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Ternary transition metal phosphides: High-temperature superconductors

(superconductivity)

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ABSTRACT Two systems of ternary transition metal phosphides with the ordered Fe_2P-type hexagonal structure are reported. They have the general formula MRuP and MOsP, in which M can be Ti, Zr, or Hf. An onset of the superconducting transition temperature as high as 13.0 K is reported for the ZrRuP compound.

Many ternary transition metal phosphides with the general formula MM′P and the ordered Fe_2P-type hexagonal structure (C22) (1) are known: TiMnP, MnNiP, FeNiP, CoNiP, MoNiP, WNiP, MnRuP, CrRhP, MnRhP, CrPdP, and CaAgP (2–7). Mössbauer studies and x-ray intensity measurements show that in general M and M′ are metal elements with M occupying the 3(*g*) positions of the space group $P\bar{6}2m$, and M′ occupying the 3(*f*) positions. As a rule, M is to the left of M′ in the periodic table. In the case that M and M′ have similar atomic sizes, there is a possibility that a slight disorder may occur. For example, in the FeNiP compounds, 25–30% of the 3(*g*) positions are occupied by Ni. The crystallographic ordering is reported to be very sensitive to the heat treatment of the samples, and it is possible that the ordering may effect the magnetic properties of the compounds (6, 8–10).

With the presence of the 3*d* transition metals Cr, Mn, Fe, Co, or Ni, most of the compounds reported were ordered ferromagnetically, and no superconductivity was reported in this particular group of ternary transition metal phosphides.

During the study of the Zr–Ru–P ternary system, many samples had been found to become superconducting above 10 K. Because there are no superconducting transition temperatures (T_cs) reported above 6 K in the related binary systems (11), and because most ternary phosphide phases are reported with the 1-1-1 composition,[‡] ZrRuP was made; it was found to form the ordered Fe_2P-type structure, with an onset of superconductivity as high as 13.0 K.

EXPERIMENTAL DETAILS

All samples were prepared from transition metals with purities of 99.9% and red phosphorus with a purity of better than 99.999%. Mixtures of the powders were pressed into small pellets and sintered between 800 and 1200°C in sealed quartz tubes under an argon atmosphere. Some samples were synthesized by making the binary RuP and OsP compounds first. After the measurements, all sintered compounds were arc-melted under an argon atmosphere in a Zr-gettered arc furnace and then annealed between 800 and 1200°C.

Table 1. Superconducting transition temperatures (T_c) and lattice parameters for two systems of hexagonal ternary phosphides

Compound	T_c, K	*a*, Å (±0.006)	*c*, Å (±0.004)	vol, Å^3	Heat treatment*
TiRuP	1.33 onset	6.325	3.542	122.7	am
ZrRuP	12.34–10.56	6.459	3.778	136.5	am, 900°C, a, q
HfRuP	12.70–11.08	6.414	3.753	133.7	s 1000°C, sc
TiOsP	†	6.285	3.625	124.0	s 1000°C, sc
ZrOsP	7.44–5.70	6.460	3.842	138.8	s 1000°C, sc
HfOsP	6.10–4.96	6.417	3.792	135.1	s 1000°C, sc

* am, Arc-melted; s, sintered; sc, slow cooled; q, quenched; a, annealed. All heat treatments specified are the last step only.

† No transition observed above 1.2 K.

Powder x-ray diffraction data were taken on a GE XTD-6 diffractometer (CuK_α radiation), equipped with a diffracted-beam crystal monochrometer, at a scanning rate of 0.2° in 2θ per minute. Line intensities were determined by weighing paper tracings of the diffracted peaks, and the program "Lazy Pulverix" was used to calculate the line intensities (12).

Superconducting transition temperatures were obtained from low frequency (20-Hz) ac magnetic susceptibility measurements. The T_c ranges reported denote 10–90% transition widths.

RESULTS AND DISCUSSION

The superconducting transition temperatures, lattice parameters, unit cell volumes, and preparation methods of the ordered Fe_2P-type hexagonal structure in the MRuP and MOsP systems are shown in Table 1. The univ cell volumes indicate that Ti, Zr, and Hf are all four-valent in these compounds. Comparisons of the sum of the atomic volumes and the unit cell volumes indicate three formula units per unit cell, as expected. The structural study of the hexagonal phase was carried out on a sample of ZrRuP. Reasonable agreement between the calculated and observed intensities was obtained with atoms placed in the same positions reported in the isostructural ZrRuSi compound (13) (space group $P\bar{6}2m\text{-}D^3_{3h}$): 3 Zr in 3(*g*)($x$, 0, ½) with $x_{Zr} = 0.580$; 3 Ru in 3(*f*)(x, 0, 0) with $x_{Ru} = 0.248$; 2 P in 2(*c*) (⅓, ⅔, 0) and 1 P in 1 (*b*)(0, 0, ½). Refinement of the x_{Zr} and x_{Ru} parameters was carried out by minimizing the discrepancy factor $R(R = \Sigma|I_{obs} - I_{calc}|/\Sigma I_{obs})$ with respect to x_{Zr} and x_{Ru} for the first 21 diffraction lines, reducing the R factor from 19% to 10% with $x_{Zr} = 0.585 \pm 0.004$ and $x_{Ru} = 0.235 \pm 0.004$. The observed x-ray line intensities and those calculated by using the above Zr and Ru position parameters are shown in Table 2, along with the calculated and observed

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[‡] Many ternary phosphides with the Co_2P-type, Cu_2Sb-type, and Cr_2P-type structures have the general formula MM′P.

Table 2. Powder diffraction data for ZrRuP

hkl	d_{obs}, Å	d_{calc}, Å	I_{obs}*	I_{calc}
100	5.598	5.594	79	96
001	3.781	3.778	18	19
110	3.228	3.229	143	78
101	3.132	3.131	206	236
200	2.796	2.797	41	34
111	2.455	2.455	963	1000
201	2.248	2.248	668	677
210	2.114	2.114	722	693
002	1.891	1.889	246	261
300	1.864	1.865	164	91
211	1.845	1.845	182	198
102	1.790	1.790	7	9
301	—	1.672	0	1
112	1.630	1.631	31	24
220	1.615	1.615	34	27
202	1.565	1.565	13	13
310	1.551	1.551	66	61
221	1.484	1.485	20	21
311	1.435	1.435	243	244
212	1.409	1.409	356	376
400	1.399	1.398		53

* Average of two different scans to eliminate preferred orientations.

d-spacings. The calculated interatomic distances are shown in Table 3.

A proposed structure of the ZrRuP is shown in Fig. 1. The Ru_3s form the two-dimensional triangular clusters in the basal plane, and these clusters are connected with each other through the Zr–Ru bonds with Zr atoms located in the $z = \frac{1}{2}$ plane.

All T_cs reported in Table 1 are the highest ones obtained during various sample preparation methods and heat treatments. For example, as shown in Fig. 2, one of the ZrRuP samples (no. 60) gave an onset of superconductivity at 10.7 K after arc-melting of the sintered sample. The T_c increased steadily as the annealing temperature of the arc-melt sample was increased from 900 to 1200°C (procedures 2–5 in Fig. 2). The highest onset of 13.02 K was obtained in the final step by annealing the 1200°C-annealed sample again at 900°C for 1 week and then quenching it in water. It appears that, through annealing, the T_c increases with the increase of the crystallographic order. However, the broad transition width $\Delta T_c = 1.8$ K indicates that sharper and higher superconducting transition temperatures may still be obtained.

In the case of sintered samples, the numbers of sinterings as well as the sintering temperature are important not only for the synthesis of the right phase, but also for the T_c of this phase. One of the HfRuP samples (no. 74) exhibited a broad and low T_c (Fig. 3) after sintering of the pressed powder pellet at 900°C for 1 week. Crushing the pellet and resintering the repressed pellet at 1100°C increased the T_c sharply. No increase was then achieved by further sintering at 1100°C. However, returning the sample to the sintering temperature of 1000°C did increase the T_c again. The T_c of 12.70 K for the HfRuP compound reported in Table 1 was reached by sintering at 1200°C before putting the sample back to 1000°C. To our knowledge, this compound has the highest T_c ever reported for a true Hf phase.

Table 3. Interatomic distances for ZrRuP (in Å)

Zr:	4 Zr	3.37	Ru:	2 Zr	2.95
	2 Ru	2.95		4 Zr	3.00
	4 Ru	3.00		2 Ru	2.63
	4 P	2.71		2 P	2.42
	1 P	2.68		2 P	2.53
P(2*c*):	6 Zr	2.71	*P*(1*b*):	3 Zr	2.68
	3 Ru	2.53		6 Ru	2.42

Standard deviations are less than 0.01 Å.

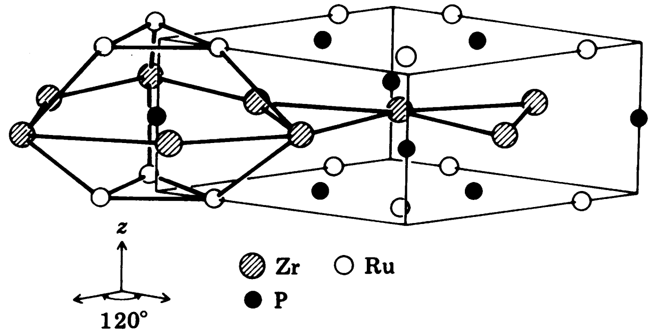

FIG. 1. Proposed structure of the hexagonal ZrRuP. Lines are drawn to indicate the Ru_3 two-dimensional triangular clusters and the linking of these clusters through Zr—Ru bonds.

The report of this group of transition metal phosphides marks the discovery of a class of high-temperature superconducting phosphides ($T_c > 10$ K). In fact, it is also one of the few true ternary systems of high-temperature superconductors. Two other examples are the double molybdenum sulfides (14) and the rare earth rhodium borides (15).

From the projection of the Ru- and Zr-sublattices onto the [001] plane as shown in Fig. 4, the two-dimensional triangular clusters of Ru_3s have a nearest-neighbor Ru–Ru distance of 2.63 Å, which is smaller than the average distance of 2.68 Å in the element (16). As a result of this contraction, the decrease of the 4*d* bandwidth (i.e., the increase of density of states at the Fermi energy) is likely to be responsible for the high superconducting transition temperature of the ZrRuP compound.

The role of the phosphorus ions is not easily understood from a comparison of the different compounds in this system. Fortunately, the compound ZrRuSi is found to be isostructural to ZrRuP (13) and is not superconducting above 1.2 K. The effect of replacing the phosphorus by the more electronegative silicon is an increase in the neartest-neighbor Ru–Ru distance to 2.87 Å (13), which is 0.19 Å larger than in the element Ru ($T_c = 0.51$ K) and is 0.24 Å larger than in the ZrRuP compound. This larger distance is probably the cause for the absence of superconductivity in this isostructural compound.

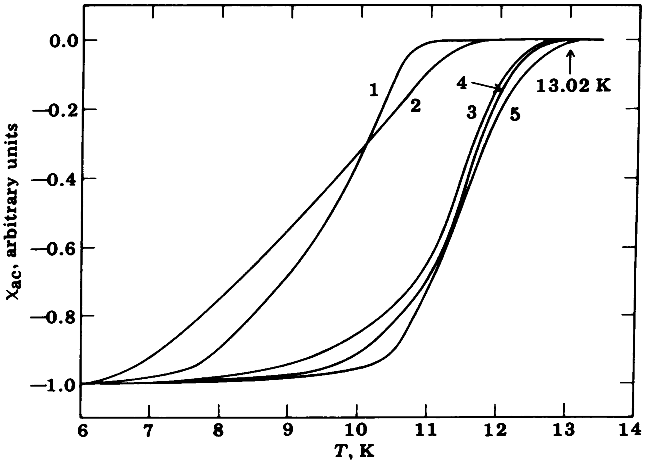

FIG. 2. Low-temperature magnetic susceptibility vs. temperature for the superconducting ZrRuP sample (no. 60) prepared by successively: 1, arc-melting the sintered sample; 2, annealing at 900°C for 2 weeks; 3, annealing at 1000°C for 7 days; 4, annealing at 1100°C for 5 days; 5, annealing at 1200°C for 3 days, then at 900°C for 7 days. The onset of 13.02 K is the value at 1% transition.

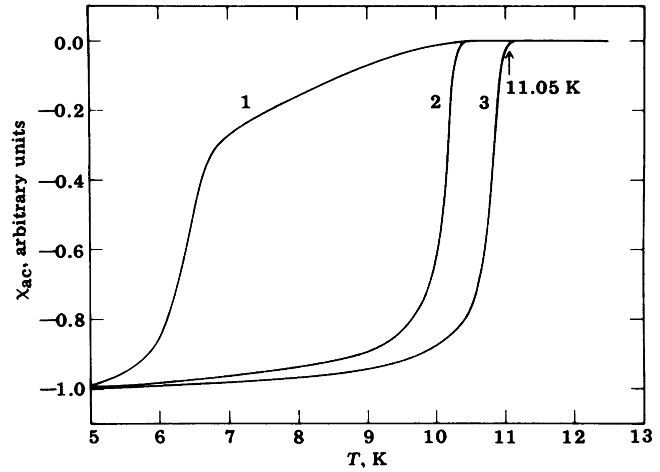

FIG. 3. Low-temperature magnetic susceptibility vs. temperature for the HfRuP sample (no. 74) prepared by successively: 1, sintering at 900°C for 7 days; 2, sintering at 1100°C for 2 days; 3, sintering at 1000°C for 5 days. The onset of superconductivity is 11.05 K.

The low T_c of the TiRuP compound (onset 1.33 K) is quite puzzling, because it is unusual to have an order of magnitude difference in the T_c between a Ti compound and its isoelectronic Zr compound. The possible existence of a magnetic moment in the titanium ions is ruled out through the paramagnetic behavior of TiRuP for $T > T_c$ from magnetic susceptibility and resistivity measurements. The possibility of a random distribution of Ti and Ru atoms in the 3(*g*) and 3(*f*) positions is also ruled out through the x-ray intensity calculation by putting the Ti in 3(*g*) with $x_{Ti} = 0.585$ and Ru in 3(*f*) with $x_{Ru} = 0.247$, giving a discrepancy factor of 12%. The observed and calculated x-ray line intensities along with the observed and calculated *d* spacings are shown in Table 4. By using the x_{Ru} parameter in the intensity calculation, we found that the nearest-neighbor Ru-Ru distance in TiRuP is 2.70 Å, a value very close to that in the element Ru. This probably is the reason why the T_c of the TiRuP compound is so close to the 0.51-K T_c of the Ru element.

Because P and As are in the same column of the periodic table, superconducting compounds with the same structure are expected to form in the ternary transition metal arsenides. This assumption has already been confirmed by preliminary results in the arsenides. The detailed results will appear soon (17).

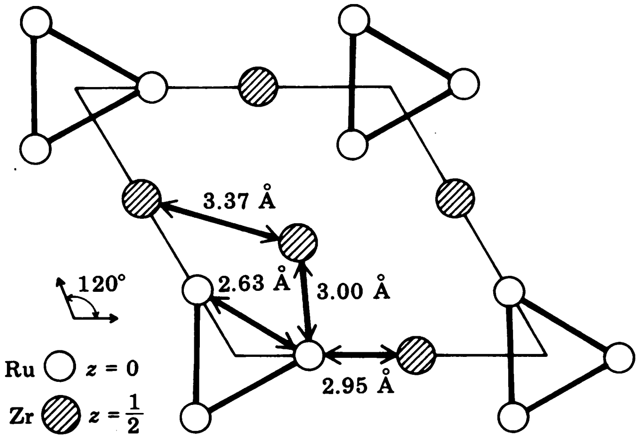

FIG. 4. Projection of the Ru- and Zr-sublattices onto [001] in the proposed structure for hexagonal ZrRuP. Lines are drawn to indicate the Ru_3 clusters. The shortest intermetallic distances are indicated.

Table 4. Powder diffraction data for TiRuP

hkl	d_{obs}, Å	d_{calc}, Å	I_{obs}	I_{calc}
100	5.468	5.478	223	251
001	3.539	3.542	165	224
110	3.161	3.162	219	213
101	2.974	2.974	105	137
200	—	2.739	0	1
111	2.359	2.359	1015	1000
201	2.165	2.167	710*	601
210	2.069	2.070	772	715
300	1.825	1.826		144
211	1.787	1.787	818	439
002	1.771	1.771		235
102	—	1.685	0	22
301	1.622	1.623	47	19
220	—	1.581	0	6
112	1.545	1.545	41	54
310	1.517	1.519	45	33
202	—	1.487	0	1
221	1.444	1.444	36	22
311	1.395	1.396	93	101
400	1.369	1.369	141	96
212	1.345	1.346	230	346

* The intensity of this peak fluctuated in various samples, depending on the preparation method.

In conclusion, the discovery of the ordered Fe_2P-type structure in the MRuP and the MOsP systems not only gives us a group of high-temperature superconductors, but also may help us to arrive at an empirical criterion for the occurrence of superconductivity in ternary systems.

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