Electrical Conductivity and Superconductivity of ZrNi_4P_2 and MRu_4P_2 ($\text{M} = \text{Zr}$ and Hf) Prepared at High Pressure

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Ternary metal phosphides ZrNi_4P_2 and MRu_4P_2 ($\text{M} = \text{Zr}$ and Hf) with ZrFe_4Si_2 -type structure have been prepared at high temperatures and high pressures. A superconductivity of ZrNi_4P_2 is not observed down to 2 K though it behaves as a metal. The superconductivity for ZrRu_4P_2 and HfRu_4P_2 is found at around 11 K and 9.5 K, respectively. The upper critical field (H_{c2}) obtained from H_{c2} vs temperature curve for ZrRu_4P_2 is 12.2 tesla(T) at 0 K.

[electrical conductivity, superconductivity, high pressure, ZrRu_4P_2 , new superconductor]

1. Introduction

A ternary nickel phosphide ZrNi_4P_2 crystallizes in the tetragonal ZrFe_4Si_2 -type structure, space group $\text{P4}_2/\text{mmn}$. Figure 1 shows the structure of ZrNi_4P_2 . The phosphide has the characteristic structure with tetrahedral Ni_4 clusters in a marcasite-type host structure. The Ni_4 clusters with common edges develop as infinite linear chains along the [001] direction[1]. Extended Hückel molecular orbital and tight binding band structure calculations have been carried out for ZrNi_4P_2 [2]. Magnetic properties of LnNi_4P_2 (Ln = lanthanide) are studied at low temperatures[3]. Recently, the superconductivity in ZrRu_4P_2 with ZrFe_4Si_2 -type structure has been observed at around 11 K[4].

In this paper the electrical properties of ZrNi_4P_2 and MRu_4P_2 ($\text{M} = \text{Zr}$ and Hf) are discussed.

2. Experimental

Using a wedge-type cubic-anvil high-pressure apparatus, ZrNi_4P_2 , ZrRu_4P_2 and HfRu_4P_2 were prepared at high temperatures and high pressures[4]. The sample assembly for the

preparation of ternary metal phosphides is similar to that used for the synthesis of black phosphorus[5]. The ternary metal phosphides were prepared by reaction of stoichiometric amounts of each metal and red phosphorus powders at around 850 °C for MRu_4P_2 ($\text{M} = \text{Zr}$ and Hf), and 1100 °C for ZrNi_4P_2 under 4 GPa. The reaction time is between 30 and 180 minutes. The samples were characterized by the powder x-ray diffraction using $\text{CuK}\alpha$ radiation and silicon as a standard. Figure 2 shows the x-ray diffraction pattern of ZrNi_4P_2 at room temperature. The diffraction lines of ZrNi_4P_2 are assigned by the index of ZrFe_4Si_2 -type structure. The lattice parameters of ZrNi_4P_2 obtained from the data are $a = 6.944(2) \text{ \AA}$, $c = 3.576(3) \text{ \AA}$, $V = 172.4(3) \text{ \AA}^3$. The x-ray diffraction profiles of MRu_4P_2 ($\text{M} = \text{Zr}$ and Hf) are similar to those of ZrNi_4P_2 . The lattice constants of ZrRu_4P_2 are $a = 6.992(3) \text{ \AA}$, $c = 3.699(3) \text{ \AA}$, $V = 180.8(2) \text{ \AA}^3$.

Copper or gold lead was attached to polycrystals of the samples with a silver-epoxy paste, and four-lead electrical resistivity measurements were performed at low temperatures. The

Fig. 1. Crystal structure of ZrNi_4P_2 .

Fig. 2. X-ray diffraction pattern of ZrNi_4P_2 prepared at around 1100 °C and 4 GPa.

resistance of ZrRu_4P_2 was measured as a function of the applied magnetic field at various constant temperatures[6]. The dc magnetic susceptibility of the polycrystalline samples was measured in the range of 1.8-300 K with a Quantum Design MPMS SQUID magnetometer.

3. Results and Discussion

Figure 3 shows the resistivity normalized to room temperature for ZrNi_4P_2 and ZrRu_4P_2 at low temperatures. The resistivity of both phosphides rapidly decreases with decreasing temperature. The superconductivity of ZrNi_4P_2 is not observed down to 2 K though it behaves as a metal. The resistivity vs temperature curve for ZrNi_4P_2 is very similar to that of binary nickel phosphides, Ni_2P , NiP and NiP_3 with metallic character[7]. The susceptibility of ZrNi_4P_2 is essentially temperature-independent, showing the

Fig. 3. Normalized electrical resistivity vs temperature curves for ZrNi_4P_2 and ZrRu_4P_2 .

Fig. 4. Normalized electrical resistivity vs temperature curves for MRu_4P_2 ($M = \text{Zr}$ and Hf).

Pauli paramagnetism[8]. The magnetic susceptibility of the binary nickel phosphides also indicates the Pauli paramagnetism[7,9]. The electrical and magnetic properties of ZrNi_4P_2 resemble those of the binary nickel phosphides.

Figure 4 shows the resistivity vs temperature curves of MRu_4P_2 ($M = \text{Zr}$ and Hf). The resistivity of both phosphides rapidly decreases with decreasing temperature, and sharply drops at around 11 K for ZrRu_4P_2 and 9.5 K for HfRu_4P_2 . The sample of ZrRu_4P_2 was annealed at around 800 °C for a week. The T_c of 11 K for ZrRu_4P_2 is the highest value of those obtained for the samples prepared under various reactions and annealing conditions. The T_c 's observed for ZrRu_4P_2 are between 8 and 11 K. The sample of HfRu_4P_2 was not annealed. Both ternary ruthenium phosphides are new superconductors.

Figure 5 shows the resistance ratio (R/R_0) vs temperature curves of ZrRu_4P_2 prepared at various temperatures under 4 GPa. The electrical behavior of these samples considerably depends on the preparation temperatures. When the reaction temperature is above 1000 °C, the resistivity does not become zero at around the T_c . This tendency becomes more remarkable as the reaction temperature is higher. Some new diffraction lines are observed in the pattern of the samples prepared at higher temperatures.

The resistance of ZrRu_4P_2 is measured as a function of the applied magnetic field at constant temperatures between 0.6 and 8.4 K. The T_c decreases with increasing applied magnetic field. The superconducting transition becomes broader at lower temperatures. Figure 6 shows the upper critical field (H_{c2}) vs temperature curve for ZrRu_4P_2 . The H_{c2} - T curve is fitted by the pair breaking model[10] as shown by a dotted line. H_{c2} obtained

Fig. 5. Normalized resistivity vs temperature curves for ZrRu_4P_2 prepared at various temperatures under 4 GPa.

Fig. 6. Upper critical field(H_{c2}) vs temperature curve for $ZrRu_4P_2$.

from this data is 12.2 tesla(T) at 0 K when the mid point of the resistivity jump is taken as T_c . The coherence length(ξ) of $ZrRu_4P_2$ can be estimated from the formula $H_{c2} = \Phi_0 / 2\pi\xi^2$. The coherence length of the compound is 52 Å.

Several interesting superconductors of ternary ruthenium phosphides have been found. $ZrRuP$ and $HfRuP$ with Fe_2P -type structure have the T_c of about 13 K[11,12]. The Fe_2P -type structure is the layer structure. Each layer in the hexagonal lattice is occupied by either Zr and P or Ru and P atoms. The compound $LaRu_4P_{12}$ with skutterudite structure is a superconductor with T_c of 7.2 K[9]. We have already studied the magnetic field dependence of the resistance at constant temperatures for both phosphides; H_{c2} at 0 K is 17.5 T for $ZrRuP$ [6] and 3.65 T for $LaRu_4P_{12}$ [9]. H_{c2} of $ZrRu_4P_2$ is lower than that of $ZrRuP$, and is much higher than that of $LaRu_4P_{12}$.

The superconducting data of three ternary ruthenium phosphides, $ZrRuP$, $ZrRu_4P_2$ and $LaRu_4P_{12}$, are summarized in Table 1. The T_c and H_{c2} of $ZrRuP$ and $ZrRu_4P_2$ which are metal rich compounds are much higher than those of $LaRu_4P_{12}$ which is a phosphorus rich compound. The superconductivity of $ZrRu_4P_2$ and $ZrRuP$ is mainly due to Ru 4d character near the Fermi level. On the other hand, the band calculation suggests that the highest-occupied band of $LaRu_4P_{12}$ has a more phosphorus(s, p)orbital character rather than Ru 4d in the vicinity of the Fermi level[13]. The remarkable difference in the superconducting properties for the ternary ruthenium phosphides may closely be related to the difference in the electronic states in the vicinity of the Fermi level.

Table 1. Superconducting data of three ruthenium phosphides.

Compound	$ZrRu_4P_2$	$ZrRuP$	$LaRu_4P_{12}$
Structure	tetragonal $ZrFe_4Si_2$ -type	hexagonal Fe_2P -type	cubic $CoAs_3$ -type
Density(g/cm ³)	9.894	8.151	6.327
Metal:Phosphorus	5:2	2:1	5:12
Valence electrons /formula unit	46	17	75
T_c (K)	11	13	7.2
H_{c2} (T)	12.2	17.5	3.65
Coherence length(Å)	52.0	43.4	95.0

References

- [1] J. Y. Pivan, R. Guérin, E. H. ElGhadraoui and M. Rafiq, *J. Less Common Met.*, **153**, 282(1989).
- [2] A. L. Beuze, M. C. Zerrouki, R. Lissillour, R. Guérin, and W. Jeitschko, *J. Alloys Comp.*, **191**, 53(1993).
- [3] S. Députier, O. Peña, T. Le Bihan, J. Y. Pivan and R. Guérin, *Physica*, **B233**, 26(1997).
- [4] I. Shirotni, G. Iwasaki, I. Kaneko, C. Sekine, S. Todo and T. Yagi, *Solid State Commun.*, **104**, 217(1997).
- [5] I. Shirotni, *Mol. Cryst. Liq. Cryst.*, **86**, 1943(1982).
- [6] I. Shirotni, K. Tachi, K. Takeda, S. Todo, T. Yagi and K. Kanoda, *Phys. Rev.*, **B52**, 6197(1995).
- [7] I. Shirotni, E. Takahashi, N. Mukai, K. Nozawa, M. Kinoshita, T. Yagi, K. Suzuki, T. Enoki and S. Hino, *Jpn. J. Appl. Phys., Suppl.* **32-3**, 294(1993).
- [8] T. Le Bihan, Report of Diplome d'Etudes Approfondies, Université de Rennes, June (1990).
- [9] I. Shirotni, T. Adachi, K. Tachi, S. Todo, K. Nozawa, T. Yagi and M. Kinoshita, *J. Phys. Chem. Solids*, **57**, 211(1996).
- [10] M. Tinkam, *Introduction to Superconductivity*, McGraw-Hill(1975).
- [11] H. Barz, H. C. Ku, G. P. Meisner, Z. Fisk and B. T. Matthias, *Proc. Natl. Acad. Sci., U.S.A.*, **77**, 3132(1980).
- [12] I. Shirotni, N. Ichihashi, K. Nozawa, M. Kinoshita, T. Yagi, K. Suzuki and T. Enoki, *Jpn. J. Appl. Phys., Suppl.* **32-3**, 695(1993).
- [13] D. Jung, M. H. Whango and S. Alvarez, *Inorg. Chem.*, **29**, 2252(1990).