

# Electronic structure of the superconducting compounds *o*-ZrRuP and MoRuP

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The electronic energy band structures of ordered Co<sub>2</sub>P-type intermetallic superconducting compounds *o*-ZrRuP and MoRuP have been calculated using the full-potential linearized augmented plane wave method within the local-density approximation. We found that MoRuP ( $T_c = 16$  K) has quasi-one-dimensional Fermi surfaces, similar to hexagonal *h*-ZrRuX ( $X = \text{P, As, Si}$ ) which have  $T_c > 10$  K. Since *o*-ZrRuP has no such Fermi surface, and we conclude that its existence is important for the appearance of higher  $T_c$  in this series.

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## I. INTRODUCTION

The discovery of superconductivity in ZrRuP (Ref. 1) has stimulated intensive studies of metallic phosphides. Now a family of the compounds  $TT'X$  ( $T, T'$  is a transition metal element;  $X = \text{Si, Ge, P, As}$ ) was found, and so far more than ten compounds are known to be superconducting. Some of these compounds are superconducting above 10 K, and the highest  $T_c$  is  $\sim 16$  K in MoRuP.<sup>2</sup> Moreover, this system is closely related to a family of skutterdite compounds  $RT_4X_{12}$  ( $R$  is a rare earth element,  $T = \text{Fe, Ru, Os}$ , and  $X = \text{P, As, Sb}$ ) which show a variety of electronic and magnetic properties, such as Kondo insulating behavior, large thermoelectricity, and superconductivity.<sup>3-6</sup>

Three different structural types are known for these compounds, namely, the Fe<sub>2</sub>P-type hexagonal structure (*h*- $TT'X$ ), the Co<sub>2</sub>P-type orthorhombic structure (*o*- $TT'X$ ), and the TiFeSi-type orthorhombic structure (*o'*- $TT'X$ ). In general, *h*- $TT'X$  has a higher  $T_c$  than *o*- $TT'X$ . Many *h*- $TT'X$  compounds have  $T_c$  above 10 K, while most of *o*- $TT'X$  compounds have no higher  $T_c$  than 4 K. 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, namely only about 0.74 states/eV atom.<sup>7</sup>

ZrRuP has two polytypes, namely *h*-ZrRuP ( $T_c = 13$  K) and *o*-ZrRuP ( $T_c = 4$  K). A mechanism that leads to a higher  $T_c$  in *h*-ZrRuP than in *o*-ZrRuP was proposed by Seo *et al.*<sup>8</sup> They performed a band-calculation study for *h*-ZrRuP and *o*-ZrRuP using the extended Hückel tight-binding method. They found the Fermi surface (FS) of *h*-ZrRuP to be highly one dimensional (1D) but no such 1D FS in *o*-ZrRuP. From the fact that the calculated density of states at  $E_F$  [ $D(E_F)$ ] are almost the same for both compounds, it is concluded that the nesting of the FS causes a charge-density-wave (CDW) instability, lower phonon frequencies and thus a higher  $T_c$ .<sup>9</sup> Another evidence of this mechanism is seen in the isoelectronic compound *h*-HfRuAs. In this case, CDW actually takes place and the doubling of lattice constant  $c$  occurs at low temperature.<sup>10</sup>

It seems that this mechanism of enhancing  $T_c$  by FS nesting is quite attractive, however, their calculated value of  $D(E_F)$  was only  $\sim 30\%$  of the experimental value. On the other hand, we also calculated the band structure of *h*-ZrRuP

using the local density approximation with full potential linearized augmented plane wave (LDA-FLAPW) approach,<sup>11</sup> and obtained excellent agreement between our calculated  $D(E_F)$  and the experimental value. Therefore we conclude that the LDA works well for this system, and perform FLAPW calculations for other compounds. In this paper we focus on *o*-ZrRuP and MoRuP (hereafter we call it *o*-MoRuP), which have different  $T_c = 4$  and 16 K, respectively. We also found a quasi-1D FS in *o*-MoRuP, as commonly seen in *h*- $TT'X$  with  $T_c > 10$  K. This fact supports the above-mentioned mechanism of high- $T_c$  in this system.

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 discussions in Sec. III. Finally, conclusions are given in Sec. IV.

## II. METHOD OF CALCULATION

The scheme we used in our calculations is the standard (FLAPW) method. The present energy-band calculation was

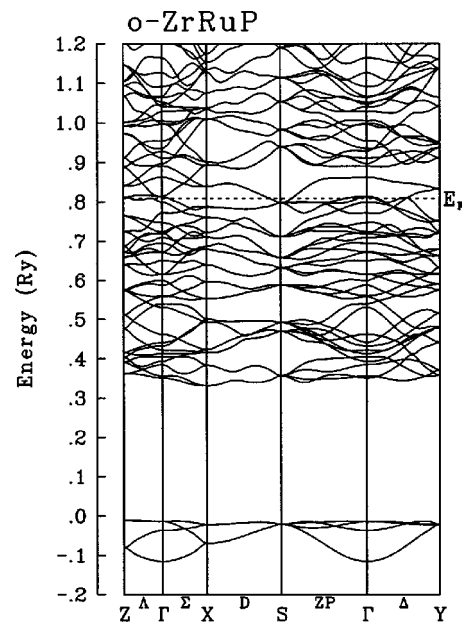


FIG. 1. Energy band structure of *o*-ZrRuP. The Fermi energy is denoted by  $E_F$ .

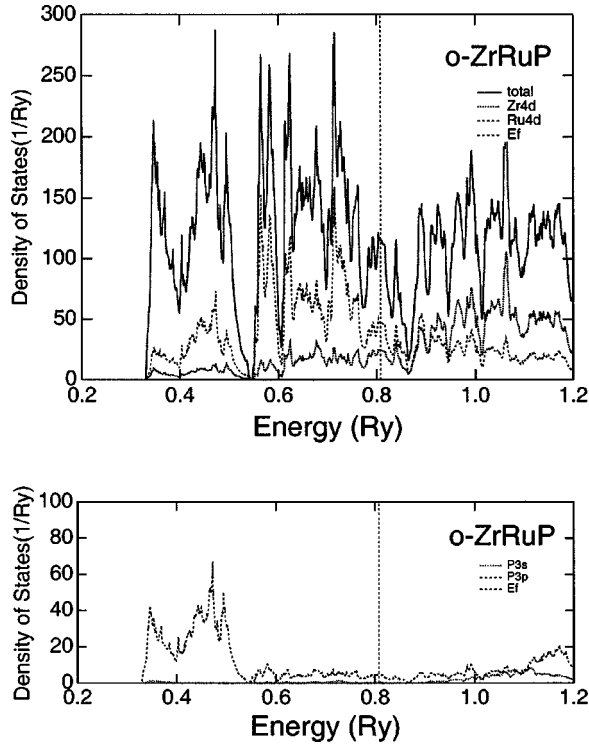


FIG. 2. Calculated density of states (DOS) curve for *o*-ZrRuP (in states per Ry and per unit cell containing four ZrRuP).

performed using the computer code KANSAL-94. For the exchange-correlation potential we adopted the local-density approximation, according to Gunnarson and Lundqvist.<sup>12</sup> The space group is *Pnma*, and which is handled by the code TSPACE.<sup>13</sup> The lattice constants and fractional atomic coordinates used in our calculation are taken from experiments.<sup>14,15</sup> Muffin-tin (MT) radii are set as  $0.19a$  for Zr/Mo/Ru and  $0.165a$  for P, where  $a$  denotes the lattice constant. The semi-core  $4p^6$  electrons of Zr/Mo/Ru are calculated as valence electrons by using a second energy window. States that are deeper in energy are treated as core levels, and are calculated inside the MT spheres in each self-consistent step. Plane wave basis functions with a wave vector  $|\mathbf{k} + \mathbf{G}| < K_{\max} = 6.82(2\pi/a)$ , where  $\mathbf{k}$  is a wave vector in the Brillouin zone and  $\mathbf{G}$  is a reciprocal-lattice vector, are used and resulted in about 970 LAPWs. The self-consistent potentials are calculated at 27  $\mathbf{k}$ -points in the irreducible Brillouin zone (IBZ, 1/8th of the BZ). The density of states (DOS) are deduced from the eigenstates at 225 points in the same IBZ by the ordinary tetrahedron method.

### III. RESULTS AND DISCUSSION

The energy band dispersion of *o*-ZrRuP is shown in Fig. 1 along the principal symmetry axes in the Brillouin zone. Total and partial density of states (MT-sphere-projected DOS) are shown in Fig. 2. The states in the energy range of  $-0.1$ – $0.0$  and  $0.35$ – $0.55$  Ry are mainly P  $3s$  and P  $3p$  orbitals, respectively. Transition metal  $d$ -orbitals are widely spread in energy; however, roughly speaking, Ru  $4d$  component is

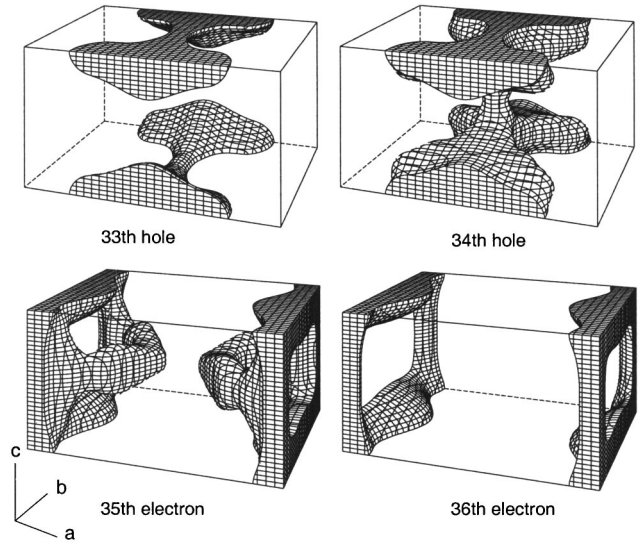


FIG. 3. A perspective view of FSs in *o*-ZrRuP.

dominant in the energy range of  $0.6$ – $0.85$  Ry, and Zr  $4d$  component is dominant above  $0.9$  Ry. This situation is almost the same as in *h*-ZrRuP,<sup>11</sup> however, the overlap between the Ru  $4d$  and Zr  $4d$  bands are larger in *o*-ZrRuP, due to Zr-Ru bonds. This is in contrast to the band structures of  $\text{LaFe}_4\text{P}_{12}$  (Refs. 16 and 17) and  $\text{LaRu}_4\text{P}_{12}$ ,<sup>18</sup> in which Fe/Ru  $d$  orbitals form narrow bands while  $P p$  orbitals form wide bands, which even at the Fermi level have a considerable contribution to the DOS.

The overall band structure looks similar to the result by Seo *et al.*,<sup>8</sup> however, the DOS at the Fermi level  $D(E_F)$  is  $116$  (states/Ry/f.u.) =  $0.71$  (states/eV/atom), which is considerably higher than their value of  $0.29$  (states/eV/atom). Our value of  $D(E_F)$  is almost the same as that of *h*-ZrRuP.<sup>11</sup> The experimental value derived from specific heat measurement is  $0.74$  (states/eV/atom),<sup>7</sup> which is in striking good agreement with our calculated result. The FSs of *o*-ZrRuP are shown in Fig. 3. There are four Fermi surfaces in *o*-ZrRuP (33rd–36th bands), and each FS contains  $0.13$  holes,  $0.34$  holes,  $0.31$  electrons, and  $0.14$  electrons, respectively. We see no prominent 1D-FS in contrast to *h*-ZrRuP. This is probably the reason for the relatively low  $T_c$  ( $=4$  K), as was already discussed by Seo *et al.*<sup>8</sup>

The total and partial density of states (MT-sphere-projected DOS) of *o*-MoRuP are shown in Fig. 4. Since the Mo  $4d$  levels are lower in energy than the Zr  $4d$ , and also since the unit cell of *o*-MoRuP is smaller than that of *o*-ZrRuP, Mo  $4d$  states are more hybridized with Ru  $4d$  states. This is seen in the wider Ru  $4d$  bandwidth. The total  $D(E_F)$  is  $136$  (states/Ry/f.u.) =  $0.84$  (states/eV/atom), which is slightly larger than that of *o*-ZrRuP. Due to the deeper level of Mo  $4d$  and the increase in the number of valence electrons,  $D(E_F)$  is dominated by the Mo  $4d$  partial DOS rather than Ru  $4d$ , in contrast to the case of *o*-ZrRuP.

The FSs of *o*-MoRuP are shown in Fig. 5. There are also four Fermi surfaces (37th–40th bands) in *o*-MoRuP, and each FS contains  $0.07$  holes,  $0.45$  holes,  $0.30$  electrons, and

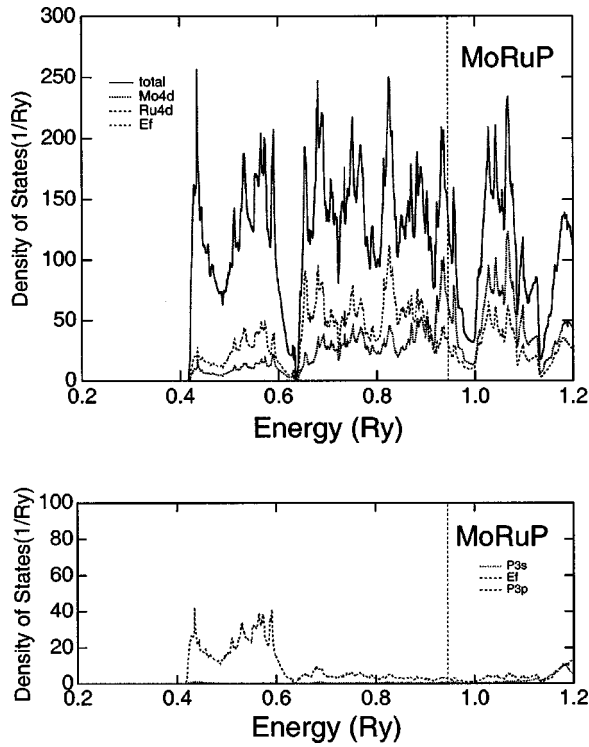


FIG. 4. Calculated density of states (DOS) curve for *o*-MoRuP (in states per Ry and per unit cell containing four MoRuP).

0.22 electrons, respectively. Clearly there is a portion of quasi-one-dimensional FS along the *ac* plane for the 39th and 40th bands of *o*-MoRuP. As for the anisotropy, the dispersion of the band along the *c* axis is the smallest, contrary to the naive expectation that the dispersion of the *b* axis should be the smallest because of the layered stacking along the *b* axis. This FS does not appear in *o*-ZrRuP even when  $E_F$  is shifted to a higher energy, in order to accommodate the same number of valence electrons as in *o*-MoRuP. This means that the

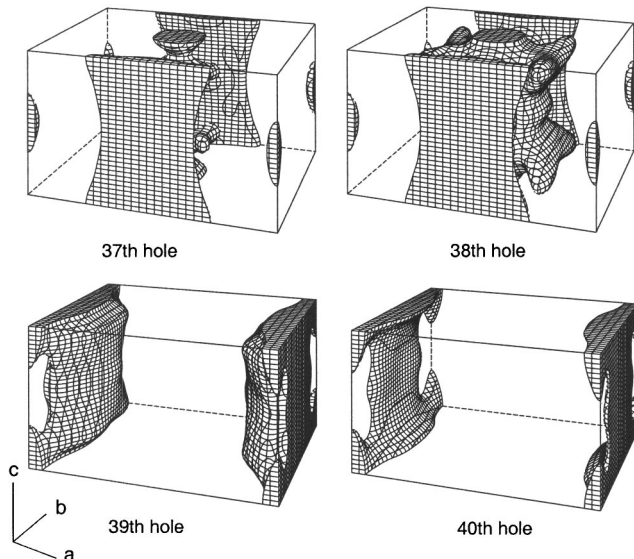


FIG. 5. A perspective view of FSs in *o*-MoRuP.

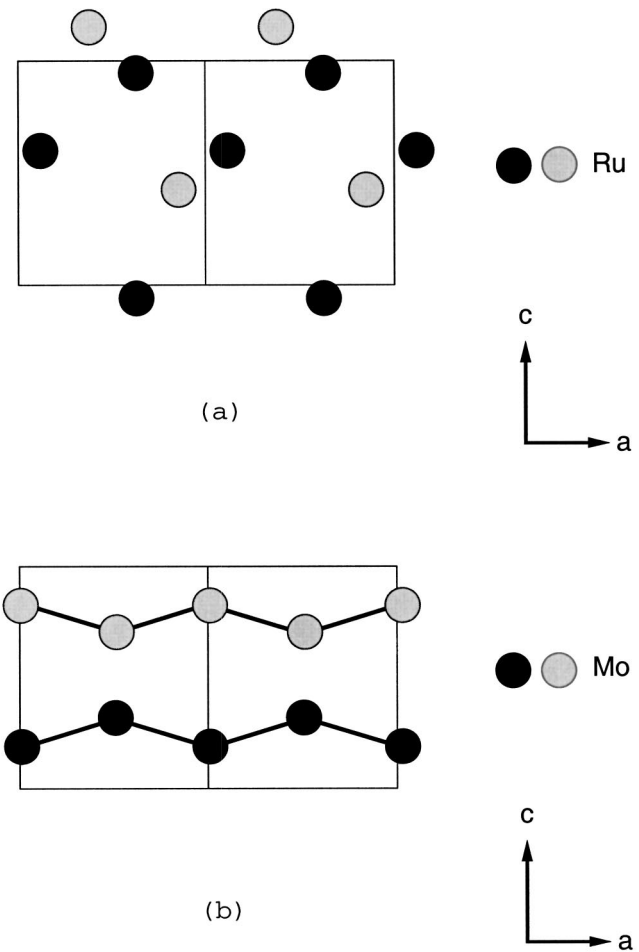


FIG. 6. Crystal structure of (a) *o*-ZrRuP and (b) *o*-MoRuP with an *ac* plane. Circles denote (a) Ru and (b) Mo, respectively. Light-colored circles are on the  $y=1/4$  plane, and dark-colored circles are on  $y=3/4$ . (a) Zr, P and (b) Ru, P are not shown because their contributions to  $D(E_F)$  are small.

rigid-band model does not hold between *o*-ZrRuP and *o*-MoRuP for FSs, in contrast to the case of *h*-ZrRuP and *h*-ZrRuSi.<sup>11</sup>

The different shapes of FSs between *o*-ZrRuP and *o*-MoRuP are explained as follows: The main contribution to  $D(E_F)$  (and thus to the FS) are from Ru 4*d* states in *o*-ZrRuP and Mo 4*d* states in *o*-MoRuP, respectively. In Fig. 6 we show the *ac* plane of the crystal structure, emphasizing these atoms. We can clearly see that there are Mo chains along the *a* axis in *o*-MoRuP [the nearest Mo-Mo distance is 3.069 Å (Ref. 19)] but no Ru chain in *o*-ZrRuP. These chains derive a quasi-1D FS in *o*-MoRuP, which in turn result in a softening of phonons, like the case of *h*-ZrRuP. However, this one dimensionality is not as strong as that in *h*-ZrRuP, because there is also a Mo-Mo bond (whose distance is 3.213 Å) in the *b* direction.

#### IV. CONCLUSIONS

In this paper, the electronic energy band structure has been calculated for *o*-ZrRuP and *o*-MoRuP by the FLAPW

method within the LDA. We found that the  $D(E_F)$  is rather similar in both compounds; however *o*-MoRuP has much more pronounced low-dimensional FSs, due to the Mo chain in this structure. This is probably the reason why *o*-MoRuP has a higher  $T_c$  than *o*-ZrRuP, similar to the case of *h*-ZrRuP vs *o*-ZrRuP.

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