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Influence of the Magnetic Moment on the Atomic Distance in Amorphous Ce_xRu_{100-x} *

Ying-Jie Li(李英杰)[1**], Ikuo Nakai(中井生央)[2],
Yusuke Amakai(雨海有佑)[3], Shigeyuki Murayama(村山茂幸)[3]

[1]*Inner Mongolia Key Laboratory for Physics and Chemistry of Functional Materials, Physics and Electronic Information College, Inner Mongolia Normal University, Hohhot 010022*
[2]*Department of Electrical and Electronic Engineering, Tottori University, Tottori 680-8552, Japan*
[3]*Department of Materials Science and Engineering, Muroran Institute of Technology, Muroran 050-8585, Japan*

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We perform the extended x-ray absorption fine structure (EXAFS) measurement to investigate the local structure of amorphous alloys Ce_xRu_{100-x} ($x = 9$, 43 and 80). The interatomic distances of the nearest Ru–Ce and Ru–Ru pairs derived from EXAFS are fully independent of Ce concentration. On the other hand the distance between neighboring Ce atoms increases sharply with the Ce content, which is exactly proportional to the Ce effective magnetic moment. We discuss the relation between the atomic distance and the effective magnetic moment from the point of view of the magneto-volume effect.

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Amorphous Ce–Ru alloy systems (a-Ce_xRu_{100-x}, where x is the Ce concentration in atomic percent) have a variety of electronic properties such as heavy-fermion-like behavior in the Ce-rich concentration range ($x \geq 67$) and the superconductivity in the Ru-rich region ($x \leq 39$) in low temperatures below 5 K.[1–3] The electronic properties are strongly dependent on the valence of Ce atoms of a-Ce_xRu_{100-x}, which are 3.44, 3.29 and 3.13 for $x = 9$, 43 and 80, respectively.[4] In Ru-rich region ($x \leq 39$), the Ce $4f$ electron behaves itinerantly so that the superconductivity comes out. In a Ce-rich region ($x \leq 39$), it acts as a localized electron and the heavy-fermion-like behavior is displayed. We found from the x-ray absorption spectroscopy near the Ce L_3 edge that the energy of the onset of the continuum depends linearly on Ce valence for a-Ce_xRu_{100-x} and a C15 Laves phase intermetallic compound $CeRu_2$ (x-$CeRu_2$). The valence provides evidence that the $4f$ electron is the origin of the heavy-fermion-like behavior of a-Ce_xRu_{100x}. Recently it was observed that the magnetic susceptibility of a-Ce_xRu_{100-x} with temperature-independent term subtracted obeys the Curie–Weiss law and that the effective magnetic moment per Ce atom decreases rapidly with decreasing Ce content.[3] Electronic properties of materials are quite sensitive to their structure and electronic states. In other words, great differences of electronic properties are often observed even in materials which consist of the same kinds of elements. This is due to the fact that another key to determining the electronic properties is the local structure of materials, which means the atomic arrangement around a specific atom. We here give an example of α-Ce and γ-Ce with the same face-centered cubic structure: the lattice constant and the valence are 4.85 Å and tetravalent in α-Ce; those of γ-Ce are 5.16 Å and trivalent. The magnetic susceptibility shows that the γ-Ce has a magnetic moment of about $2.54\mu_B$, while the α-Ce possesses no magnetic moment.[5] In a-Ce_xRu_{100-x} as in the example, we expect that the local structure considerably influences the magnetic and electronic properties. This motivates us to investigate the local structure of a-Ce_xRu_{100-x}.

The extended x-ray absorption fine structure (EXAFS) gives us knowledge about the local atomic arrangement around a specific atom such as coordination number and interatomic distance.[6,7] Since EXAFS is specially sensitive to the short-range order and does not require any long-range order, it is one of the best measuring techniques when we try to study the local structure of amorphous materials with no long-range order. To obtain the local structure of a-Ce_xRu_{100-x}, we attempt to measure the EXAFS spectra at the Ce and Ru K edges.

Ingots of the Ce–Ru alloying system were prepared by melting an appropriate amount of Ce (99.9%) and Ru (99.9%) in an argon arc furnace. A dc high-rate sputtering fabricated an amorphous phase of the Ce–Ru system. As a reference material, x-$CeRu_2$ was also prepared. The x-ray diffraction was measured by using Cu K_α radiation in a conventional θ–2θ scan mode. The composition of a-Ce_xRu_{100-x} was detected to be $x = 9$, 43 and 80 by electron probe x-ray microanalysis. The EXAFS measurements near Ru and Ce K

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**Corresponding author. Email: lyingjie@imnu.edu.cn
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edges were carried out by using synchrotron radiation at the beamline NW10A of Photon Factory.[8] The storage ring was operated at 6.5 GeV with an initial beam current of about 50 mA. The optics system was the Si (311) double crystal monochromator. All the spectra were measured at 10 K in the transmission mode by using the ionization chambers filled with appropriate sorts of gases for the x-ray energy. The incident energy of photons was calibrated against the energy value for a peak near the Cu K edge.

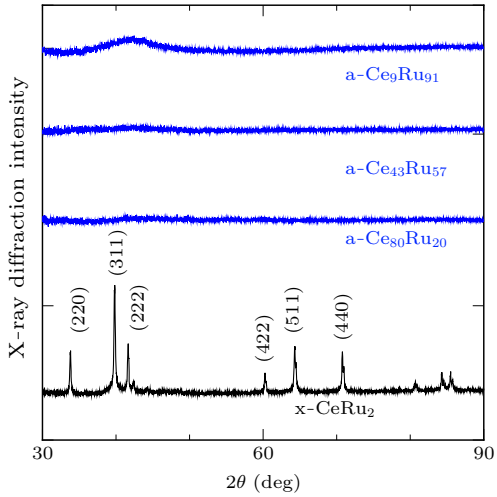

Fig. 1. X-ray diffraction patterns of amorphous alloys a-Ce_xRu_{100-x} and the C15 Laves phase compound x-$CeRu_2$. A halo pattern appears around 40 degrees for a-Ce_xRu_{100-x}. The typical indices of reflections are labeled for x-$CeRu_2$.

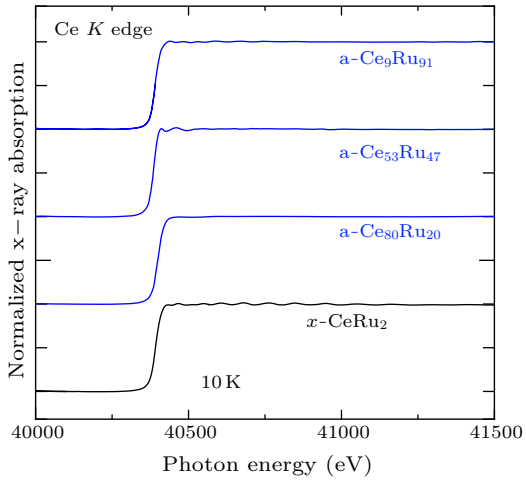

Fig. 2. Normalized x-ray absorption near the Ce K edge at 10 K for a-Ce_xRu_{100-x} and the C15 Laves phase compound x-$CeRu_2$ plotted against photon energy.

In Fig. 1 we show the x-ray diffraction (XRD) patterns of a-Ce_xRu_{100-x} and x-$CeRu_2$. No other reflections except a broad bump near about 40° are detected for a-Ce_xRu_{100-x}, which means that they are in the amorphous phase. The pattern proves that x-$CeRu_2$ has the C15 Laves phase structure with the lattice constant of 7.53812 Å. In x-$CeRu_2$ the Ce atom has 12 nearest neighbors of Ru at 3.1251 Å and 4 Ce atoms at 3.2641 Å, while Ru is surrounded by 6 Ru atoms at 2.6651 Å and 6 Ce atoms at 3.1251 Å. Figure 2 represents the normalized x-ray absorption spectra near the Ce K edge measured at 10 K as a function of photon energy for a-Ce_xRu_{100-x} and x-$CeRu_2$. EXAFS oscillations of a-Ce_xRu_{100-x} in the energy region above the absorption edge is noticeably smaller than that of x-$CeRu_2$, which is a distinguishing feature of amorphous materials.

In Fig. 3 weighted EXAFS signals $k^3\chi(k)$ derived from the spectra of the Ce and Ru K edges at 10 K for a-Ce_xRu_{100-x} and x-$CeRu_2$ are drawn against the wave vector of photoelectron k. We fit the Fourier filtered $k^3\chi(k)$ spectrum to the following formula using the least squares method,

$$k^3\chi(k) = \sum_i A_i(k)\sin[2kR_i + \delta_i(k)], \tag{1}$$

with the amplitude

$$A_i(k) = k^2 N_i |f_i(k,\pi)| \exp(-2(\sigma_i^2 k^2 + R_i/\lambda))/R_i^2, \tag{2}$$

where N_i is the coordination number, $f_i(k,\pi)$ is the backscattering amplitude, σ_i is the Debye–Waller factor, R_i is the interatomic distance between the absorbing atom and the ith scattering one, δ_i is the phase shift, and λ is the mean free path of photoelectron. We apply the standard code FEFF8.4 in EXAFS analysis to calculate the parameters such as $f_i(k,\pi)$ and δ_i based on the model structure of x–$CeRu_2$.[9]

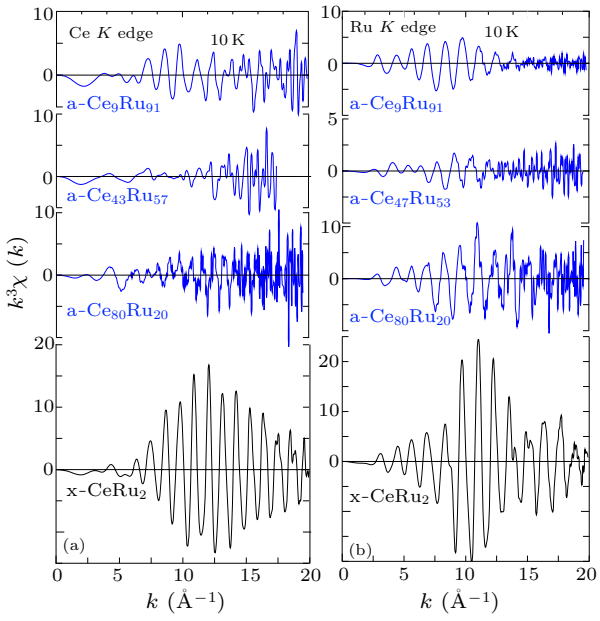

Fig. 3. EXAFS spectrum $k^3\chi(k)$ as a function of wave vector $\boldsymbol{k}$ at Ce and Ru K edges of a-Ce_xRu_{100-x} and the C15 Laves phase compound x-$CeRu_2$.

The interatomic distances thus estimated for a-Ce_xRu_{100-x} and x-$CeRu_2$ at 10 K are plotted as a

function of Ce concentration in Fig. 4. The interatomic distance of Ru–Ce for a-Ce_xRu_{100-x} is remarkably shorter than that of x-$CeRu_2$ (3.13 Å); the Ru–Ru distance is close to that of x-$CeRu_2$ (2.67 Å). However they are completely independent of Ce content within the error of analysis. On the other hand, the situation in Ce–Ce pairs is totally different from that of Ru–Ce and Ru–Ru ones. The distance between the nearest neighboring Ce atoms for a-Ce_xRu_{100-x} makes a relatively sharp increase with the Ce content, which is considerably larger than that of x-$CeRu_2$ (3.26 Å). These features on the interatomic distance suggest that the local structure of a-Ce_xRu_{100-x} is decidedly different from that of x-$CeRu_2$.

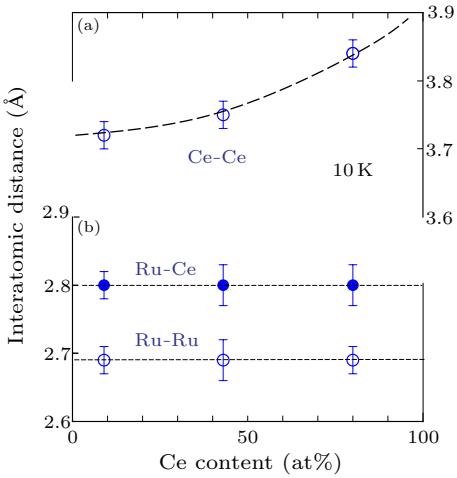

Fig. 4. The interatomic distance of Ce–Ce, Ru–Ce and Ru–Ru pairs for a-Ce_xRu_{100-x} at 10 K. The Ce–Ce distance increases sharply with the Ce content, while the Ru–Ce and Ru–Ru distances are independent of the Ce concentration.

The effective magnetic moment per Ce atom derived from the Curie–Weiss law shows a rapid decrease from $1.8\mu_B$ for a-$Ce_{80}Ru_{20}$ to $0.16\mu_B$ for a-$Ce_{39}Ru_{61}$.[3] According to the decreasing tendency, it is reasonable to assume that the moment disappears in the low Ce content. This dependence of the moment on Ce concentration is very similar to that of Ce–Ce distance. Figure 5 depicts the Ce effective magnetic moment versus the Ce–Ce interatomic distance, which demonstrates an absolutely linear relationship between them. It is well known as Vegard's law that the lattice constant of solid solutions depends linearly on the atomic content in the first approximation. The deviation from the law happens often in real materials due to several causal factors. Shiga pointed out that the magnetic factor is a considerably important one in the 3d transition metal alloys and proposed a simple and clear expression in the form[10]

$$a = A(1-x) + B\,x + C\,m, \tag{3}$$

where a is the lattice constant of the binary solid solution with adjustable parameters A, B and C, x is the atomic concentration of one constituent, and m is the average magnitude of atomic magnetic moment. The first two terms in Eq. (3) imply the conventional Vegard law and the last term represents the contribution to the lattice constant due to the magneto-volume effect. He also demonstrated that Eq. (3) is valid for a number of 3d transition metal alloys which is interpreted consistently in the framework of mean atomic size.[11] That is, the concept of the atomic size explains the lattice constant which implies the totally averaged parameter over the whole area of the specimen. Therefore, it is reasonable to apply the expression to the interatomic distance evaluated from EXAFS that means the local parameter averaged over the whole area of specimen. Though our system not only includes a 4f rare earth element while it is in an amorphous phase, it is worth investigating whether the expression holds in the a-Ce_xRu_{100-x} system. Applying it to the local structure, we should replace the lattice constant with the interatomic distance between Ce atoms. The solid line in Fig. 5 shows the fit to Eq. (3). The parameters thus estimated for a-Ce_xRu_{100-x} are $A = 3.72$ Å, $B = 3.72$ Å and $C = 0.067$ Å/μ_B. It is a rather surprising conclusion that both A and B are exactly the same. This means that, if the Ce atom should have no magnetic moment, the interatomic distances for all of the neighboring atomic pairs would be absolutely independent of the Ce concentration, or it would not obey the conventional Vegard law at all. In other words, the a-Ce_xRu_{100-x} system maintains an extremely rigid local structure of amorphous phase which can be changed only by the magnetic factor of magnetic moment instead of the chemical factor of Ce content. Also, it should be noted that the value of C for a-Ce_xRu_{100-x} is about twice as large as that of 3d transition metal alloys.[11]

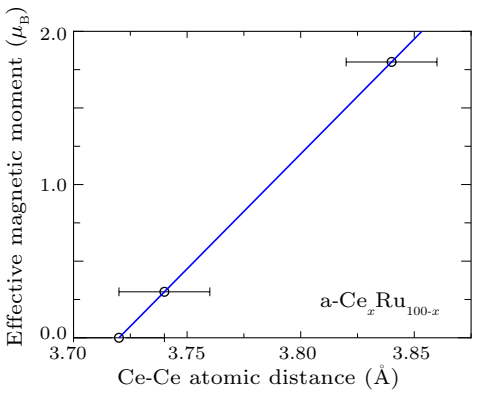

Fig. 5. The effective magnetic moment per Ce atom versus the interatomic distance between nearest neighbor Ce atoms for a-Ce_xRu_{100-x}. The line indicates an exactly linear relation between them.

In fact, the magnetovolume effect has been found in a number of 3d transition metals and alloys such as ferromagnetic FeNi Invar alloys and an antiferromag-

netic YMn_2 intermetallic compound.[12,13] The spin fluctuation theory suggests that the effect comes from variation in the amplitude of the magnetic moment.[14] In the work, we demonstrate the linear relation between the Ce–Ce interatomic distance and the magnitude of Ce magnetic moments. According to Shannon *et al.*,[15] the radius of the octahedral Ce ion decreases with increasing its valence: from 1.01 Å in Ce^{3+} to 0.87 Å in Ce^{4+}. In a-Ce_xRu_{100-x}, the Ce–Ce distance increases with decreasing the Ce valence. If the Ce ionic radius depended on the valence, the interatomic distance between Ce and Ru should be changed with the Ce concentration. However, it is not dependent on the Ce content. Therefore it is reasonable to conclude that the increase of the Ce–Ce distance is not attributed to the change of the valence. The idea based on the magneto-volume effect can reasonably explain the variation of the interatomic distance in a-Ce_xRu_{100-x} on the Ce content.

In summary, we have determined the interatomic distance of the nearest neighboring Ce–Ce, Ru–Ce and Ru–Ru pairs from the EXAFS spectra of a-Ce_xRu_{100-x} (x = 9, 43 and 80) at 10 K near Ce and Ru K edges. The Ru–Ce and Ru–Ru distances are totally independent of Ce content. On the other hand the distance between the nearest neighboring Ce atoms increases rapidly with the Ce concentration and also depends linearly on the Ce effective magnetic moment. These findings lead us to the conclusion that the magneto-volume effect plays an essential role in the local structure of the amorphous rare earth system a-Ce_xRu_{100-x}.

References

[1] Obi Y, Murayama S, Amakai Y, Okada Y and Asano K 2006 *Physica* B **378** 857
[2] Amakai Y, Murayama S, Takano H, Mizutani M, Asano K, Obi Y and Takanashi K 2007 *J. Magn. Magn. Mater.* **310** 416
[3] Amakai Y, Murayama S, Obi Y, Takano H, Momono N and Takanashi K 2009 *J. Phys. Conf. Ser.* **150** 042004
[4] Li Y J, Ohnishi N, Nakai I, Amakai Y and Murayama S 2009 *J. Phys. Soc. Jpn.* **78** 094717
[5] Grimberg A J T 1973 *PhD Thesis* (Amsterdam: University of Amsterdam)
[6] Sayers D E, Stern E A and Lytle F W 1971 *Phys. Rev. Lett.* **27** 1204
[7] Stern E A 1974 *Phys. Rev.* B **10** 3027
[8] Nomura M, Koike Y, Sato M, Koyama A, Inada Y and Asakura K 2007 *AIP Conf. Proc.* **882** 896
[9] Ankudinov A L, Nesvizhskii A I and Rehr J J 2003 *Phys. Rev.* B **67** 115120
[10] Shiga M 1972 *Solid State Commun.* **10** 1233
[11] Shiga M 1974 *AIP Conf. Proc.* **18** 463
[12] Chikazumi S, Mizoguchi T, Yamaguchi Y and Buckwith P 1968 *J. Appl. Phys.* **39** 939
[13] Shiga M 1988 *Physica* B **149** 293
[14] Takahashi Y and Nakano H 2006 *J. Phys.: Condens. Matter* **18** 521
[15] Shannon R D and Prewitt C T 1969 *Acta Crystallogr.* B **25** 925