

Hidden-order state in URu₂Si₂: High-quality single crystal and novel techniques

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URu₂Si₂ is one of the heavy fermion compounds where the effective mass of the conduction electron is large compared to that of ordinary metals. This compound has been particularly investigated because of its remarkable features. One is the occurrence of superconductivity below 1.4 K where the ‘heavy electrons’ form Cooper pairs. Another one is a phase transition occurring at higher temperature 17.5 K. Early researches suggested this is due to a magnetic phase transition, because the 5f electrons carries magnetic moments and it is natural to assume that they order below the transition temperature. However, any efforts to detect the signature of the magnetic ordering have failed since its discovery in 1985 [1]. Other possibilities such as the ordering of multipolar moments of 5f electron were investigated but no clear evidence was found. The nature of the ‘hidden-order’ state is now one of the important subjects in condensed-matter physics.

To tackle this problem we carefully prepared a high quality single crystal of URu₂Si₂ to eliminate impurity effects which become significant at low-temperatures. Using the Czochralski pulling method and subsequent solid-state electrotransport annealing under ultra high vacuum [2], we succeeded to prepare an extremely pure single crystal. The purity of the metallic compound is measured by the residual resistivity ratio (RRR) where the residual resistivity at very low temperature reflects impurity concentration. Our sample shows RRR ~1000, much larger than the samples prepared by other researchers. Figure 1 shows the temperature dependence of electrical resistivity of URu₂Si₂ clearly showing the hidden-order transition at T₀=17.5 K and superconducting one at 1.4 K. Among the 5 samples, No. 1 shows the lowest residual resistivity. This single crystal was investigated further using two experimental techniques, high energy-resolution photoemission spectroscopy [3] and torque magnetometry using a micro cantilever [4].

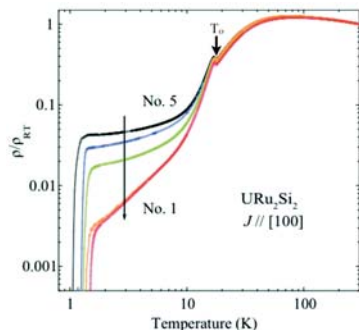


Fig. 1 Temperature dependence of electrical resistivity in URu₂Si₂.

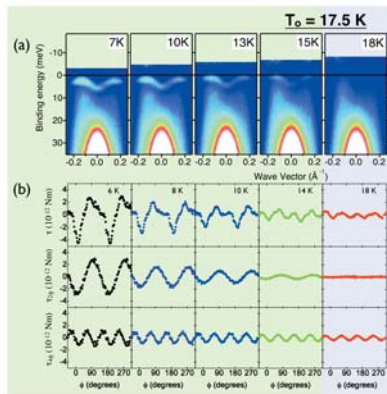


Fig. 2 (a) Photoemission spectra [3] and (b) magnetic torque [4] of URu₂Si₂ as a function of temperature.

The results are summarized in Fig. 2. Fig. 2(a) shows the intensity mapping of the photoelectron as functions of the binding energy and wave vector. At 18 K the spectrum consists of a strong intensity around 30 meV (originating from the surface effect) and hole band cutting the Fermi energy ($E = 0$ meV). On cooling below the transition temperature 17.5 K, a new feature appears around 2-5 meV. The intensity of the narrow band increases with decreasing temperature. Fig. 2(b) is the result of the magnetic torque measurements. The upper panels show the total magnetic anisotropy as a function of magnetic field angle within the tetragonal basal plane, while the middle and bottom panels correspond to the decomposed two-fold and four-fold components, respectively. Because of the tetragonal structure of URu₂Si₂, the magnetic anisotropy should follow the tetragonal (four-fold) rotational symmetry. Above 17.5 K, in fact, the magnetic torque can be expressed by a four-fold oscillation. However in the hidden-order state, a two-fold component, which breaks the crystal symmetry, appears.

These observations clearly demonstrate the emergence of a new electronic state in the hidden-order state and provide new insights for the exotic phase transition observed in highly correlated electron systems.

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A specific Ce anomaly during sorption of rare earth elements on biogenic Mn oxide produced by *Acremonium* sp. strain KR21-2

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Microbial oxidation of Mn(II) occurs at rates of up to 5 orders of magnitude greater than abiotic Mn(II) oxidation [1]. Mn(II)-oxidizing microorganisms are thought to play an important role in the formation of Mn oxides in most natural environments [2]. It is well known that oxidation of Ce(III) by synthetic Mn oxide causes Ce sorption anomaly in rare earth element (REE) partitioning pattern [3]. However, the sorption behavior of REE and Ce oxidation process by biogenic Mn oxide have not been clarified. In the present study, we examined the relevance of microorganisms to the Ce(III) oxidation process by biogenic Mn using *Acremonium* sp. strain KR21-2 [4]. To accomplish this, we made sorption experiments of REEs between biogenic Mn oxides and aqueous solution.

We used *Acremonium* sp. strain KR21-2 as a model of Mn-oxidizing fungi, as described above. The hyphae and biogenic Mn oxide were put into 100 mL of 10 mmol/L NaCl solution which contains 100 ng/mL REE each. The initial pH was then adjusted with NaOH and HCl solutions. Sample solutions after 25 h were collected by filtration with a 0.2 μm filter. REE concentrations in the solutions were determined with ICP-MS. We characterized REE species in the solutions using size exclusion column (SEC) HPLC-ICP-MS. Cerium L_{III}-edge X-ray absorption near edge structure (XANES) spectra were recorded at beamline 12C at the Photon Factory, KEK (Tsukuba, Japan), to determine the oxidation state of Ce sorbed on biogenic Mn oxide.

The distribution coefficient of REE, $K_d(\text{REE})$, between solid and solution is defined as the following equation: $K_d(\text{REE}) = ([\text{REE}]_{\text{solid}} - [\text{REE}]_{\text{aq}})/c[\text{REE}]_{\text{aq}}$, where the term c (g/mL) is the ratio of solid to solution. The $K_d(\text{REE})$ patterns for the mixture of hyphae and biogenic Mn oxide (called biogenic Mn oxide hereinafter) at pH 3.83 showed a positive Ce anomaly, suggesting Ce(III) oxidation on biogenic Mn oxide (Fig. 1). Such large positive Ce anomaly was also reported in sorption of REE on abiotically synthesized Mn oxide [3]. The polarity of

Ce anomaly shifted from positive to negative with increasing pH, and negative Ce anomaly was observed at pH 6.64 (Fig. 1), indicating Ce was preferentially remained in solution phase.

Cerium L_{III}-edge XANES spectra were shown in Fig. 2. The trivalent Ce reference species of Ce₂(CO₃)₃·8H₂O and the Ce(III) aqueous solution show a single white line peak at 5726 eV. In contrast, two distinct peaks were observed for the Ce(IV) compound of Ce(SO₄)₂·nH₂O around 5729 and 5737 eV. The XANES spectra of the Ce sorbed biogenic Mn oxide samples at pH 3.83, 6.16 and 6.64 show double white line peaks 5726 and 5737 eV. In particular, the second peak around 5737 eV common to the Ce(IV) references clearly indicates that Ce(III) was oxidized to Ce(IV) by the biogenic Mn oxide samples.

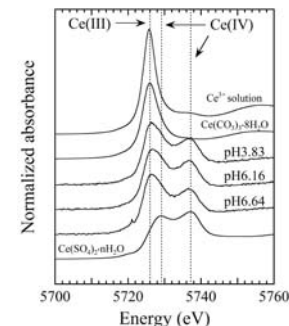


Fig. 2 Ce L_{III}-edge XANES spectra.

In the present study the positive Ce anomaly for the biogenic Mn oxide was observed at pH 3.83, and decreased with increasing pH (Fig. 1). Furthermore, negative Ce anomaly was observed at pH 6.64. The trend observed for our data is quite opposite to that observed for the previous studies using abiotically synthesized Mn oxide, where the degree of positive Ce anomaly increased with increasing pH [3]. The negative Ce anomaly indicates that a larger fraction of Ce was present in solution phase (i.e. < 0.2 μm fraction) than that of La and Pr (Fig. 1). SEC-HPLC-ICP-MS analysis demonstrated that the specific organic molecules had preferentially complexed with Ce(IV) in solution phase. A line of our data indicates that the negative Ce anomaly at pH 6.64 arose from Ce(III) oxidation on the biogenic Mn oxide and subsequent complexation of Ce(IV) with organic ligands released from fungal cells.

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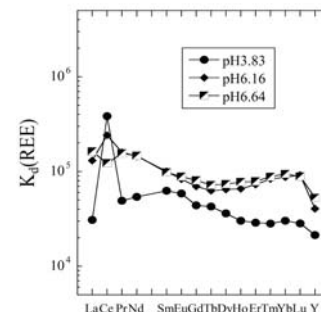


Fig. 1 $K_d(\text{REE})$ patterns at different pHs.