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2001 J. Phys.: Condens. Matter 13 9393

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Superconductivity and crystal structure of $\text{ZrRu}_{1-x}\text{Rh}_x\text{P}$ alloys prepared at high pressure

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Received 12 June 2001

Published 28 September 2001

Online at stacks.iop.org/JPhysCM/13/9393

Abstract

$\text{ZrRu}_{1-x}\text{Rh}_x\text{P}$ alloys ($x = 0, 0.01, 0.05, 0.1, 0.15, 0.20, 0.25, 0.3, 0.4, 0.5$ and 1) have been prepared at around 1300 and 1600 °C under 4 GPa. ZrRuP ($x = 0$) prepared at these temperatures has a hexagonal Fe_2P -type structure at room temperature. When the Ru atoms in ZrRuP are slightly displaced by the Rh atoms, the structure of the alloys changes drastically from the hexagonal form to the orthorhombic Co_2P -type structure. The x-ray diffraction patterns of the alloys ($x = 0.05, 0.1$ and 0.15) mainly indicate the orthorhombic Co_2P -type structure, though there are several weak lines of the hexagonal phase. Above $x = 0.2$ the alloys have a single phase of the orthorhombic form. Electrical and magnetic properties of the alloys $\text{ZrRu}_{1-x}\text{Rh}_x\text{P}$ have been studied at low temperatures. The superconducting transitions of hexagonal and orthorhombic ZrRuP occur at around 12 and 4 K, respectively. The transition temperature, T_c , decreases rapidly with increasing x for both phases of $\text{ZrRu}_{1-x}\text{Rh}_x\text{P}$. The Rh atoms suppress the onset temperature of the superconductivity in the alloys.

1. Introduction

Ternary ruthenium phosphide ZrRuP crystallizes in two modifications, a hexagonal Fe_2P -type structure (h- ZrRuP) [1] and an orthorhombic Co_2P -type structure (o- ZrRuP) [2]. Each layer in the Fe_2P -type structure is occupied by either Zr and P atoms or Ru and P atoms. Two-dimensional triangular clusters of Ru_3 are formed, and linked with each other through the Ru–P bonds in the basal plane [1]. In contrast, the orthorhombic structure has layers that are filled with Zr, Ru and P atoms, and these layers are all equivalent [2]. The orthorhombic phase of ZrRuP transforms to the hexagonal Fe_2P -type structure at around 1100 °C and 3.5 GPa [3].

h- ZrRuP has a considerable superconducting transition temperature (T_c) of about 13 K and a high upper critical field (H_{c2}) of 17 T [1, 4, 5]. On the other hand, the T_c of o- ZrRuP is about 4 K [2, 4]. ZrRuSi also has two modifications, the Fe_2P -type and Co_2P -type structures [5, 7]. The superconducting properties of ZrRuSi are very similar to those of ZrRuP [5, 7]. ZrRuSi

has one less valence electron than ZrRuP. Generally, the electrical properties of many materials depend remarkably on the number of valence electrons. However, the superconductivity of ZrRuP and ZrRuSi is insensitive to the number of valence electrons [5, 7]. The electronic band structures of ZrRuP and ZrRuSi have been studied by Seo *et al* [8] and Hase [9].

ZrRhP with 18 valence electrons has the Co₂P-type structure and shows the superconducting transition at around 1.5 K [2]. The cell volume of ZrRhP matches that of o-ZrRuP and is slightly smaller than that of h-ZrRuP. The cell volumes per formula unit, lattice constants and T_c s of h-ZrRuSi, h-ZrRuP, o-ZrRuP and ZrRhP are summarized in table 1.

Table 1. Cell volumes per formula unit, lattice constants and T_c s of h-ZrRuSi, h-ZrRuP, o-ZrRuP and ZrRhP.

	h-ZrRuSi	h-ZrRuP	o-ZrRuP	ZrRhP
Valence electrons/ formula unit	16	17	17	18
Structure	Hexagonal Fe ₂ P-type	Hexagonal Fe ₂ P-type	Orthorhombic Co ₂ P-type	Orthorhombic Co ₂ P-type
a (Å)	6.684	6.459	6.417	6.438
b (Å)			7.322	7.393
c (Å)	3.672	3.778	3.862	3.787
c/a	0.549	0.585	0.602	0.588
Cell volume/ formula unit (Å ³)	47.3	45.5	45.4	45.4
T_c (K)	12.2	13	4	1.5

We have prepared the alloys ZrRu_{1-x}Rh_xP at high temperatures and high pressures. Electrical and magnetic properties of the alloys have been studied at low temperatures. When a small proportion of the Ru atoms in h-ZrRuP are replaced by Rh atoms, the T_c and the structure of the alloys drastically change. In this report the superconducting property and the crystal structure of the alloys ZrRu_{1-x}Rh_xP are discussed.

2. Experimental procedure

Ternary metal phosphides were prepared with a wedge-type cubic-anvil high-pressure apparatus at high temperatures and high pressures [4]. The sample container, made of pyrophyllite, is formed into a cube 21 mm on an edge. The sample assembly for the preparation of these compounds is similar to that used for the synthesis of black phosphorus [10]. The starting materials are put into a crucible made of BN. The crucible, with a graphite heater, is inserted into the pyrophyllite cube.

The alloys ZrRu_{1-x}Rh_xP ($x = 0, 0.01, 0.05, 0.1, 0.15, 0.20, 0.25, 0.3, 0.4, 0.5$ and 1) were prepared by reaction of stoichiometric amounts of each metal and phosphorus powders at around 4 GPa. The reaction temperatures were between 1200 and 1600 °C. These compounds were characterized by powder x-ray diffraction using Cu K α radiation and silicon as a standard.

Copper or gold leads were attached to polycrystals of the samples with silver filled by epoxy, and four-lead electrical resistivity measurements were performed at low temperatures. The dc magnetic susceptibility of the polycrystalline samples was measured in the range 1.8–300 K with a Quantum Design SQUID magnetometer.

3. Results

h- and o-ZrRuP have been prepared at high temperatures and high pressures [4]. The temperature of preparation for o-ZrRuP is lower than that for h-ZrRuP at high pressure. The density for the forms of ZrRuP is 8.172 g cm^{-3} for the orthorhombic form and 8.148 g cm^{-3} for the hexagonal phase at room temperature and ambient pressure. This result suggests that the hexagonal form is a high-temperature phase of ZrRuP. By use of synchrotron radiation, we have studied *in situ* x-ray diffraction of ZrRuP at high temperatures and high pressures; the orthorhombic phase of this compound transforms to the hexagonal one at around 1100°C under 3.5 GPa [3]. h-ZrRuP is quenched, though the hexagonal form is the high-temperature phase.

Figure 1 shows x-ray diffraction patterns of $\text{ZrRu}_{1-x}\text{Rh}_x\text{P}$ ($x = 0, 0.01, 0.05$ and 0.15) prepared at around 1300°C and 4 GPa. The x-ray diffraction profile of ZrRuP ($x = 0$) shows the hexagonal Fe_2P -type structure at room temperature. When the Ru atoms in ZrRuP are slightly displaced by the Rh atoms, the structure of the alloys changes drastically. The pattern

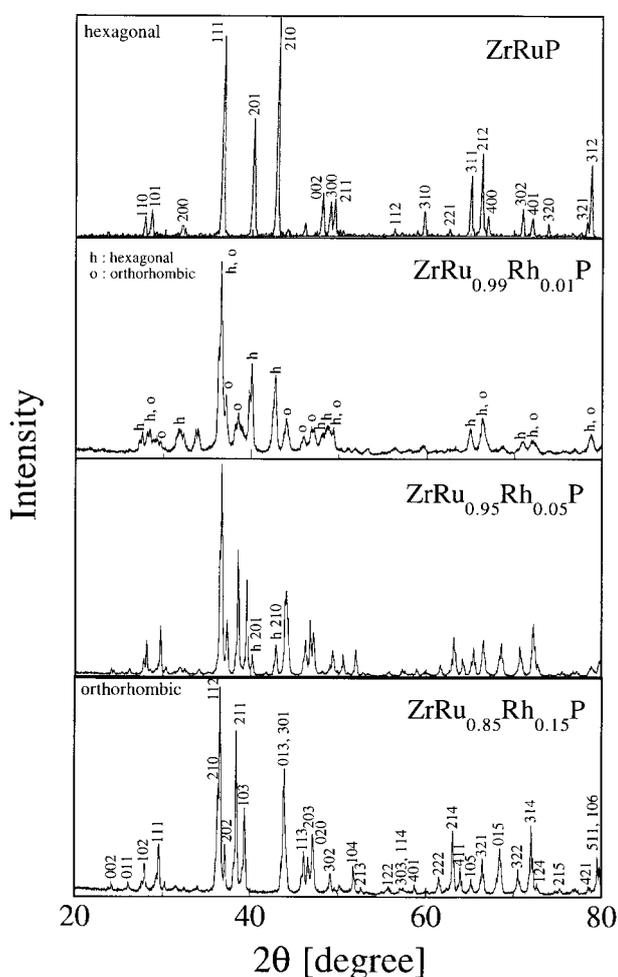


Figure 1. X-ray diffraction patterns of $\text{ZrRu}_{1-x}\text{Rh}_x\text{P}$ ($x = 0, 0.01, 0.05$ and 0.15) prepared at around 1300°C and 4 GPa.

of $\text{ZrRu}_{0.95}\text{Rh}_{0.05}\text{P}$ mainly indicates the orthorhombic Co_2P -type structure, though there are several weak lines of the hexagonal phase. Below $x = 0.15$ the hexagonal and orthorhombic phases coexist. The alloys with x above 0.2 almost become single phase, with the Co_2P -type structure.

Alloys were also prepared at around 1600 °C and 4 GPa. As the hexagonal phase in the alloys becomes more stable at higher temperatures, the proportion of hexagonal phase in the product increases. The cell volume (181.5 \AA^3) of ZrRhP matches that of o-ZrRuP [2]. However, the single phase of the hexagonal form of the alloys cannot be obtained. Figure 2 shows the phase diagram for the alloys $\text{ZrRu}_{1-x}\text{Rh}_x\text{P}$ prepared at high pressure. The stable region for the hexagonal phase is very small. Thus, Rh atoms dominate the structure of the alloys.

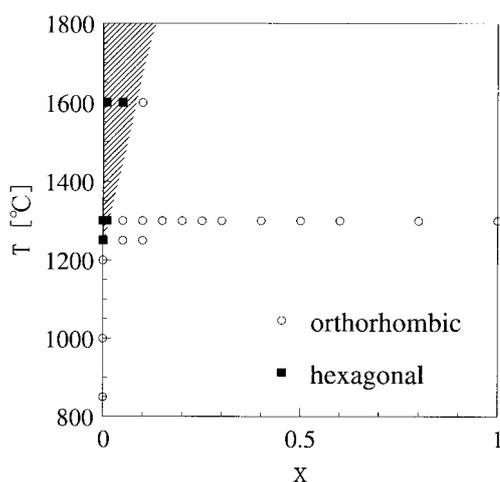


Figure 2. The phase diagram of $\text{ZrRu}_{1-x}\text{Rh}_x\text{P}$ prepared at high temperatures under 4 GPa.

Figure 3 shows lattice constants plotted as a function of the component of the alloys $\text{ZrRu}_{1-x}\text{Rh}_x\text{P}$ with the orthorhombic Co_2P -type structure. As is shown in table 1, the lattice constants of o-ZrRuP and ZrRhP differ considerably, though the cell volumes of the two compounds are equal. The a - and b -axes in the alloys increase with increasing x . In contrast, the c -axis decreases with increasing x . For the alloys with x below 0.1, the lattice parameters of the hexagonal phase have also been studied. The a -axis is not sensitive to x . The c -axis decreases with increasing x . Thus, the interlayer interactions in both structures increase with increasing x . The behaviour of the lattice parameters may be closely related to the phase transition of the alloys.

Figure 4 shows resistivity versus temperature curves for the alloys $\text{ZrRu}_{1-x}\text{Rh}_x\text{P}$ ($x = 0, 0.05, 0.15, 0.2$ and 0.3) prepared at around 1300 °C and 4 GPa. The alloys show superconductivity between 2 and 12 K. Two electrical anomalies for $x = 0.05, 0.1$ and 0.15 are found in the resistivity–temperature curve. Both T_c s arise from the coexistence of the hexagonal and orthorhombic phases in the alloy. The alloy with $x = 0.2$ shows superconductivity in the orthorhombic form only. T_c for the alloys with x above 0.3 becomes below 2 K, and is close to the T_c (1.5 K) of ZrRhP .

Figure 5 shows the temperature dependence of the dc magnetic susceptibility measured in an applied field of 5 Oe for $\text{ZrRu}_{1-x}\text{Rh}_x\text{P}$ ($x = 0, 0.05, 0.15, 0.3$ and 0.5) prepared at around 1300 °C and 4 GPa. h-ZrRuP cooled in zero field shows a magnetic shielding equal to approximately 100% of that expected for perfect diamagnetism. The existence of hysteresis between zero-field cooling and field cooling indicates that the phosphide is a

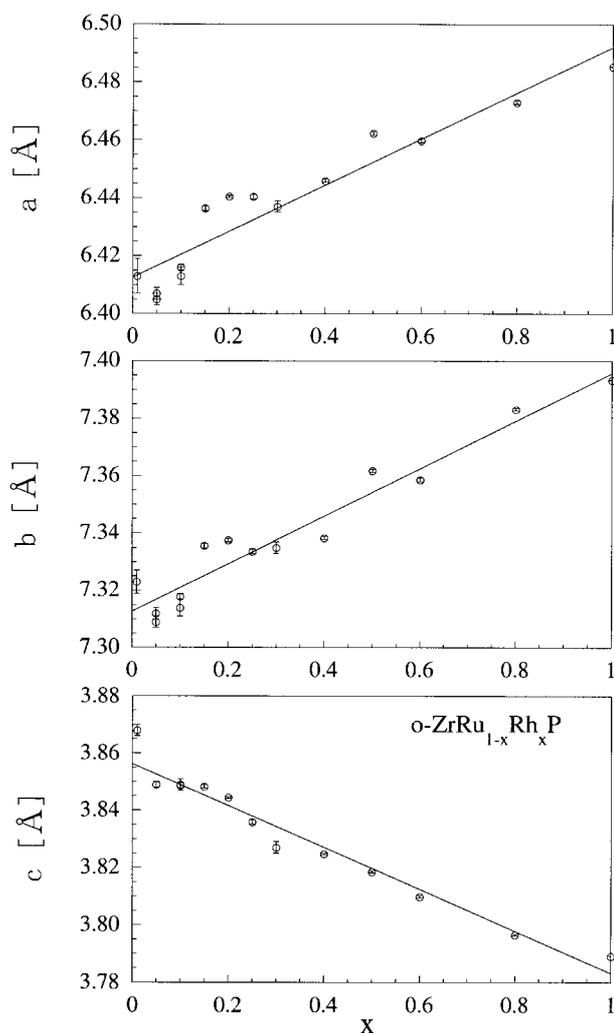


Figure 3. Lattice constant versus x curves for $\text{ZrRu}_{1-x}\text{Rh}_x\text{P}$ with the orthorhombic Co_2P -type structure.

type II superconductor [11]. Two magnetic anomalies are found at around 3.5 and 10 K in the susceptibility–temperature curve of $\text{ZrRu}_{0.95}\text{Rh}_{0.05}\text{P}$. Superconductivity is observed for both phases.

When the alloys $\text{ZrRu}_{1-x}\text{Rh}_x\text{P}$ ($x = 0.05$ and 0.1) are held at 1000°C for five days in a sealed silica tube, the hexagonal phase transforms to the orthorhombic form which is the low-temperature phase. Figure 6 shows the resistivity versus temperature curves for the orthorhombic form of these alloys. Both alloys show the superconducting transition at around 3 K.

$\text{ZrRu}_{1-x}\text{Rh}_x\text{P}$ alloys ($x = 0.01, 0.05$ and 0.1) were also prepared at around 1600°C and 4 GPa. These alloys are rich in the hexagonal phase, though the hexagonal and orthorhombic phases coexist. The resistivity–temperature curves for the alloys ($x = 0.01$ and 0.05) show mainly the superconductivity of the hexagonal phase. Two anomalies are found for $x = 0.1$.

Figure 7 shows T_c plotted as a function of x for the alloys. The T_c s of the hexagonal and orthorhombic phases of $\text{ZrRu}_{1-x}\text{Rh}_x\text{P}$ decrease rapidly with increasing x . In particular, the T_c of the hexagonal phase of the alloys sharply decreases from 13 K at $x = 0$ to 4.5 K at $x = 0.15$. The Rh atoms suppress the temperature of the onset of the superconductivity in the alloys.

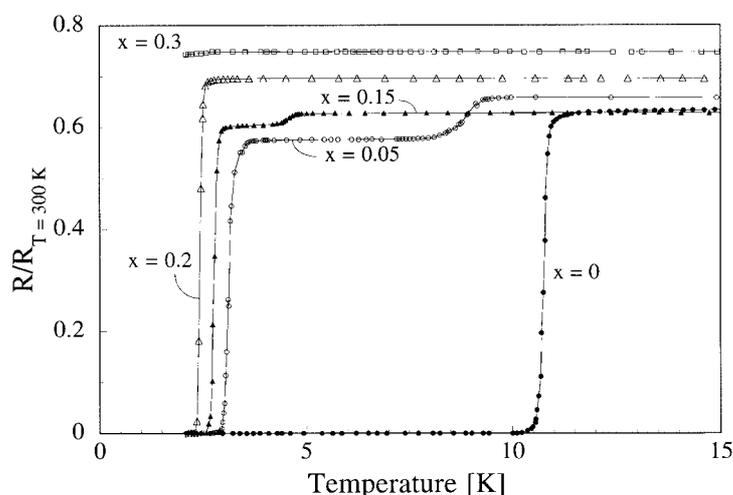


Figure 4. Resistivity versus temperature curves for $\text{ZrRu}_{1-x}\text{Rh}_x\text{P}$ ($x = 0, 0.05, 0.15, 0.2$ and 0.3) prepared at around 1300°C and 4 GPa .

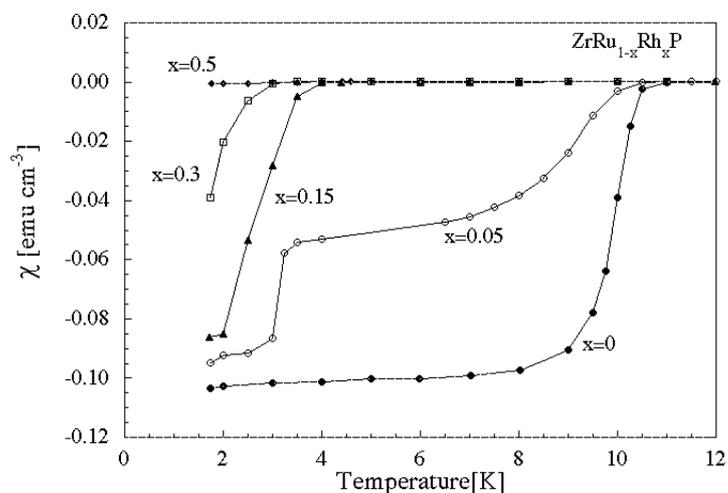


Figure 5. The temperature dependence of the dc magnetic susceptibility measured in an applied field of 5 Oe for $\text{ZrRu}_{1-x}\text{Rh}_x\text{P}$ ($x = 0, 0.05, 0.15, 0.3$ and 0.5) prepared at around 1300°C and 4 GPa .

4. Discussion

The specific heat measurements of h- and o-ZrRuP have already been carried out at low temperatures; the electronic density of states at the Fermi energy [$D(E_F)$] is relatively low at $0.76\text{ eV}^{-1}/\text{atom}$ and $0.72\text{ eV}^{-1}/\text{atom}$ for h- and o-ZrRuP, respectively [12, 13]. Seo *et al* have calculated the electronic band structures of h- and o-ZrRuP by the extended Huckel tight-binding method; the $D(E_F)$ value at the Fermi level is $0.21\text{ states eV}^{-1}/\text{atom}$ for h-ZrRuP and $0.29\text{ states eV}^{-1}/\text{atom}$ for o-ZrRuP [8]. These values are considerably smaller than those obtained from the specific heat measurements of both phosphides. Recently, Hase has calculated the band structure of h-ZrRuP by the full-potential linearized augmented-plane-

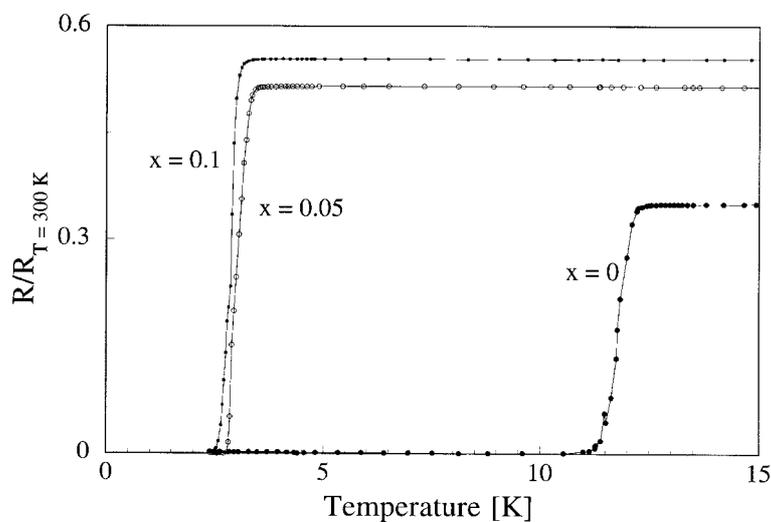


Figure 6. Resistivity versus temperature curves for the orthorhombic form of $\text{ZrRu}_{1-x}\text{Rh}_x\text{P}$ ($x = 0.05$ and 0.1) held at 1000°C for five days in a sealed silica tube.

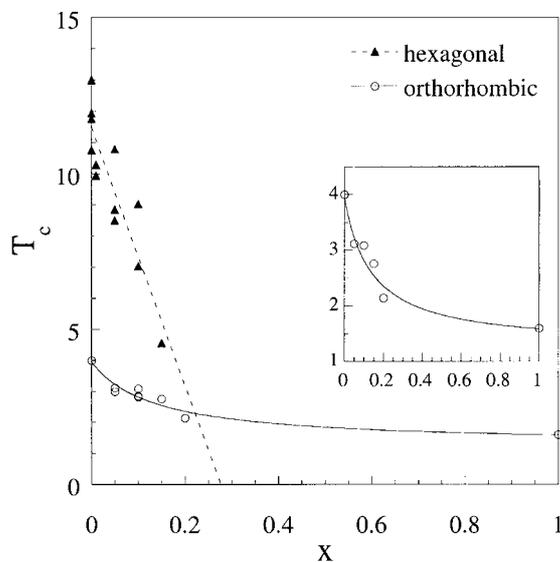


Figure 7. T_c versus x curves for the hexagonal and orthorhombic phases of $\text{ZrRu}_{1-x}\text{Rh}_x\text{P}$.

wave method within the local-density approximation [9]. The calculated density of states at the Fermi level (0.71 states $\text{eV}^{-1}/\text{atom}$) in h-ZrRuP is very close to the experimental result. The number of d electrons in the Rh atom is one more than that for the Ru atom. Thus, the Fermi level in the alloys h-ZrRu $_{1-x}$ Rh $_x$ P is expected to rise with increasing x . The density of states calculated near the Fermi level increases with increasing Fermi energy [8]. However, the experimental results show that the T_c of the alloys rapidly decreases with increasing x . This cannot be explained by these band calculations [8, 9].

Stewart *et al* have reported that the electron–phonon coupling parameter obtained from the

specific heat measurement is 0.79 for h-ZrRuP and 0.48 for o-ZrRuP [12, 13]. The electron-phonon coupling of h-ZrRuP is larger than that of o-ZrRuP. The resistivity of both forms of ZrRuP has been measured at low temperatures and high pressures. Both T_c s decrease with increasing pressure, at the rates of -53 mK GPa^{-1} for h-ZrRuP and -98 mK GPa^{-1} for o-ZrRuP; these changes mainly arise from the change of the electron-phonon coupling parameter with pressure [14]. Seo *et al* have pointed out that the electron-phonon coupling is important in making T_c higher for h-ZrRuP than for o-ZrRuP [8]. The T_c of $\text{ZrRu}_{1-x}\text{Rh}_x\text{P}$ decreases rapidly with increasing x . The anomalous suppression of T_c for the alloys cannot be explained by the change of $D(E_F)$. The change of the electron-phonon coupling parameter must play an important role in the superconductivity of the alloys.

Seo *et al* have pointed out that h-ZrRuP has a nearly half-filled one-dimensional (1D) band along the c -direction. A CDW instability associated with a 1D band is a likely cause for the occurrence of the change from h-TT'X (T and T': transition metals, Fe₂P-type structure) to o'-TT'X (the 'dimerized' form of h-TT'X, TiFeSi-type structure) in HfRuAs and TiRuAs phases. h-ZrRuP does not undergo a distortion from h-TT'X to o'-TT'X because the CDW instability is not strong enough. However, this instability appears to provide soft phonons conducive to superconductivity, leading to a high T_c for h-ZrRuP. As o-ZrRuP does not possess a partially 1D band, its T_c is low. o'-TT'X does not show superconductivity [8].

Recently, we have found that ZrRhSi with the orthorhombic Co₂P-type structure has the high T_c of 10.3 K [15]. o-ZrRuP and ZrRhSi are isostructural and isoelectronic compounds. The T_c of ZrRhSi is much higher than that of o-ZrRuP, comparable to that of h-ZrRuP. o'-ZrRuGe with the TiFeSi-type structure shows superconductivity at around 10.5 K [5]. The high T_c of ZrRhSi with the Co₂P-type structure and ZrRuGe with the TiFeSi-type structure cannot be explained by their theory. Thus, ZrRhSi and ZrRuGe are very interesting superconductors.

As mentioned above, when a small proportion of the Ru atoms in h-ZrRuP are replaced by Rh atoms, the T_c and the structure of the alloys change drastically. The Rh atoms dominate the structure and the superconductivity of the alloys. h-ZrRuP has a partially filled 1D band along the c -direction [8, 9]. However, the 1D chains along the c -axis may be broken by the Rh atoms in the alloys. The anomalous suppression of T_c for the alloys may be closely related to the breaking of the 1D chains.

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