

## Superconductivity of ZrRuSi prepared at high pressure

Ichimin Shirotani, Kenji Tachi, and Keiki Takeda

*Muroran Institute of Technology, 27-1, Mizumoto, Muroran-shi 050, Japan*

Sakae Todo and Takehiko Yagi

*The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan*

Kazushi Kanoda

*Institute for Molecular Science, Myodaiji, Okazaki-shi 444, Japan*

(Received 24 May 1995)

Hexagonal ZrRuSi with the Fe<sub>2</sub>P-type structure (*h*-ZrRuSi) and orthorhombic ZrRuSi with the Co<sub>2</sub>P-type form (*o*-ZrRuSi) were prepared at high temperatures and high pressures. These metal silicides are interesting layer compounds. A resistivity of ZrRuSi was measured at low temperatures. The superconductivity was observed between 7–12 K for *h*-ZrRuSi and between 3–5 K for *o*-ZrRuSi. These silicides are superconductors. The resistivity of *h*-ZrRuSi and *h*-ZrRuP was measured at various constant temperatures as a function of applied magnetic field. The upper critical field ( $H_{c2}$ ) obtained from resistance vs magnetic field curves was 1 tesla at 0 K for *h*-ZrRuSi. This is a surprisingly small value. On the contrary, *h*-ZrRuP has large  $H_{c2}$  of 17.5 tesla at 0 K. The physical properties of these superconductors are discussed.

The compound ZrRuP crystallizes in two modifications, the Fe<sub>2</sub>P-type hexagonal structure (*h*-ZrRuP) (Ref. 1) and Co<sub>2</sub>P-type orthorhombic structure (*o*-ZrRuP).<sup>2</sup> *h*-ZrRuP is an interesting layer compound. Each layer in the hexagonal lattice is occupied by either Zr and P atoms or Ru and P atoms. The two-dimensional triangular clusters of Ru<sub>3</sub> are formed, and linked with each other through the Ru-P bonds in the basal plane. The Ru<sub>3</sub> clusters are also connected with each other through the Zr-Ru bonds with Zr atoms located in the  $z = \frac{1}{2}$  plane. The Ru-Ru distance in the clusters is 2.63 Å,<sup>1</sup> which is shorter than the average of 2.68 Å in pure Ru metal. In contrast, the orthorhombic structure has layers which are filled with Zr and Ru atoms and these layers are all equivalent.<sup>2</sup> The orthorhombic phase of ZrRuP transforms to the hexagonal one at high temperatures and high pressures.<sup>3</sup>

*h*-ZrRuP shows an interesting superconductivity, an onset of superconducting transition temperature ( $T_c$ ) as high as 13 K.<sup>1</sup> The superconductivity of *o*-ZrRuP is found around 3.5 K.<sup>2</sup> ZrRuP is usually prepared by an arc-melted method. We have prepared *h*- and *o*-ZrRuP at high temperatures and high pressures.<sup>4</sup> The  $T_c$ 's of both ZrRuP are about 13 K for the hexagonal phase and 4 K for the orthorhombic phase.

*h*-ZrRuSi is found to be isostructural to *h*-ZrRuP.<sup>1,5</sup> The effect of replacing the phosphorus atom by the more electronegative silicon atom is an increase in the nearest-neighbor Ru-Ru distance to 2.87 Å. ZrRuSi prepared by the arc-melted method does not show the superconductivity above 1.2 K.<sup>1</sup> We have prepared *h*- and *o*-ZrRuSi at high temperatures and high pressures, and observed the superconductivity at around 7–12 K for *h*-ZrRuSi and 3–5 K for *o*-ZrRuSi.

In this paper the physical properties of the superconductors ZrRuSi prepared at high pressure are discussed.

### EXPERIMENT

Using a wedge-type cubic-anvil high pressure apparatus,<sup>4</sup> ZrRuSi was prepared at high temperatures and high pressures. The upper and lower stages of the high pressure apparatus consist of three anvils that slide on the wedge formed in shallow *v*-shaped grooves. The anvil movement is completely synchronized by means of a wedge system. The anvils prepared by the cemented tungsten carbide have a 16×16 mm<sup>2</sup> top-square face. The sample container made of pyrophyllite is formed into a cube of 21 mm on an edge. The sample assembly for the preparation of ZrRuSi is similar to that used for the synthesis of black phosphorus.<sup>6</sup> ZrRuSi was prepared by reaction of stoichiometric amounts of Zr, Ru, and Si powders at around 4 GPa. The samples prepared at high pressure were characterized by powder x-ray diffraction using Cu  $K\alpha_1$  radiation and silicon as a standard. Figure 1 shows the x-ray-diffraction pattern of ZrRuSi prepared at around 1400 °C and 4 GPa. These diffraction lines of the metal silicide agreed with those of *h*-ZrRuSi reported by Jonson and Jeitschko.<sup>5</sup> The lattice constants of *h*-ZrRuSi obtained by us were  $a = 6.6812 \pm 0.0005$  Å and  $c = 3.6715 \pm 0.0006$  Å. Some weak diffraction peaks indicated by the arrows were identified as lines of the orthorhombic phase. X-ray-diffraction profile of ZrRuSi prepared at 950 °C and 4 GPa was similar to that of *o*-ZrRuP. These diffraction lines were almost assigned by an index of Co<sub>2</sub>P-type structure. Some lines of the hexagonal phase were observed in this pattern. The preparation of the single phase of *o*-ZrRuSi is very difficult because the density of both phases is almost equal.

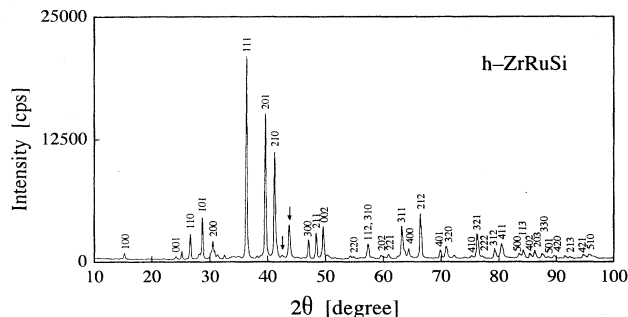


FIG. 1. X-ray-diffraction pattern of *h*-ZrRuSi prepared at around 1400°C and 4 GPa.

Copper or gold lead was attached to a polycrystal of ZrRuSi with silver filled by epoxy, and four-lead electrical resistivity measurements were performed at low temperatures. The resistivity of *h*-ZrRuP and *h*-ZrRuSi was measured at various constant temperatures as a function of applied magnetic field.

#### RESULTS AND DISCUSSION

Figure 2 shows an electrical resistivity vs temperature curve for *h*-ZrRuSi prepared at 1400°C and 4 GPa. The compound was annealed at 1000°C for a week. The resistivity decreased slowly with decreasing temperature, but sharply dropped at around 12 K. The  $T_c$  of 12 K is the highest one obtained during various sample preparations and the annealing conditions. The  $T_c$ 's observed for *h*-ZrRuSi were between 7 and 12 K. The ac susceptibility of ZrRuSi was measured at low temperatures. The susceptibility abruptly decreased at around 12 and 4 K. The anomaly at around 4 K is due to the superconducting transition of *o*-ZrRuSi because there is a small amount of *o*-ZrRuSi in the sample as is shown in Fig. 1. We have already reported similar magnetic behavior for ZrRuP prepared at high pressure.<sup>4</sup> The orthorhombic and hexagonal phases of ZrRuSi easily coexisted because the density of both phases is almost equal. The diffraction peaks of both phases were clearly observed for ZrRuSi prepared at 1300°C and 4 GPa. Figure 3 shows the resistivity of

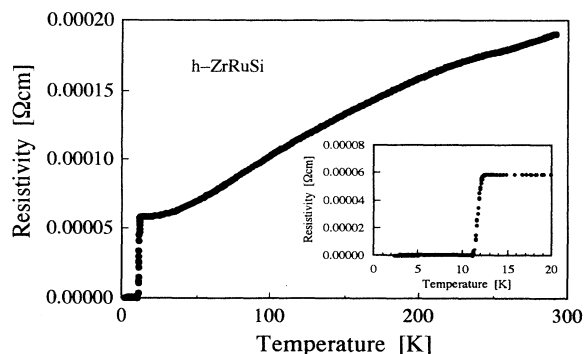


FIG. 2. Electrical resistivity of *h*-ZrRuSi at low temperatures.

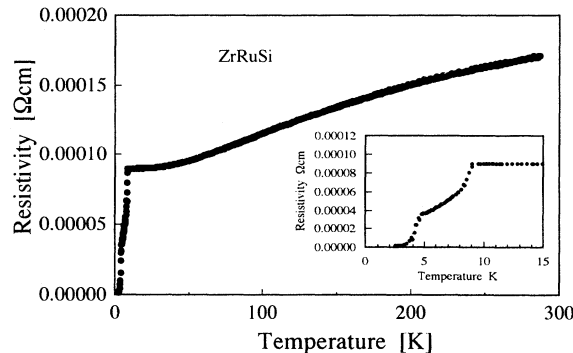


FIG. 3. Electrical resistivity vs temperature curve for ZrRuSi prepared at around 1300°C and 4 GPa.

this specimen at low temperatures. The sample was annealed at 1000°C for a week. The resistivity decreased rapidly at around 9 and 5 K. These arise from the superconducting transition for *h*- and *o*-ZrRuSi. The  $T_c$ 's observed for *o*-ZrRuSi were between 3 and 5 K. The superconductivity of ZrRuSi prepared by the arc-melted method is not found above 1.2 K.<sup>1</sup> However, we have found the superconductivity of *h*- and *o*-ZrRuSi prepared at high pressure at around 12 and 5 K, respectively.

Figure 4 shows the resistance of *h*-ZrRuSi plotted as a function of the applied magnetic field at constant temperatures between 0.5 and 5.5 K. The critical magnetic field increased monotonically when the temperature was above 3.1 K. However, an anomaly in the resistance vs magnetic-field curves was observed below this temperature. The superconductivity of ZrRuSi is very sensitive to the conditions of the sample preparation and the heat

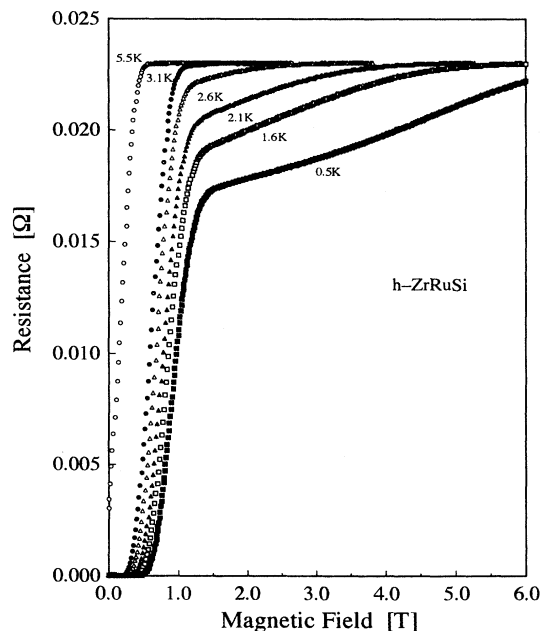


FIG. 4. Resistance vs applied magnetic-field curves for *h*-ZrRuSi at various temperatures.

treatment. This anomaly may closely be related to the coexistence of both phases and the crystallinity though the origin is not understood still. The upper critical field ( $H_{c2}$ ) obtained from  $H_{c2}$  vs temperature curve was 1 tesla at 0 K when the midpoint was taken as the  $T_c$ . This is a surprisingly small value. Figure 5 shows the resistance vs applied magnetic-field curves for  $h$ -ZrRuP at various constant temperatures. The anomaly in the resistance curves was not observed for  $h$ -ZrRuP.  $H_{c2}$  of  $h$ -ZrRuP was 17.5 tesla at 0 K. This value was much larger than  $H_{c2}$  of  $h$ -ZrRuSi. The coherence length ( $\xi$ ) of  $h$ -ZrRuSi and  $h$ -ZrRuP can be estimated from the formula  $H_{c2} = \Phi_0 / 2\pi\xi$ . The coherence length was 181.5 Å for  $h$ -ZrRuSi and 43.4 Å for  $h$ -ZrRuP. These values differ remarkably for both superconductors.

$h$ -ZrRuSi and  $h$ -ZrRuP are interesting layer compounds. Each layer in the hexagonal lattice is occupied by either Zr and  $X$  ( $=P, Si$ ) atoms or Ru and  $X$  atoms. The two-dimensional triangular clusters of  $Ru_3$  are formed, and linked with each other through the Ru- $X$  bonds in the basal plane. The Ru-Ru distances in the clusters are 2.63 Å for  $h$ -ZrRuP and 2.871 Å for  $h$ -ZrRuSi. Barz *et al.* suggest that the high- $T_c$  in  $h$ -ZrRuP is due to the short Ru-Ru distance in the clusters.<sup>1</sup> However, the  $T_c$  of  $h$ -ZrRuSi is over 10 K though the Ru-Ru distance in  $h$ -ZrRuSi is about 8.4% longer than that of  $h$ -ZrRuP. This result indicates that the  $T_c$  of both compounds is not sensitive to the Ru-Ru distance in the clusters.

$h$ -ZrRuP,  $h$ -ZrRuAs, and  $h$ -HfRuP with  $Fe_2P$ -type structure have high- $T_c$  over 10 K.<sup>1,4,7</sup> On the other hand, the  $T_c$  of  $o$ -ZrRuP, NbRhP, and TaRhP with the  $Co_2P$ -type structure are around 3–4 K.<sup>2,4</sup> We have found that  $T_c$ 's of  $h$ -ZrRuSi and  $o$ -ZrRuSi were about 12 and 5 K, respectively. The  $T_c$  of the hexagonal phase of

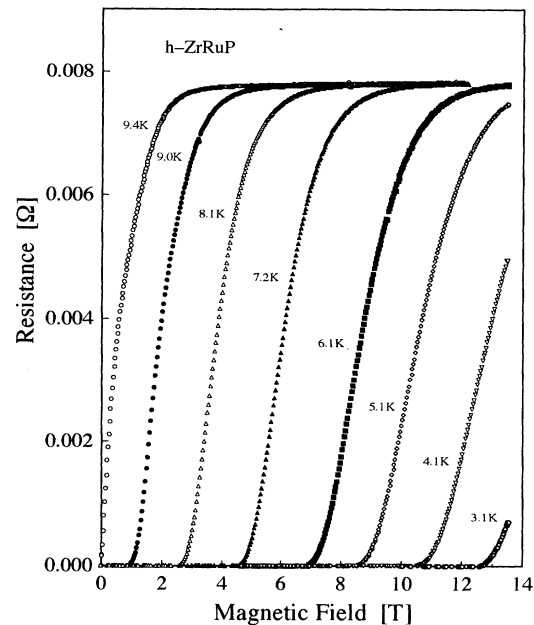


FIG. 5. Resistance vs applied magnetic-field curves for  $h$ -ZrRuP at various temperatures.

the metal silicide is higher than that of the orthorhombic phase.

#### ACKNOWLEDGMENTS

The authors wish to thank Professor S. Kagoshima and Dr. H. Shinagawa, University of Tokyo, for their support and useful suggestions.

<sup>1</sup>H. Barz, H. C. Ku, G. P. Meisner, Z. Fisk, and B. T. Matthias, Proc. Natl. Acad. Sci. U.S.A. **77**, 3132 (1980).

<sup>2</sup>R. Müller, R. N. Shelton, J. W. Richardson, and R. A. Jacobson, J. Less-Common Met. **42**, 177 (1983).

<sup>3</sup>I. Shirovani, T. Adachi, N. Ichihashi, K. Tachi, T. Kikegawa, and O. Shimomura, *Photon Factory Activity Report* (National Laboratory for High Energy Physics in Japan, Japan, 1993), Vol. 11, p. 435; I. Shirovani, K. Tachi, N. Ichihashi, T. Adachi, T. Kikegawa, and O. Shimomura, Phys. Lett. A (to be

published).

<sup>4</sup>I. Shirovani, N. Ichihashi, K. Nozawa, M. Kinoshita, T. Yagi, K. Suzuki, and T. Enoki, Jpn. J. Appl. Phys. Suppl. **32-3**, 695 (1993).

<sup>5</sup>V. Johnson and W. Jeitschko, J. Solid State Chem. **4**, 123 (1972).

<sup>6</sup>I. Shirovani, Mol. Cryst. Liq. Cryst. **86**, 1943 (1982); I. Shirovani, S. Shiba, K. Takemura, O. Shimomura, and T. Yagi, Physica B **190**, 1191 (1992).