Relation between the atomic distance and the Ce valence of amorphous Ce$_x$Ru$_{100-x}$

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Abstract. We report the local structure of amorphous alloys Ce$_x$Ru$_{100-x}$ ($x=9$, 43 and 80) and a C15 Laves phase compound CeRu$_2$ determined from an extended x-ray absorption fine structure measurements near Ru K edge and Ce K edge. The structure analyses indicate that the Ce-Ru and Ru-Ru interatomic distances of amorphous Ce$_x$Ru$_{100-x}$ are constant for all of the Ce concentration, while the Ce-Ce distance increases with increasing the Ce content. The interatomic distance of Ru-Ru in the amorphous alloy system is as same as that of the CeRu$_2$ compound. The Ce-Ce interatomic distance of amorphous Ce$_x$Ru$_{100-x}$ is closely connected with the Ce valence.

1. Introduction

The Ce-Ru amorphous alloy system (a-Ce$_x$Ru$_{100-x}$, where $x$ means the Ce concentration in atomic percent) has a wide variety of electronic properties. It shows the heavy fermion like behavior in the Ce-rich region ($x\geq 67$) and the superconductivity in the Ru-rich concentration ($x\leq 39$) [1-3]. The electronic properties of a-Ce$_x$Ru$_{100-x}$ depend strongly on the Ce 4f electrons and therefore the valence of Ce atoms [4]. The C15 cubic Laves phase intermetallic compound CeRu$_2$ (x-CeRu$_2$) shows superconductivity of which the Ce valence is 3.36 [4-6]. We have found the linear relation between the energy of transition to the continuum and the valence of Ce atoms for both a-Ce$_x$Ru$_{100-x}$ and x-CeRu$_2$ and also the Ce valence values of 3.44, 3.29 and 3.13 for a-Ce$_x$Ru$_{100-x}$ of $x=9$, 43 and 80, respectively. These findings provide evidence that the 4f electron is the origin of the heavy fermion like behavior in a-Ce$_x$Ru$_{100-x}$ [4]. In general the electronic properties of alloys and compounds are quite sensitive to their crystallographic structure. Especially the local atomic arrangement around a specific atom influences predominantly to the electronic states of the atom. For example, although both $\alpha$-cerium and $\gamma$-cerium possess a face centered cubic structure, their interatomic distances between Ce atoms are quite different from each other: 3.65 Å for $\gamma$-cerium and 3.41 Å for $\alpha$-cerium [7]. The valence of $\alpha$-cerium is reported to be tetravalent, while the $\gamma$-cerium is trivalent [8]. Also in the case of a-Ce$_x$Ru$_{100-x}$ the local structure is a crucial factor of determining the electronic properties. Because the extended x-
ray absorption fine structure (EXAFS) is especially sensitive to the short range order [9], it is one of the best techniques for detecting the local structure of amorphous materials with no long range order. The oscillatory part of EXAFS contains the atomic local structure information such as coordination number and bond length [10, 11]. Here we report on the local structure of the Ce $K$ edge and Ru $K$ edge in $a$-$Ce_{x}Ru_{100-x}$.

2. Experimental Details

Ingots of the $Ce_{x}Ru_{100-x}$ alloys were prepared by arc melting of the appropriate amounts of 99.9% Ce and 99.9% Ru in an argon atmosphere. The amorphous phase of $Ce_{x}Ru_{100-x}$ was fabricated by DC high-rate sputtering. The compound $x$-$CeRu_{2}$ was also prepared as a reference material. Another references used were 99.9% cerium trifluoride ($x$-$CeF_{3}$) and 99.9% cerium dioxide ($x$-$CeO_{2}$).

The x-ray diffraction patterns were measured using Cu $K\alpha$ radiation in a conventional $\theta$$-2\theta$ scan mode. The chemical composition of $a$-$Ce_{x}Ru_{100-x}$ was fixed to be $x$=9, 43 and 80 by electron-probe microanalysis.

The EXAFS measurements near Ru and Ce $K$ edges were carried out at the beamline NW10A with a Si (311) double crystal monochromator in Photon Factory [11]. The storage ring was operated at 6.5 GeV with an initial current of about 50 mA. All the spectra were measured at 10 K and 300 K in the transmission mode using the ionization chambers filled with a mixed gas of 50% $N_{2}$ and 50% Ar in front of the sample and a pure Kr gas behind it for Ru $K$ edge; for Ce $K$ edge a pure Kr gas was filled in both the ionization chambers. The incident energy of photons was corrected with the energy for a prepeak near the Cu $K$ edge.

3. Results and Discussion

Figure 1 shows the x-ray diffraction patterns of $a$-$Ce_{x}Ru_{100-x}$ with the references $x$-$CeRu_{2}$, $x$-$CeO_{2}$ and $x$-$CeF_{3}$. No reflections except a broad bump near about 40 degree are detected for $a$-$Ce_{x}Ru_{100-x}$, which means that it is in the amorphous phase. We obtain the following by the Rietveld refinement of these patterns. The compound $x$-$CeRu_{2}$ crystallizes in the C15 Laves phase structure with the lattice constant of 7.5381 Å, in which the Ce atom has twelve nearest neighbors of Ru at 3.1251 Å and four Ce atoms at 3.2641 Å, while Ru is surrounded by six Ru atoms at 2.6651 Å and six Ce atoms at 3.1251 Å. The oxide $x$-$CeO_{2}$ is the CaF$_2$ structure with the Fm$3m$ space group and lattice constant of 5.4109 Å, where the Ce has twelve neighboring Ce atoms at 3.8262 Å and eight O atoms at 2.3431 Å. The fluoride $x$-$CeF_{3}$ has the P6$mmc$ space group symmetry and lattice constant of 7.0930 Å, in which Ce has four nearest Ce atoms at 4.0570 Å and seven F atoms at 2.4448 Å, 2.4260 Å, 2.3862 Å, 2.4056 Å and 2.3866 Å.

![Figure 1. X-ray diffraction patterns of $a$-$Ce_{x}Ru_{100-x}$ ($x$=9, 43 and 80) and the compound $x$-$CeRu_{2}$, along with cerium dioxide $x$-$CeO_{2}$ and cerium trifluoride $x$-$CeF_{3}$ for comparison. A halo pattern appears around 40 degree for $a$-$Ce_{x}Ru_{100-x}$. The typical index of the plane is labelled for the crystalline materials.](image)

![Figure 2. Normalized x-ray absorption near the Ru $K$ edge at 10 K for $a$-$Ce_{x}Ru_{100-x}$ and $x$-$CeRu_{2}$ plotted against photon energy.](image)
The EXAFS signals are derived from the routine procedure of background removal, spline smoothing and normalization. Figure 2 represents normalized x-ray absorption spectra near the Ru $K$ edge measured at 10 K as a function of photon energy $E$ for a-Ce$_x$Ru$_{100-x}$ and x-CeRu$_2$. The radial structure functions $\Phi(R)$ obtained from Fourier transform of $k^2\chi(k)$ are displayed in Figs. 3(a) and (b) for a-Ce$_x$Ru$_{100-x}$ and x-CeRu$_2$. The thick and thin lines denote the magnitude and the imaginary part of $\Phi(R)$. In Fig. 3(a) the peaks at 2.45 Å and 3.45 Å for a-Ce$_x$Ru$_{100-x}$ correspond to the Ru and Ce atoms around the central Ce atom. Surprisingly the peak of the Ce-Ru pair disappears for a-Ce$_{80}$Ru$_{20}$. We have not yet figured out the puzzle. It is why we have not shown the structural parameter for the Ce-Ru pair in Table 1. In x-CeRu$_2$ the peak at 2.30 Å and 3.00 Å indicate the Ru and Ce atoms. To estimate the structural parameters, we reconvert $\Phi(R)$ into $k^2\chi(k)$ with the Fourier filtering technique for each peaks of $\Phi(R)$. The Fourier filtered $k^2\chi(k)$ spectrum is fitted to the following EXAFS formula by the least squares method [9, 12],

$$\chi(k) = \sum N_i |f_i(k, \pi)| \exp(-2(\sigma_i^2 k^2 + R_i^2 \lambda)) / k R_i^2 \cdot \sin(2kR_i + \delta_i(k)), \quad (1)$$

where $N_i$ is the coordination number, $f_i(k, \pi)$ is backscattering amplitude, $\sigma_i$ is Debye-Waller factor, $R_i$ is the interatomic distance between the absorber and the $i$-th neighboring atom, $\delta_i$ is the phase shift. The program FEFF8.4 is now widely used for estimate $f_i(k, \pi)$ and $\delta_i$ from some model structure [13]. Unfortunately we have no idea about the structure of our amorphous specimens. They are insensitive to the interatomic distance and mainly determined by atomic pair distribution function. Therefore we consider that in the amorphous phase with unknown structure they are similar to those of x-CeRu$_2$. As an example the Fourier filtered spectrum of a-Ce$_9$Ru$_{91}$ at Ru $K$ edge is illustrated in Fig. 4 by the open circle. The solid line shows the best fit to the spectrum. The parameters about the local structure thus determined are listed in Tables 1 and 2. We obtain quite small coordination numbers for a-Ce$_{43}$Ru$_{57}$. This may be because that the structure function for a-Ce$_{43}$Ru$_{57}$ in Fig. 3 is weaker than that of the others and that we made a simplified Gaussian analysis for a-Ce$_{43}$Ru$_{57}$ with higher disorder. The interatomic distance for x-CeF$_3$, x-CeO$_2$ and x-CeRu$_2$ are quite close to the corresponding value estimated from the lattice constant using the x-ray diffraction. In a-Ce$_x$Ru$_{100-x}$
Table 1. Structural parameters of $\text{a-Ce}_x\text{Ru}_{100-x}$ with $x$-$\text{CeF}_3$, $x$-$\text{CeO}_2$ and $x$-$\text{CeRu}_2$ determined from the Ce $K$ edge EXAFS where $A$ is an absorbing atom, $B$ is a backscattering atom, $N$ is the coordination number, $R$ is the interatomic distance, $\sigma$ is the Debye-Waller factor.

| Ce K edge | Temp | A-B       | $N$ | $R$ / Å | $\sigma$ / Å |
|-----------|------|-----------|-----|---------|--------------|
| $x$-$\text{CeF}_3$ | 300 K | Ce-F       | 7   | 2.41 (0.01) | 0.09 (0.01) |
|           |      | Ce-Ce     | 4   | 4.07 (0.01) | 0.09 (0.01) |
| $x$-$\text{CeO}_2$ | 300 K | Ce-O       | 8   | 2.33 (0.01) | 0.09 (0.01) |
|           |      | Ce-Ce     | 12  | 3.83 (0.01) | 0.07 (0.01) |
| $x$-$\text{CeRu}_2$ | 300 K | Ce-Ru     | 12  | 3.13 (0.01) | 0.13 (0.01) |
|           |      | Ce-Ce     | 4   | 3.26 (0.01) | 0.10 (0.01) |
| $x$-$\text{CeRu}_2$ | 10 K  | Ce-Ru     | 12  | 3.13 (0.01) | 0.07 (0.01) |
|           |      | Ce-Ce     | 4   | 3.26 (0.01) | 0.06 (0.01) |
| $\text{a-Ce}_9\text{Ru}_{91}$ | 300 K | Ce-Ru     | 8.3 (0.4) | 2.79 (0.02) | 0.11 (0.01) |
|           |      | Ce-Ce     | 1.3 (0.1) | 3.72 (0.02) | 0.08 (0.01) |
| $\text{a-Ce}_9\text{Ru}_{91}$ | 10 K  | Ce-Ru     | 9.0 (0.4) | 2.79 (0.02) | 0.10 (0.01) |
|           |      | Ce-Ce     | 1.4 (0.1) | 3.72 (0.02) | 0.07 (0.01) |
| $\text{a-Ce}_{43}\text{Ru}_{57}$ | 300 K | Ce-Ru     | 0.4 (0.1) | 2.79 (0.03) | 0.10 (0.01) |
|           |      | Ce-Ce     | 0.4 (0.1) | 3.75 (0.02) | 0.08 (0.01) |
| $\text{a-Ce}_{43}\text{Ru}_{57}$ | 10 K  | Ce-Ru     | 0.9 (0.3) | 2.78 (0.03) | 0.09 (0.01) |
|           |      | Ce-Ce     | 0.9 (0.3) | 3.74 (0.02) | 0.07 (0.01) |
| $\text{a-Ce}_{50}\text{Ru}_{20}$ | 300 K | Ce-Ru     | ---- | ---- | ---- |
|           |      | Ce-Ce     | 10.1 (1.1) | 3.84 (0.02) | 0.10 (0.01) |
| $\text{a-Ce}_{50}\text{Ru}_{20}$ | 10 K  | Ce-Ru     | ---- | ---- | ---- |
|           |      | Ce-Ce     | 10.1 (1.1) | 3.84 (0.02) | 0.11 (0.01) |

Table 2. Structural parameters of $\text{a-Ce}_x\text{Ru}_{100-x}$ and $\text{x-CeRu}_2$ determined from the Ru $K$ edge EXAFS where $A$ is an absorbing atom, $B$ is a backscattering atom, $N$ is the coordination number, $R$ is the interatomic distance, $\sigma$ is the Debye-Waller factor.

| Ru K edge | Temp | A-B       | $N$ | $R$ / Å | $\sigma$ / Å |
|-----------|------|-----------|-----|---------|--------------|
| $\text{x-CeRu}_2$ | 300 K | Ru-Ce     | 6   | 3.13 (0.02) | 0.13 (0.01) |
|           |      | Ru-Ru     | 6   | 2.67 (0.01) | 0.09 (0.01) |
| $\text{x-CeRu}_2$ | 10 K  | Ru-Ce     | 6   | 3.13 (0.02) | 0.08 (0.01) |
|           |      | Ru-Ru     | 6   | 2.67 (0.01) | 0.06 (0.01) |
| $\text{a-Ce}_9\text{Ru}_{91}$ | 300 K | Ru-Ce     | 0.8 (0.3) | 2.80 (0.02) | 0.10 (0.01) |
|           |      | Ru-Ru     | 7.8 (1.0) | 2.68 (0.02) | 0.11 (0.01) |
| $\text{a-Ce}_9\text{Ru}_{91}$ | 10 K  | Ru-Ce     | 0.8 (0.3) | 2.80 (0.02) | 0.08 (0.01) |
|           |      | Ru-Ru     | 7.8 (1.0) | 2.68 (0.02) | 0.10 (0.01) |
| $\text{a-Ce}_{43}\text{Ru}_{57}$ | 300 K | Ru-Ce     | 1.1 (0.2) | 2.80 (0.03) | 0.12 (0.01) |
|           |      | Ru-Ru     | 1.1 (0.2) | 2.69 (0.03) | 0.11 (0.01) |
| $\text{a-Ce}_{43}\text{Ru}_{57}$ | 10 K  | Ru-Ce     | 1.7 (0.4) | 2.80 (0.03) | 0.11 (0.01) |
|           |      | Ru-Ru     | 1.7 (0.4) | 2.69 (0.03) | 0.10 (0.01) |
| $\text{a-Ce}_{50}\text{Ru}_{20}$ | 300 K | Ru-Ce     | 7.7 (1.0) | 2.80 (0.03) | 0.10 (0.01) |
|           |      | Ru-Ru     | 1.9 (0.2) | 2.69 (0.02) | 0.11 (0.01) |
| $\text{a-Ce}_{50}\text{Ru}_{20}$ | 10 K  | Ru-Ce     | 7.7 (1.0) | 2.80 (0.03) | 0.09 (0.01) |
|           |      | Ru-Ru     | 1.9 (0.2) | 2.69 (0.02) | 0.10 (0.01) |
we confirm that the Ce-Ru interatomic distance deduced from the Ce $K$ edge is equal to that of the Ru $K$ edge within the accuracy of fitting. In a-Ce$_x$Ru$_{100-x}$ the distance between Ce atoms goes up from 3.72 Å to 3.84 Å with increasing Ce content, which is much longer than that of x-CeRu$_2$. On the other hand the Ce-Ru interatomic distance is rather shorter than that of x-CeRu$_2$ and independent of the Ce fraction. The Ru-Ru distance is also independent of the Ce content and very close to that of x-CeRu$_2$. The Ce-Ru and Ru-Ru distance of a-Ce$_x$Ru$_{100-x}$ does not obey the Vegard’s law.

It has been found that a-Ce$_x$Ru$_{100-x}$ shows a rapid increase in the effective magnetic moment per Ce atom derived from the Curie-Weiss law [3] and a linear decrease in the valence of Ce atoms with increase in the Ce concentration [4]. The Ce atom is in the mixed valence state between trivalent 4$^f_1$ and tetravalent 4$^f_0$ levels. It can be considered that the Ce valence or the number of 4$^f$ electrons is a crucial factor in determining the electronic properties of a-Ce$_x$Ru$_{100-x}$. To check this, we plot the relation of the Ce-Ce interatomic distance against the Ce valence in Fig. 5. The Ce-Ce distance increases rapidly with decreasing the Ce valence or increasing 4$^f$ electrons. The findings suggest that the volume of the Ce atom should be determined by the number of 4$^f$ electrons.

In Fig. 6 the Debye-Waller factor is represented for a-Ce$_x$Ru$_{100-x}$ and x-CeRu$_2$. In general it consists of the static disorder due to the structural configuration and the dynamic disorder caused by thermal vibration of atoms [14]. The Debye-Waller factor drawn in Fig. 6 includes the static disorder only because of measuring at 10 K. In a-Ce$_x$Ru$_{100-x}$ it is independent of the Ce content as shown by the broken line as same as the interatomic distance mentioned above and a little larger than that of x-CeRu$_2$. As tabulated in Tables 1 and 2 the Debye-Waller factor at 300 K for a-Ce$_x$Ru$_{100-x}$ is as same as that of 10 K, which means that the

Figure 4. Fourier filtered spectrum $k^3\chi(k)$ (open circle) plotted against wave vector $k$ for a-Ce$_9$Ru$_{91}$ at Ru K edge. The solid line denotes the best fit.

Figure 5. The Ce-Ce interatomic distance as a function of the Ce valence for a-Ce$_x$Ru$_{100-x}$. The broken line is a guide for the eyes.

Figure 6. The Debye-Waller factors of the Ru-Ru and Ce-Ru pairs for a-Ce$_x$Ru$_{100-x}$ (circle) and x-CeRu$_2$ (square). The broken line is a guide for the eyes.
disorder almost comes from the static origin. On the other hand for x-CeRu$_2$, it increases with increase in temperature.

4. Conclusion
The structural parameters for a-Ce$_x$Ru$_{100-x}$ such as the coordination number, the interatomic distance and the Debye-Waller factor have been determined from the Ce and Ru K edge EXAFS spectra. The nearest neighboring interatomic distance between Ce atoms increases remarkably with increasing the Ce concentration. On the other hand the Ce-Ru and Ru-Ru distances are thoroughly independent of the Ce content, which means that they do no obey the Vegard’s law. We have found the strong dependence of the Ce-Ce distance on the Ce valence or the number of 4f electrons.

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