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Single crystal growth and characterization of URu_2Si_2

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We review recent progress in single crystal growth and study of electronic properties in URu_2Si_2. Czocharalski pulling, using purified uranium metal and subsequent annealing under ultra-high vacuum, is successfully applied to this compound, and it yields the highest residual resistivity ratio. These high-quality single crystals allow us to investigate Fermi surfaces using quantum oscillation and to make detailed transport measurements at low temperature.

Keywords: single crystal growth; Fermi surface

1. Introduction

Preparation of high-quality single crystal samples is one of the most essential components of experimental study in condensed matter science. Sample impurities often lead to a significant modification to the intrinsic properties of materials. In general, an impurity acts as a scattering centre. In metals, the conduction electrons are scattered by impurities raising the low-temperature residual resistivity. When an impurity carries magnetic moment, situation becomes more serious. It changes the spin angular momentum of a conduction electron through the Kondo effect, leading to an increase of resistivity with decreasing temperature and compensation of the magnetic moment. The increase in the residual resistivity is more serious when it is larger than the resistivity arising from intrinsic scattering.

Superconductivity is also sensitive to impurities, particularly in the case of unconventional superconductivity.

In URu_2Si_2, most fundamental properties were clarified soon after the discovery of its superconductivity and the so-called 'hidden-order' phase transitions [1]. It has also been pointed out that there is a significant sample dependence on the physical properties, such as superconducting transition temperature and weak antiferromagnetic ordered moment observed in neutron scattering in the hidden order state.

It is now well understood that the 'weak antiferromagnetism' observed in neutron scattering experiments is fictitious and arises from residual stress in the sample [2]. In fact, a clear antiferromagnetism is observed above a relatively small hydrostatic or uniaxial critical

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pressure [3,4]. The ground state at ambient pressure is, therefore, in unidentified hidden order state which coexists with unconventional superconductivity at low temperature.

These are the characteristics of highly correlated electron systems. Because of an enhanced density of states at Fermi level, the conduction electron system is, in general, unstable for a symmetry breaking which reduces the density of states and hence its total energy. A small perturbation to the system, such as impurity doping or application of pressure, would therefore induce significant modifications.

In this paper, we review the present status of the crystal growth of URu_2Si_2 and the progress of physical property investigation using the high-quality single crystals.

2. Single crystal growth and characterization

Single crystals of URu_2Si_2 and related compounds are, in general, grown by the Czochralski pulling in an arc furnace. To improve quality, we have made the following modifications to the conventional method.

The uranium metal as a starting material has been purified using the solid state electrotransport (SSE) under ultrahigh vacuum. This process is particularly important because the purity of uranium is usually lower than the purity of commercially available ruthenium and silicon material. It should also be noted that the SSE is efficient in removing transition metal impurities such as iron and nickel [5]. The Czochralski-grown single crystal was subsequently annealed using the same technique.

High quality crystals with smaller dimensions can also be grown from Sn-flux. We obtained the single crystals with quality as high as the best sample grown by Czochralski pulling, although the size was much smaller.

The samples were characterized by electron microprobe for chemical composition and by single-crystal X-ray diffraction for crystallographic parameters including the site occupancy and atomic displacement parameters. We did not detect any impurity elements or off-stoichiometry within the experimental accuracy, typically, around 1%.

Figure 1 shows the crystal structure determined by the Single-crystal X-ray diffraction. The data were successfully analyzed using the tetragonal $ThCr_2Si_2$-type structure (space group I4/mmm), as previously reported. In this structure, U and Ru atoms sit in the special positions (0 0 0) and (0 1/2 1/4), respectively. On the other hand, the position of Si has a positional parameter (0 0 z_{Si}).

The importance of the z_{Si} parameter in $ThCr_2Si_2$-type structure in general has been discussed on the basis of the bonding nature between Si sites [6]. In fact, recent band calculations study demonstrated that the small change in z_{Si} significantly modifies the Fermi surfaces [7]. For URu_2Si_2, the z_{Si} is reported as 0.373 [8] or 0.372 without significant temperature dependence.

Figure 1 also shows experimentally determined thermal ellipsoids for each atom with probability of 50%, demonstrating absence of possible disorder or defects. It is interesting to compare the crystallographic parameters of URu_2Si_2 with those of the reference compounds $ThRu_2Si_2$ and $LnRu_2Si_2$ (*Ln*: rare earth elements). Figure 2 shows the unit cell volume of the $LnRu_2Si_2$ and the $AnRu_2Si_2$ compounds (*An*: actinide elements). In the actinide compounds, $ThRu_2Si_2$ is usually regarded as a reference compound to URu_2Si_2 because Th does not have $5f$ electrons. On the other hand, $LaRu_2Si_2$ is a reference compound to $CeRu_2Si_2$ for the same reason.

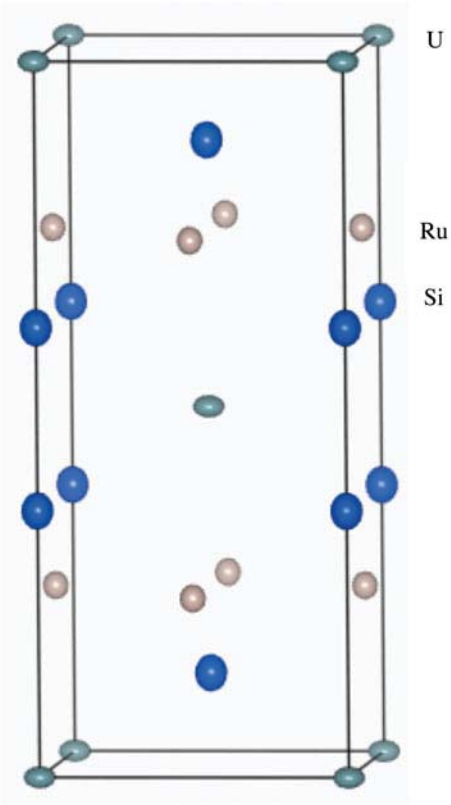

Figure 1. (colour online) Crystal structure of URu_2Si_2 determined by the single-crystal X-ray diffraction. The ellipsoids at the atomic sites are drawn using the anisotropic atomic displacement parameters.

In the lanthanide series, the unit cell volume gradually shrinks with increasing atomic number, following a lanthanide contraction. This is an indication that rare earth atoms take a trivalent state in these compounds. The volume of $CeRu_2Si_2$ is significantly smaller than the lanthanide contraction, suggesting a smaller average atomic volume of cerium. From this behaviour, the itinerant character of $4f$ electron in $CeRu_2Si_2$ is discussed. The unit cell volume of $CeRu_2Si_2$ further decreases with decreasing temperature below a characteristic temperature of about 10 K. Heavy fermion behaviour in $CeRu_2Si_2$ with an enhanced effective mass of itinerant $4f$ electron are correlated with this volume anomaly [9].

In the actinide series, on the other hand, the volume does not follow the simple contracting tendency. Among actinide compounds $ThRu_2Si_2$ has a well defined Th^{4+} state. It is anticipated that 'actinide contraction' line can be assumed, followed in this case by tetravalent actinide atoms, instead of by trivalent atoms in the lanthanide contraction.

Arguing in this manner, URu_2Si_2 has a significantly smaller unit cell volume than expected for tetravalent state, indicating itinerant character of $5f$ electrons.

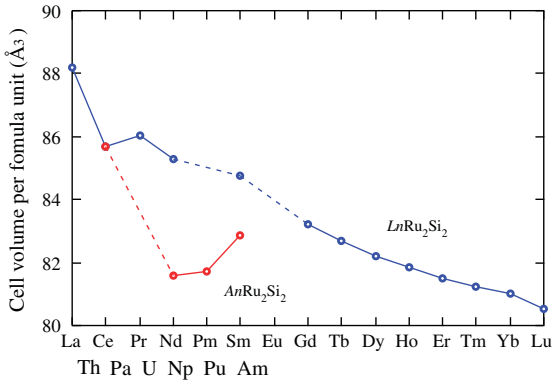

Figure 2. (colour online) Unit cell volume of $An\mathrm{Ru_2Si_2}$ (*An*: actinide) and $Ln\mathrm{Ru_2Si_2}$ (*Ln*: lanthanide).

3. Sample dependent behavior

Figure 3 shows the low-temperature specific heat measured on the same piece of single crystal at different annealing conditions. For the as-grown crystal, the specific heat anomaly corresponding to the superconducting transition appears below 0.7 K. After annealing at 900°C for 24 h, the onset of the anomaly shifts to 1.1 K. At the same time, the jump of the specific heat becomes larger. Further annealing shifts the onset to an even higher temperature side and the superconducting transition becomes sharper. This behaviour is consistent with earlier reports. The significant improvement by annealing strongly indicates that the sample quality is not governed by impurities or off-stoichiometry but rather by the lattice imperfections.

Even after the careful crystal growth and annealing using the same manner as described above, the quality of each crystal differs. Here, we use the residual resistivity ratio (RRR) as the measure of the sample quality. At present, we are unable to detect the significant

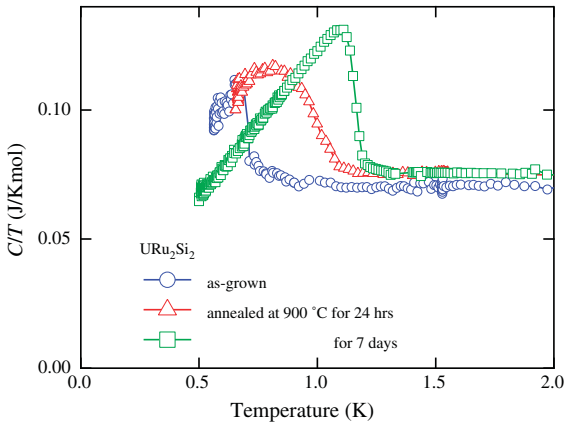

Figure 3. (colour online) Specific heat around the superconducting transition of $\mathrm{URu_2Si_2}$ single crystal with different annealing conditions.

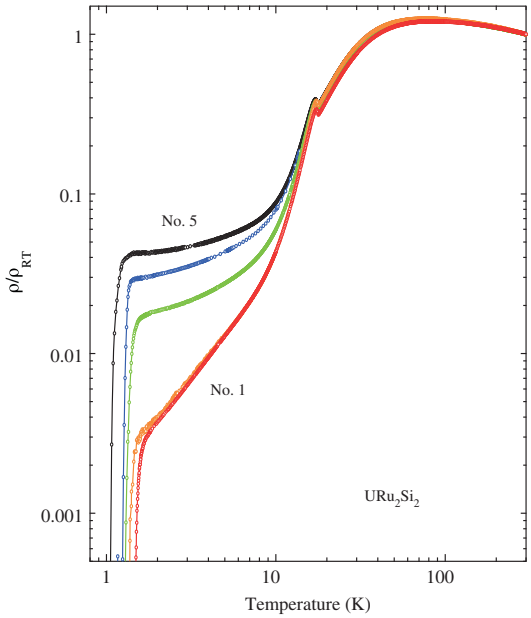

Figure 4. (colour online) Electrical resistivity of URu_2Si_2 single crystals cut from an annealed single crystal ingot [10]. The ingot was sliced into five pieces corresponding to Nos. 1–5 samples. No. 1 taken from the region close to the surface has the lowest residual resistivity, while No. 5 from the core part has the largest. Nos. 2–4 are between two extremes.

difference between the samples with different quality using other methods like EPMA or X-ray diffraction.

Figure 4 shows the electrical resistivity measured on an annealed single crystal cut from the same ingot called #15, after SSE treatment [10]. No. 1 sample was taken from the outer part of the ingot, while No. 5 corresponds to the core part of the same sample. It is remarkable that the low-temperature resistivity is almost 10 times different between No. 1 and 5. Note also that the superconducting-transition temperature correlates with residual resistivity. On the other hand, small but significant change in the hidden order transition temperature was also reported [11].

Resistivity behaviour of the best sample (No. 1) differs from the sample with larger residual resistivity. Here, residual resistivity is defined as the resistivity just above the superconducting transition at low temperature. Samples with poor quality (No. 5) behaves as T^2, as observed, in other actinide compounds in general. However, the resistivity of No. 1 sample significantly differs from it. As mentioned in introduction, resistivity behaviour reflects the electron scattering in the ordered state. The present observation is therefore expected to provide important information on the nature of hidden-order. This point will be discussed in detail in the next section.

4. High-pressure evolution of electrical resistivity in a high-quality single crystal

The electrical resistivity of URu_2Si_2 has already been reported by several research groups. It is characterized by a broad maximum ,around 80 K followed by a steep decrease with

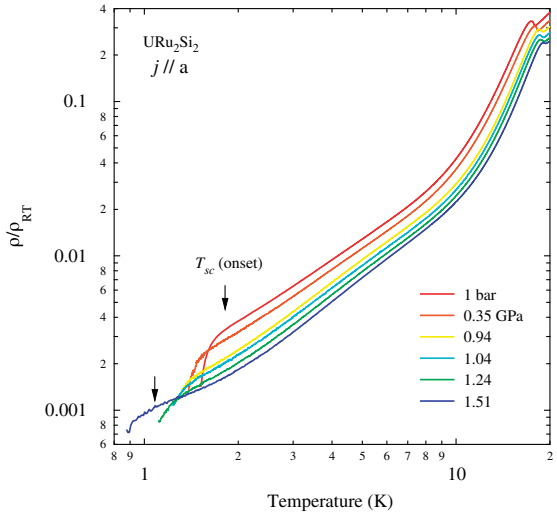

Figure 5. (colour online) Electrical resistivity of URu_2Si_2 measured at various hydrostatic pressures [12].

decreasing temperature and an anomaly at T_{HO}. Unlike most of heavy fermions with the Fermi-liquid behaviour, a clear T^2 behaviour is not seen in electrical resistivity at low temperature. The resistivity measurement on the high-quality sample with low-residual resistivity is important to detect the intrinsic scattering in the hidden order state which would reflect the excitation spectrum of quasiparticles. It is further interesting to compare the resistivity behaviour both in the hidden order state and the pressure-induced antiferromagnetic state.

Figure 5 shows the temperature dependence of the electrical resistivity measured at various pressures [12]. To elucidate intrinsic behaviour, we performed the resistivity measurement on the best sample corresponding to No. 1 in Figure 4. Two anomalies corresponding to the hidden-order transition, around 17 K and superconductivity at the lowest temperature are clearly observed at ambient pressure. With increasing pressure, the transition temperature of hidden-order (T_0) and that of superconductivity (T_{sc}) changes gradually. However, they are replaced by an antiferromagnetic ordering above a critical pressure $P_x = 0.8$ GPa. It is also remarkable that the temperature dependence of the resistivity just above the superconducting transition varies with increasing pressure. At low pressures, the resistivity as a function of temperature follows a power law in a wide temperature region, as demonstrated by the linear behaviour in the logarithmic plot. At higher pressures above the critical pressure, deviation from the linear behaviour is observed at low temperature, suggesting that the temperature dependence cannot be expressed by a single exponent. This observation indicates that resistivity measurement under pressure would give a difference in the electron scattering between hidden-order and antiferromagnetic states. Note also that the resistivity just above the resistance drop due to superconductivity is about 10^{-3} of the room temperature value at 1.51 GPa. The intrinsic RRR should be higher than 1000 for this sample.

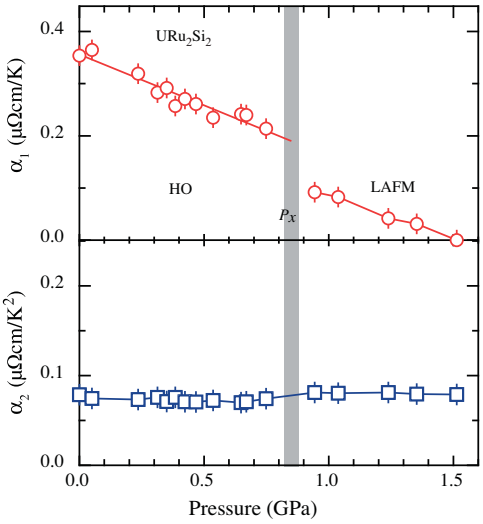

Figure 6. (colour online) Pressure dependence of the coefficients α_1 and α_2 [12].

By analyzing the present data, we found that the temperature dependence of resistivity can be decomposed in two parts: one corresponds to a 'normal' scattering proportional to T^2 due to electron-electron scattering and another one corresponds to 'anomalous' component proportional to T. Note also that at low temperatures other contributions to resistivity such as lattice vibrations can be neglected. The total resistivity can therefore be expressed as follows:

$$\rho = \rho_0 + \alpha_1 T + \alpha_2 T^2 \tag{1}$$

The pressure dependence of the contribution of each term is plotted in Figure 6. 'Anomalous' component α_1 decreases with increasing pressure and discontinuously decreases at the critical pressure. α_1 in the high-pressure antiferromagnetic phase is still finite. This is most likely due to the remaining hidden-order component existing above the first-order transition line, as suggested in the inelastic neutron scattering experiment [13]. High-pressure data at 1.51 GPa shows $\alpha_1 = 0$, suggesting that there is no remaining hidden-order state. From this we concluded that the anomalous scattering α_1 only exists in the hidden-order state. On the other hand, the 'normal' contribution α_2 is almost temperature-independent. It means that electronic state in both hidden-order and antiferromagnetic states is similar. In fact, Fermi surfaces obtained in both phases agree fairly well [14,15] in consistent with the present observation. We also note that the magnitude of the anomalous resistivity (α_1) changes as a function of pressure. Furthermore it was found that α_1/α_2 is closely related to the superconducting-transition temperature, as shown in Figure 7. As mentioned above, the normal component α_2 is almost pressure independent. The present result, therefore, demonstrates that α_1 is proportional to T_{sc}. This observation strongly suggests that the anomalous resistivity only existing in the hidden-order phase drives heavy fermion superconductivity at lower temperature.

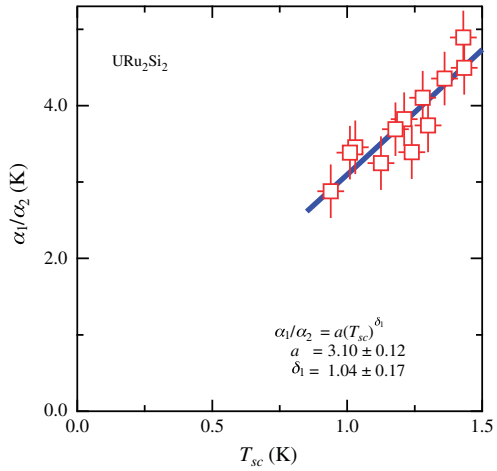

Figure 7. (colour online) The resistivity coefficient α_1/α_2 is plotted against T_{sc} [12].

5. Concluding remarks

We studied the long-standing problem in URu_2Si_2 using an extremely high-quality single-crystal growth and high-pressure techniques. As a result, hidden-order state causes an anomalous scattering on conduction electrons and, furthermore, it is intimately related to the heavy fermion superconductivity in this compound. Although the nature of the hidden-order is still unclear, the present observation indicates that the anomalous scattering is one of the very important properties characterizing the hidden-order state. The present anomalous resistivity $\alpha_1 T$ can be found in other correlated electrons systems such as high-temperature superconducting cuprates and heavy-fermion systems. On the other hand, an ordered phase which does not accompany an explicit phase transitions were often observed in those compounds. One of the prominent examples is so-called pseudo-gap phase of high-temperature superconductors. Hidden-order state and other mysterious ordering might be the general characteristics of correlated electron systems. Our high-quality single crystal stimulates scientists developing new novel measurement techniques [16–18]. We expect new findings concerning the hidden-order using these techniques.

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