Anisotropic Lattice Compression and Possible Valence Change in Kondo Compound CeAu$_2$Si$_2$

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Lattice constants and crystal structure of tetragonal Kondo compound CeAu$_2$Si$_2$ have been investigated at high pressure in order to examine pressure-induced change of crystal structure and gradual valence change of Ce atom. It is found that the lattice constants $a$ and $c$ decrease with increasing pressure without any discontinuity up to 13 GPa at room temperature. The bulk modulus $B_0$ and its pressure derivative $B'_0$ were obtained to be 112 GPa and 3.2. These values are comparable with other Kondo compounds. From the $\rho(T)$ curve at high pressure which does not change so much under high pressure, it is suggested that the valence of Ce changes sluggishly with pressure and the Kondo state of CeAu$_2$Si$_2$ is very stable at high pressure.

Key words: high pressure, structural change, electrical resistivity, Kondo effect, X-ray diffraction.

1. Introduction

The Kondo compounds including Ce have been investigated extensively because they have a lot of interesting physical properties such as magnetic ordering, quantum phase transition, superconductivity and so forth. The electronic states and the characteristic Kondo temperature $T_K$ of these compounds have been well known to be strongly affected by applying pressure since the hybridization between conduction band and 4$f$ level is influenced significantly by applying pressure. Then the valence of Ce is also changed by applying pressure, which is reflected in the pressure dependence of electrical resistance and volume or lattice constants. Since the valence fluctuation has been recently considered as a perspective candidate for superconductivity, the investigation of the mechanism may give a large progress in this research field. In this study we attempted to measure the pressure dependence of lattice constant and electrical resistance to examine the possible valence and the crystal structure change at high pressure.

2. Experimental procedure

The preparation of the single crystalline sample was described previously. The powdered sample was obtained by crashing that. Hydrostatic pressure was generated using WC Bridgman type anvils having a face of 3 mm in diameter. The powders of the sample and NaCl were placed in a small hole having 0.3 mm diameter at the center of a beryllium gasket. A mixture of 4:1 methanol/ethanol was used as a pressure transmitting medium. The diffraction lines were recorded on the imaging plate and the diffraction angles were obtained by using personal computer. The electrical resistance was measured by means of cubic anvil press up to 8 GPa at The Institute of Solid State Physics, Tohoku University, Sendai, 980-8578, Japan.

Fig.1: The lattice constants $a$ and $c$ as a function of pressure

Fig.2 The $c/a$ ratio as a function of pressure.
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3. Results

3.1 Lattice compression

Since there appear no new diffraction lines in the powder diffraction spectra, the crystal structure of ThCr$_2$Si$_2$ is stable at least up to 13 GPa. Fig. 1 shows the lattice constants of $a$ and $c$-axis as a function of pressure below 13 GPa at room temperature. It is seen that the $a$ and $c$-axis change smoothly with pressure within experimental errors. The linear compressibilities for $a$ and $c$-axis were obtained to be $\kappa_a = 3.68 \times 10^{-3}$ GPa$^{-1}$, $\kappa_c = 2.69 \times 10^{-3}$ GPa$^{-1}$, respectively. This result indicates that the $a$-axis is more compressible than the $c$-axis, i.e., the compression is anisotropic, which implies that the cohesive energy is anisotropic. Fig. 2 shows the $da/dp$ ratio as a function of pressure. Reflecting the anisotropic compressibilities, the value increases with increasing pressure. The increase of $da$ at high pressure has been also observed in other Ce Kondo compounds.$^{7,8}$

3.2 Pressure dependence of volume

Fig.3 shows the values of $V/V_0$ as a function of pressure up to 13 GPa at room temperature, where $V$ ($= ca^2$) and $V_0$ are the volumes at high and ambient pressure, respectively. $V/V_0$ decreases smoothly with increasing pressure below 13 GPa without any anomalies. The bulk modulus was obtained by assuming the Murnaghan’s equation of state, which is described as follows,

$$\frac{V}{V_0} = \left( \frac{B_0'}{B_0} \times P + 1 \right)^{1/\kappa_0} \quad (1)$$

where $B_0$ and $B_0'$ are the bulk modulus and its pressure derivative at ambient pressure, respectively. By least square fitting of the experimental data to eq.(1), we obtained $B_0 = 112$ GPa and $B_0' = 3.2$, respectively.

3.3 Electrical resistance at high pressure.

Fig.4 shows the electrical resistance ($R$) of CeAu$_2$Si$_2$ as a function of pressure up to 8 GPa. It is found that $R$ increases smoothly with increasing pressure. This result indicates that there are no large or discontinuous changes in the electronic structure up to 8 GPa such as $\gamma$-$\alpha$ transition in Ce metal,$^{9}$ which is consistent with the result of pressure dependence of volume described in foregoing sections at least up to 8 GPa. Fig. 5 indicates the $\rho(T)$ of CeAu$_2$Si$_2$ at high pressure. $\rho(T)$ has a peak around 8 K and a broad shoulder around 150 K. The former peak is due to combined Kondo effect and magnetic ordering. Indeed the susceptibility shows a rapid drop around 8 K, indicating antiferromagnetic ordering.$^{10}$ The magnitude of electrical resistivity increases with pressure in the whole temperature range.

4. Discussion

4.1 Comparison with the compression curve with those of other Ce Kondo compounds

The lattice compression of Ce Kondo compounds has been reported by many authors.$^{11}$ For example, the pressure dependence of volume of CeRh$_2$Si$_2$ was reported by Ohashi et al.$^{12}$, in which the value of $V/V_0$ changes continuously with pressure. Considering the
\( \rho(T) \) curves at high pressure, this compound shows a continuous valence transition having \( B_0 = 139 \text{ GPa} \) and \( B'_0 = 2.2 \). Table 1 shows the values of \( B_0 \) and \( B'_0 \) for typical Ce Kondo compounds\(^{13}\). It is seen that the values of \( B_0 \) are strongly dependent on sample but the values of \( B'_0 \) shows a systematic behavior in which \( B'_0 \) is large, about 6, for nonmagnetic LaAl\(_2\) but between 2 and 3 for the Ce Kondo compounds showing pressure-induced continuous valence transition\(^{14}\). In this sense, CeAu\(_2\)Si\(_2\) is classified as a Kondo compound showing pressure induced valence transition.

Table 1: \( B_0 \) and \( B'_0 \) for several Ce Kondo compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( B_0 ) (GPa)</th>
<th>( B'_0 )</th>
<th>Valence transition from ( \rho(T) ) curve</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeAu(_2)Si(_2)</td>
<td>112</td>
<td>3.3</td>
<td>moderate</td>
</tr>
<tr>
<td>CeRh(_2)Si(_2)</td>
<td>139</td>
<td>2.2</td>
<td>Yes</td>
</tr>
<tr>
<td>CeAl(_3)</td>
<td>54</td>
<td>3.0</td>
<td>Yes</td>
</tr>
<tr>
<td>CeAl(_2)</td>
<td>66</td>
<td>3.3</td>
<td>Yes</td>
</tr>
<tr>
<td>LaAl(_2)</td>
<td>70</td>
<td>6.0</td>
<td>no</td>
</tr>
</tbody>
</table>

### 4.2 Relation between the electrical resistance and valence transition

Figs.6 (a) and (b) are the pressure dependence of \( V/V_0 \) and the temperature dependent electrical resistivity \( \rho(T) \) of Kondo compound CeAl\(_2\) at high pressure\(^{15}\). CeAl\(_2\) is well-known to show a pressure-induced continuous valence transition\(^2,10\), which is reflected in the \( \rho(T) \) curves under high pressure. At ambient pressure the \( \rho(T) \) shows typical concentrated Kondo properties such as \( \log T \) dependence followed by magnetic ordering. The \( \rho(T) \) at 3 GPa has a broad peak at low temperature but it disappears at 8 GPa, in which \( \rho(T) \) shows a smooth change with increasing temperature same as that of normal metals. The Kondo temperature \( T_K \) of CeAl\(_2\) at ambient pressure is 6 K but it increases with pressure and becomes around 290 K at 6 GPa\(^{15}\). So the \( \rho(T) \) at 8 GPa shows a smooth temperature dependence similar to that of high \( T_K \) Kondo compounds. Such correspondences between \( \rho(T) \) curves at high pressure and valence changes have been observed in many Kondo compounds\(^{14,16}\).

From the result described in Fig. 5, it should be noted that the shape of \( \rho(T) \) curve is not affected strongly by pressure up to 8 GPa. This is in sharp contrast with those of CeAl\(_2\) and other Kondo compounds\(^{11,14}\), in which the \( \rho(T) \) curves are affected significantly by applying pressure as shown in Fig.6(b). Considering these facts, the valence change in CeAu\(_2\)Si\(_2\) occurs slowly compared with the case of other Ce Kondo compounds. Furthermore the \( T_K \) (~ 8 K) roughly evaluated from the peak in \( \rho \) seems not to increase so much by applying pressure. In other words, the Kondo state in CeAu\(_2\)Si\(_2\) is strongly stable at high pressure.

Usually the electronic states of Kondo compounds have been discussed on the basis of the Doniach's phase diagram\(^{17}\), in which the pressure dependence of \( T_N \) plays an important role in determining where the material exists in this diagram. From the pressure dependence of \( T_N \), it is suggested that CeAu\(_2\)Si\(_2\) is near the top of the peak of this phase diagram\(^{16,18}\). On the other hand, since CeAl\(_2\) is on the right hand side of that and very near the border of the critical pressure, \( T_N \) of CeAl\(_2\) disappears at high pressure and we observe quantum critical transition at moderate high pressure\(^{15}\). Taking these facts into account, we need high pressure more than several 10 GPa in order to give rise to induce the quantum phase transition in CeAu\(_2\)Si\(_2\).

### 5. Conclusion

In the present work, we have carried out the measurement of lattice constants and electrical resistance of CeAu\(_2\)Si\(_2\) at high pressure. The results are summarized as follows.

1) The lattice constants along \( a \) and \( c \) axes changed continuously with pressure and the bulk modulus and its pressure derivative are obtained to be 112 GPa and 3.2, respectively.

2) The electrical resistivity increases smoothly with...
increasing pressure up to 8 GPa. This fact shows that there is no phase transition below 8 GPa.

3) Comparing the present results with that of other Kondo compounds, it is suggested that the valence change in CeAu$_2$Si$_2$ occurs very slowly with increasing pressure.

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References


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