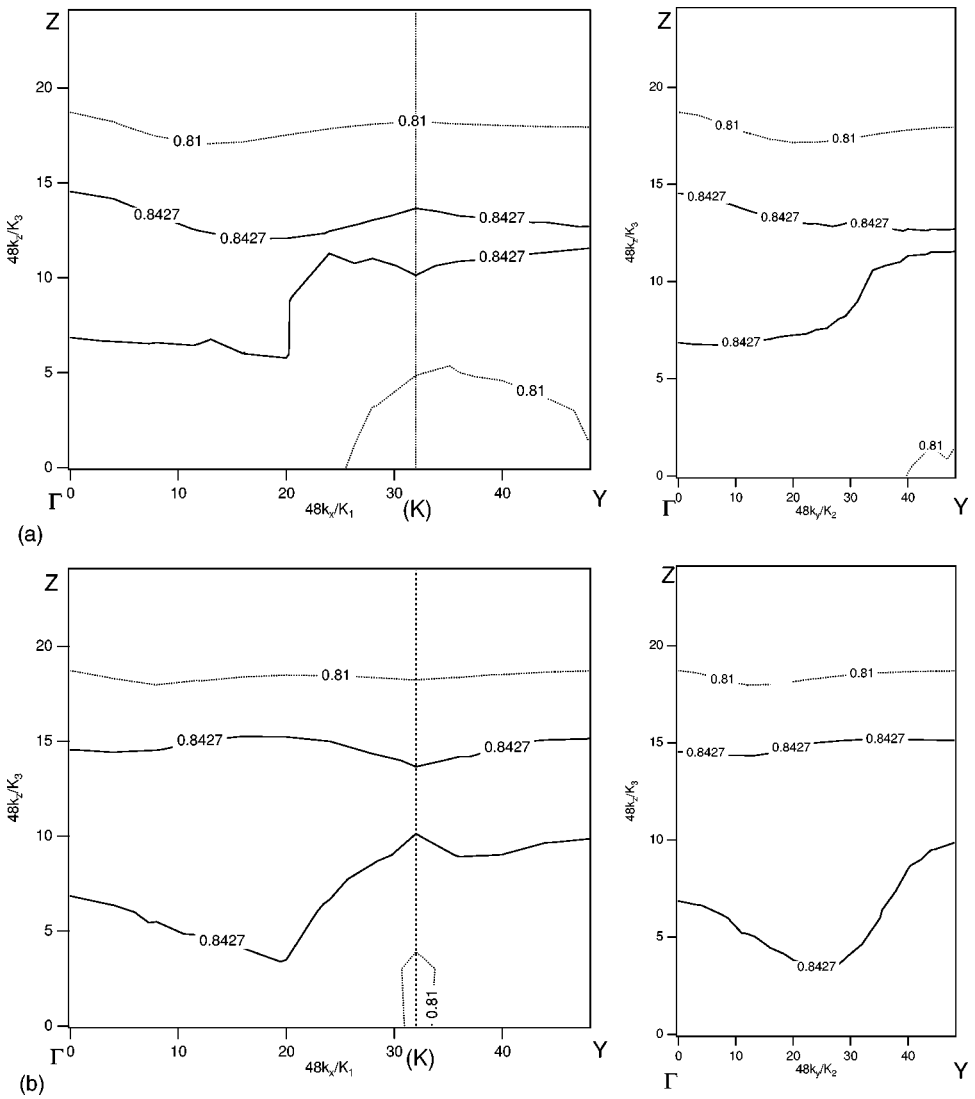

FIG. 5. The (k_x, k_z) and (k_y, k_z) energy contours of *h*-ZrRuP for (a) 25th and (b) 26th band. The unit of axes are the reciprocal lattice vector of the bco lattice for each direction (see Fig. 3). Solid curves are the Fermi surfaces ($E_F = 0.8427$ Ry). Dotted-dashed curves denote the energy contour of $E = 0.81$ Ry, which gives close resemblance to the Fermi surfaces of *h*-ZrRuSi. Vertical dotted line shows the boundary of the first Brillouin zone. The points (*K*) denotes the *K* point in the hexagonal lattice.

density-of-states curves are almost identical. Final eigenstates are obtained at 171 points in the same IBZ. The density of states (DOS) is deduced from the final eigenstates by the ordinary tetrahedron method. We have checked that the finer mesh (549 **k** points in the same IBZ) gives DOS values of *h*-ZrRuP and *h*-ZrRuSi differing only within 5%. We have used this finer mesh in order to draw the Fermi surfaces (FS's) of ZrRuP and ZrRuSi.

III. RESULTS AND DISCUSSION

The energy-band dispersion of *h*-ZrRuP along the principal symmetry axes in the Brillouin zone is shown in Fig. 2. The Brillouin zone and the notation of the **k** points are shown in Fig. 3. The total and partial density of states (MT-sphere-projected DOS) are shown in Fig. 4. The states in the energy range of -0.1–0.1 and 0.35–0.55 Ry are mainly P $3s$ and P $3p$ orbitals, respectively. Transition-metal d orbitals are rather widely spread in energy, however, roughly speaking, the Ru $4d$ component dominates in the energy range of 0.6–0.85 Ry, and the Zr $4d$ component is maximum around 0.9 Ry or higher energies.

The overall band structure looks similar to the result by Seo *et al.*,[11] however, the DOS at the Fermi level $D(E_F)$ is 86.7 states/Ry unit cell (three ZrRuP), which is considerably higher than their value of 25.7 states/Ry u.c. The experimental value derived from specific-heat measurement is 93.0 states/Ry u.c.,[10] which is in striking agreement with our calculated result. We have also obtained the $D(E_F)$ of *h*-HfRuP as 101.2 states/Ry u.c.,[16] which again agrees very well with the experimental value.[10] We note that this value is even higher than that of elemental Ru [$D(E_F) = 14.3$ states/Ry atom, $T_c = 0.5$ K], since in ZrRuP there are three f.u. per unit cell and the P atom hardly contributes to the $D(E_F)$. The partial DOS of Ru $4d$ states at E_F is 11.4 states/Ry Ru atom, which is comparable to the elemental Ru. Moreover, the interstitial contribution to $D(E_F)$ is considerably larger and can be compared to the Ru $4d$ contribution. Furthermore, the partial DOS of Zr and Ru d states overlap and suggest the valences as $Zr^{3+}(RuP)^{3-}$ rather than $Zr^{4+}(RuP)^{4-}$. We speculate that the disagreement between our and the Hückel calculation come from the treatment of the one-electron potential in both calculations. The extended Hückel approach is essentially a tight-binding one, and it sometimes underesti-

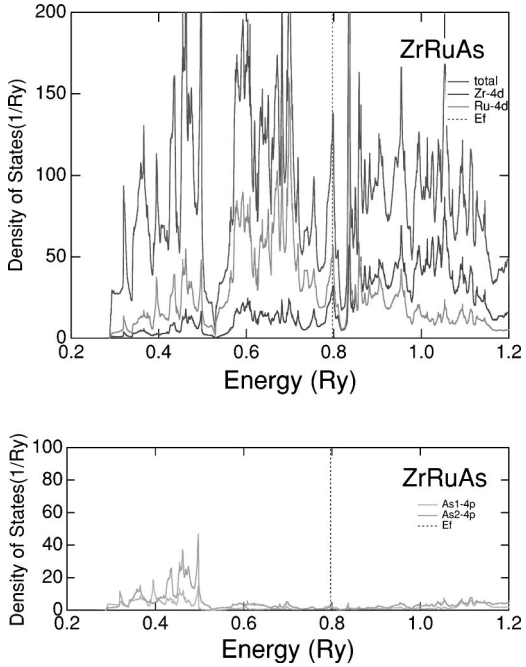

FIG. 6. DOS curve for *h*-ZrRuAs (in states per Rydberg and per unit cell containing three ZrRuAs).

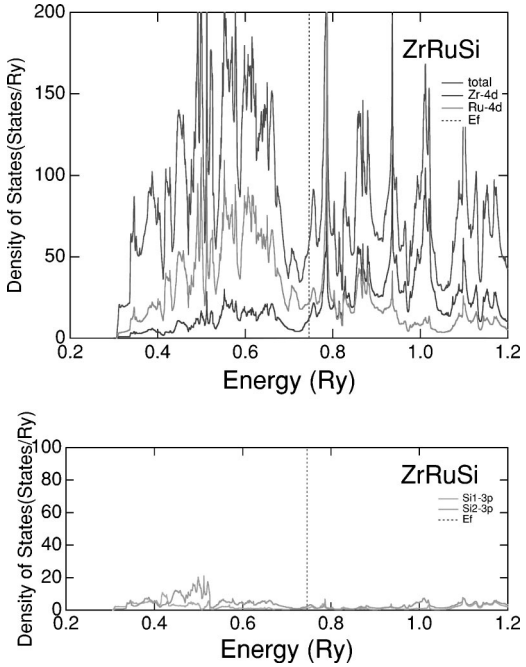

FIG. 7. DOS curve for *h*-ZrRuSi (in states per Rydberg and per unit cell containing three ZrRuSi).

mates the transfer integrals for metallic compounds. The nonsphericity of the potential may also enhance the covalent nature. In fact, we have tested this hypothesis by an LAPW calculation for ZrRuP, the MT approximation for the potential, and found that the number of *d* electrons per site in the Zr MT sphere decreases from 0.47 (FLAPW) to 0.40 (LAPW), and in the Ru MT sphere, the number of *d* electrons per site increases from 1.90 to 1.96.

The FS cross section of *h*-ZrRuP is shown in Fig. 5. There are two Fermi surfaces in ZrRuP, and these FS's somewhat resemble those of the extended Hückel result.[11] These two surfaces contain 1.83 (25th band) and 1.17 (26th band) electrons. Clearly there is a portion of one-dimensional (1D) FS at $k_z \sim \pm 15/48c^*$, especially for the 25th band. And we can see that this portion remains when the Fermi energy is slightly shifted, which means that the one dimensionality of this portion of the FS does not collapse under small changes in E_F. Thus we can safely develop a discussion on the hidden Fermi surfaces,[17] which have already been pointed out by Seo *et al.*[11] However, the details of the FS are different between the previous[11] and the present calculations, and the Fermi surface measurements, such as de Haas–van Alphen experiments, are highly desirable.

The total and partial density of states (MT-sphere-projected DOS) of *h*-ZrRuAs are shown in Fig. 6. Apparently the overall band structure is almost the same as the isoelectronic *h*-ZrRuP; however, $D(E_F)$ is as high as 131 states/Ry u.c. This is mostly due to the DOS having a sharp peak in the case of ZrRuAs. For both compounds, the main part of the $D(E_F)$ comes from the Ru *d* component. ZrRuAs has a slightly larger unit cell, especially the *a* axis (about 3% larger than in ZrRuP). This causes a smaller bandwidth of the As 4*s* band in ZrRuAs compared to the P 3*s* bandwidth of ZrRuP. Furthermore, ZrRuP has the smallest Ru_3 cluster, with the nearest Ru-Ru distance of 2.63 Å, while in ZrRuAs and ZrRuSi this value is 2.80 and 2.87 Å, respectively. In order to investigate whether this Ru-Ru distance affects the bands near the Fermi level,[1] we have calculated the band structure of ZrRuP but shifting the atomic coordinate of Ru $(x,0,0)$ to $x=0.245$, which would be the typical value of other h-$TT'X$ compounds (see Table I). The result is shown in the inset of Fig. 4. Surprisingly, such a small shift in atomic position changes $D(E_F)$ from 86.7 ($x=0.235$) to 118 ($x=0.245$), where the whole DOS shape is almost unchanged (not shown in the figure). A prominent feature is that in *h*-ZrRuP ($x=0.245$) the DOS has a single-peak structure near E_F as in *h*-ZrRuAs, whereas in *h*-ZrRuP ($x=0.235$) this peak is split into two peaks. Thus our calculation suggests that the short Ru-Ru distance plays an important role in the superconductivity in ZrRuP, through the *decrease* of $D(E_F)$. However, the total energy of *h*-ZrRuP for $x=0.245$ is higher than $x=0.235$ by 18 mRy (i.e., 2900 K), which may not be realized by moderate hydrostatic pressure. Probably this is the reason why the observed pressure dependence of T_c (dT_c/dP) is small.[18]

The total and partial density of states (MT-sphere-projected DOS) of *h*-ZrRuSi are shown in Fig. 7. Since the Si 3*s* and Si 3*p* levels are higher than P 3*s* and P 3*p*, respectively, these states are more hybridized with Ru 4*d* and Zr 4*d* states. This is seen in the wider bandwidth of the Si 3*s* than in the P 3*s* bandwidth. The total $D(E_F)$ is 59.3 states/Ry u.c., which is about half that of *h*-ZrRuP. This value is again larger than the result of Seo *et al.*,[11] however the discrepancy is not so large. The shape of DOS near E_F of

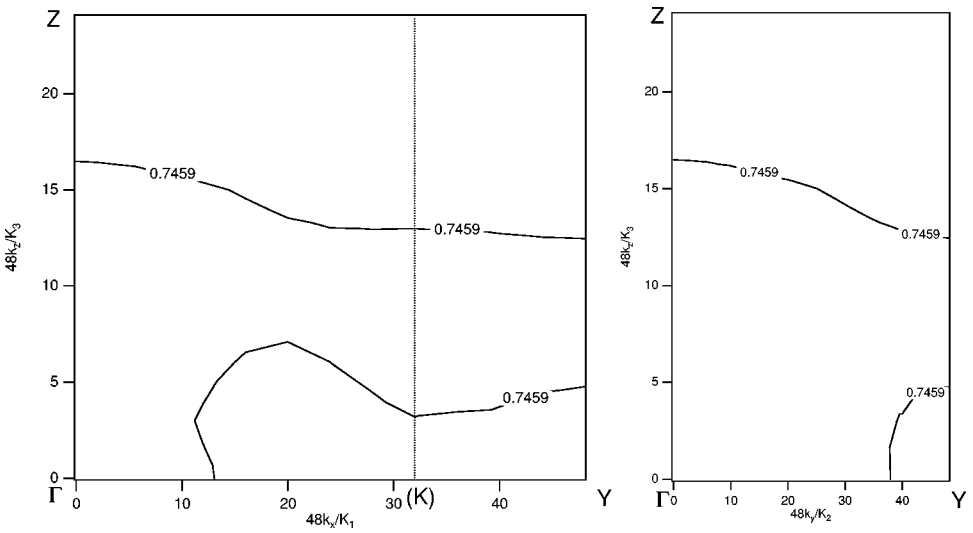

FIG. 8. The section plane of the Fermi surfaces of ZrRuSi for the 24th band. The unit of axes are the reciprocal lattice vector of the bco lattice for each direction (see Fig. 3). Solid curves are the Fermi surfaces ($E_F = 0.7459$ Ry). For the Fermi surfaces of the 25th and 26th bands, see Fig. 5.

ZrRuSi is similar to that of ZrRuP and ZrRuAs, but since the number of valence electrons is one less per f.u. than in ZrRuP and ZrRuAs, $D(E_F)$ is not at the sharp peak. Note that the number of the *d* electrons in the MT sphere in ZrRuP and ZrRuSi is 1.36 and 1.37 per Zr site, respectively. This shows that even in ZrRuSi, the ionic description $Zr^{3+}(RuSi)^{3-}$ works well, as was shown before for ZrRuP.

The Fermi surfaces of *h*-ZrRuSi can already be understood by the rigid-band model from ZrRuP. Due to the number of valence electrons being three less per unit cell than in ZrRuP, the number of electrons contained in the 25th and 26th bands is reduced to 0.49 and 0.44, respectively [see Figs. 5(a) and 5(b)]. The shapes of one-dimensional FS's are sustained for ZrRuSi and can mostly be described by the rigid-band model, namely, by shifting E_F from the bands of ZrRuP. The necessary shift of E_F, however, does not correspond to the removal of three electrons per unit cell. This is probably due to the small contribution of P and Si *p* states near the Fermi level. However, the details of FS of the 25th band in ZrRuSi are slightly different from the rigid-band model from ZrRuP. In the right panel of Fig. 5(a) the energy at the *Y* point is actually above E_F for the 25th band of ZrRuSi, thus the electron pocket around the *K* points are mutually connected. For the 26th band of ZrRuSi, the small electron pocket around the *K* point disappeared. Nevertheless, the rigid-band model from ZrRuP mostly works well for describing the FS's of ZrRuSi. Another FS appears in *h*-ZrRuSi due to the shift of E_F (see Fig. 8). This FS contains 1.08 electrons, and does not have 1D nature. In total, the one dimensionality of the FS's of ZrRuSi is smaller than that of ZrRuP.

IV. CONCLUSIONS

In this paper, the electronic energy-band structure has been calculated for *h*-ZrRu*X* (Z=P,As,Si) by the FLAPW method within LDA. The calculated density of states at the Fermi energy agrees very well with the experimental value. Mainly the Ru 4*d* states contribute near the Fermi level for *h*-ZrRu*X* (Z=P,As,Si). The one dimensionality shows up in the Fermi surfaces found in ZrRuP and ZrRuSi. The density of states at the Fermi energy is very sensitive to the in-plane Ru-Ru distance.

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*Present address: Nanoelectronics Research Institute, AIST, Tsukuba, 305-8568, Japan. Email address: i.hase@aist.go.jp

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