Muon sites in Ce(Ru,Rh)$_2$Al$_{10}$ investigated by using Density Functional Theory from the view point of electronic potential

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Abstract. Numerical investigations on muon sites in Ce-based Kondo semiconductors, Ce(Ru,Rh)$_2$Al$_{10}$ were carried out by using the Density Functional Theory. From the view point of simple electrostatic potential calculations, we found all the previously reported muon sites, suggested by different groups (Kambe S et al. 2010 J. Phys. Soc. Jpn. 79 053708 and Khalyavin D D et al., 2010 Phys. Rev. B 82 100405(R)), can be possibly chosen as muon stopping sites. We also investigated the changes in the potential of the Rh-doped case. We discovered that the electronic potential around the nearest Ru atom to the substituted Rh atom is affected and the potential becomes asymmetric around the nearest Ru ion. Although big changes in hyperfine fields at muon sites have been reported (Guo H et al. 2013 Phys. Rev. B 88 115206), the muon positions estimated from the potential calculations do not change much.

1. Introduction

CeRu$_2$Al$_{10}$ has the orthorhombic YbFe$_2$Al$_{10}$–type structure with space group Cmcm in which Ce in 4c, Ru in 8d, two Al atoms in 8g, another two Al atoms in 8f while one Al atom in 8e. A unit cell of CeRu$_2$Al$_{10}$ consists of 4 Ce, 8 Ru and 40 Al atoms [1]. Figure 1 shows the crystal structure
of CeRu$_2$Al$_{10}$. Ce atoms are in charge of the magnetism of this system and are surrounded by Al atoms forming a cage-like structure. This Ru-Al cage is suggested to form a two-dimensional plane structure stacking along the $b$-axis [2,3]. Ru atoms are in interstitial sites among those Ce-Al cages. This system has been argued to be a Kondo semiconductor and has drawn attention by its unusual electromagnetic properties [4]. Despite having nearest-neighbour distance, about 5.2 Å between Ce ions, CeRu$_2$Al$_{10}$ still exhibits an antiferromagnetic transition at $T_0 = 27.3$ K. Such a high magnetic transition temperature cannot be explained by taking into account only the RKKY interaction [5]. Meanwhile, the magnetic susceptibility is largely anisotropic while the direction of magnetic moment is along the $c$-axis in the magnetically ordered phase of CeRu$_2$Al$_{10}$ [6] and it is expected to flip to the $a$-axis when a slight amount of Ru is substituted by Rh [7]. At this moment, the insight of the magnetic properties is still inadequate to be understood. Therefore, a lot of efforts are being paid to investigate the system including the relative systems which have the same crystal structure but with different components.

In order to investigate the magnetic properties of CeRu$_2$Al$_{10}$, a µSR study has already been conducted by Kambe et al. [8]. They found the appearance of the muon-spin precession in the time spectrum below $T_0$. The internal field at the muon site which was calculated from the muon-spin precession frequency was around 30 G. This small internal field could be caused by the cancellation of the internal field at the muon site due to the antiferromagnetic spin alignment. Thus, Kambe et al. suggested some possible muon sites which located at symmetric sites between Ce atoms. On the other hand, Khalyavin et al. compared numerical estimations and experimental data for nuclear dipole fields and suggested different muon positions from those suggested by Kambe et al. [9]. Khalyavin et al. also reported two components of internal fields and the unusual temperature dependences of them. The lower-field component found by Khalyavin et al. was almost the same with that observed by Kambe et al. Another component had the larger internal field in the order of 120 G. In addition, Guo et al. has reported detailed µSR results on Rh-doped systems, Ce(Ru$_{1-x}$Rh$_x$)$_2$Al$_{10}$ [10]. They reported drastic changes in internal fields at muon sites which were related to the spin-flop caused by the Rh-doping. They confirmed that the spin-flop from along the $c$-axis to the $a$-axis was caused by a couple percent of Rh-doping.

Figure 2 summarises muon sites in CeRu$_2$Al$_{10}$ suggested by Kambe et al. [8] and Khalyavin et al. [9]. Kambe’s suggested positions located at symmetric sites in between Ce atoms around the surface on the unit cell. On the other hand, Khalyavin’s suggested sites were not on the surface but at the inside of the unit cell. They were not crystallographically the same with Kambe’s ones. Therefore, muon sites in CeRu$_2$Al$_{10}$ are still in controversial and the hyperfine interactions cannot be deeply discussed. We try to analyse those muon sites from the view point of electrostatic potential calculation by using the Density Functional Theory (DFT) and aim to
explain $\mu$SR results on CeRu$_2$Al$_{10}$. Since the direction of ordered spins changed in the Rh-doped system, we tried to deduce a change in the electrostatic potential as well as the muon sites in the Rh-doped case. In this paper, we report the results of the first trial in estimating muon sites from the potential view point of CeRu$_2$Al$_{10}$ and the first examination in observing a change in the electrostatic potential of the Rh-doped system.

**Figure 2.** Muon sites in CeRu$_2$Al$_{10}$ suggested by Kambe et al. (purple marks [8]) and Khalyavin et al. (yellow marks [9]). Kambe et al. suggested from the internal field at the muon site while Khalyavin et al. suggested from the nuclear-dipole field distribution.

2. Calculations

We have carried out the potential calculation by using the VASP program [11,12]. We used DFT by using the LDA electronic correlations since the ground state of the system would be metallic [13,14] even though physical properties of the system are categorized to be the Kondo semiconductor. The resolution of the calculation grid was $108 \times 120 \times 108$ in $a$-, $b$-, and $c$-axis. The cutoff energy of the plane wave expansion was set to be 375 eV. The electrostatic potential of one unit cell without muon was calculated in order to estimate the initial positions for injected muons. Other parameters such as the relaxation of the muon position, the local deformation of the crystal structure induced by the injected muon, the spin polarized effect on the total energy of the system and the spin-orbit coupling were not included in order to simplify calculations in this study. It has been pointed out that the zero-point vibration motion of the muon itself is important to determine final state of the muon [15]. However, we did not include this effect as well as other parameters because we would like to show in this report how simple potential estimations can explain experimental results and possible muon sites in Ce(Ru$_{1-x}$Rh$_x$)$_2$Al$_{10}$.

We used a supercomputer system in RIKEN named RIKEN Integrated Cluster of Clusters (RICC) in order to achieve the faster calculation condition. In order to estimate the change in the electrostatic potential of the Rh-doped system, we substituted one Ru with Rh in the cell. This condition was corresponding to the concentration of Rh to be about 12.5%. In such a high concentration range, the spin alignment in the magnetically ordered state is already along the $c$-axis. Although this Rh concentration value was too high to compare with the realistic sample condition which has been investigated by Guo et al. [10], we tried to achieve the basic and the simplest result in order to conceive the idea of next calculations.

3. Results and Discussions

While our calculation area covered the whole unit cell with fine meshes, we chose some characteristic areas in order to compare between the non-doped and doped system. This is because those three planes contain all estimated minimums. Figure 3 shows those characteristic planes in the unit cell. Figures 3(a) and 3(b) indicate the case of the non-doped and doped systems, respectively. One Ru atom was substituted by the Rh atom as shown in Figure 3(b) by the orange mark. The plane $\circ$ is the Ru-Al plane which is on the boundary of the unit cell and includes muon positions suggested by Kambe et al. The plane $\otimes$ is the Ce-Al plane which
includes muon positions suggested by Khalyavin et al. The plane $\Theta$ is again the Ru-Al plane which is located in the middle of the unit cell and includes muon positions suggested by Kambe et al. In the case of the Rh-doped system, we substituted one Ru atom by the Rh atom in this plane. Changes in the potential energy in each plane are also illustrated around atoms. Blue colored areas show the lower potential areas rather than the yellow/light-blue ones.

**Figure 3.** Planes contain Ru and Al ($\Theta$, $\Xi$), Ce and Al ($\Xi$), respectively. Dark-blue, light-blue, red marks are corresponding to Ce, Ru and At atoms, respectively. The plane $\Theta$ and $\Xi$ contain muon positions suggested by Kambe et al. The plane $\Xi$ contains muon positions suggested by Khalyavin et al. In order to simulate the Rh-doped system, one Ru atom in the plane $\Theta$ was substituted by the Rh atom which was corresponding the Rh concentration of 12.5%.

Figure 4 shows detailed results of the potential calculation on each plane of non-doped system. Muon positions suggested by Kambe et al. [8] and Khalyavin et al. [9] are drawn by purple and yellow marks, respectively. As indicated in Figure 4, all muon positions are located at the bottoms of potential valleys. From the comparison made between each minimum potential, it

**Figure 4.** Electrostatic potential in each plane as shown in Figure 3. Blue color areas have the higher and lower potential energy, respectively. Purple and yellow marks are muon positions suggested by Kambe et al. [8] and Khalyavin et al. [9], respectively.
was found that the differences among each minimum potential was less than a couple of Kelvin.

It should be noted that those points shown in Figure 4 could be spatially spread due to the zero-point vibration motion of the muon itself and the initially trapped muon could be hopping around site by site passing through energy barriers between suggested positions [15]. These effects are now being tested and will be published in later papers.

Our simple calculation suggests that electrostatic calculations can explain all positions proposed by Kambe et al. [8] and Khalyavin et al. [9] as the candidates that trap injected muons. Dipole field calculations from Ce atoms at those muon sites has been carried out and it was found that muon positions suggested by Kambe et al. were expected to have the smaller internal field; 20-30 G. [8] Instead, muon positions suggested by Khalyavin et al. had the larger internal field with the order of 100-200 G. [9] Since the dipole-field estimation depends on the muon position itself, we are carrying out more detailed calculations which cover more unit cells and include detailed parameters like the local crystal deformation, muon-position relaxation and changing conditions of the Ce magnetic moment as well as the spin alignment.

**Figure 5.** Differences in the potential between the non-doped and doped systems in terms of planes 1, 2 and 3. The location of each plane was as indicated in Figure 3. Purple and yellow marks in each plane are corresponding to muon positions suggested by Kambe et al. [8] and Khalyavin et al. [9], respectively. The big difference seen in the plane 3 is induced by the substituted Rh. The middle point between two minimums which appear in the plane 3 near the substituted Rh atom is corresponding to the neighboring Ru atom.

In order to investigate the difference in the potential between the non-doped and doped system, we subtracted both potential in each plane (1, 2 and 3). This operation means that the potential value on each grid of the doped system which was shown as Figure 3(b) was subtracted from that on the same position in the non-doped system which was shown as Figure 3(a). Figure 5 shows the result of differences in potential values between planes of non-doped and doped systems. Both Kambe’s and Khalyavin’s suggested muon positions are shown together in each plane by purple and yellow marks, respectively. The potential difference of the plane 1 did not change so much. This would be due to that this plane was far from the substituted Rh atom. A big change in the potential in the plane 3 appeared around the substituted Rh atom. This large difference in the potential is expected to be caused by the different valence configuration from that of Ru atom. Due to this big change in the potential at the Rh atom, the potential in the plane 2 which was just underneath the substituted Rh atom was slightly deformed. However, the electrostatic potential around suggested muon sites seemed not to be affected so much by the Rh substitution. This result leads us to suggest that muon positions would not change so much even in the Rh-doped system since the Rh concentration is much
smaller in realistic systems and that the change in the internal fields at muon positions are caused by the change in the Ce spin alignment as discussed by Guo et al. [10]

It was found that two minimums appeared in the plane $\beta$ beside the substituted Rh atom as seen in Fig. 5. Since the neighboring Ru atom and the substituted Rh atom located in the middle of the two minimums, the Rh substitution is expected to change the potential around the neighboring Ru atom to be asymmetric. Such a change may be induced by the modification of electronic outer orbitals of Ru such as $d$ orbitals because the current system has a strong mixing state between conduction and $d$ electrons. If the change in the $d$ orbital expands through the whole crystal by some reason or through a long-range magnetic correlation like the RKKY interaction, a small amount of the substitution of Ru by Rh could lead to a drastic change in the spin direction. In order to give an answer to this hypotheses, more calculations should be done on the charged state of Ru atoms, Rh atoms and on the charge density of the whole system. Those works are on-going projects and beyond the purpose of the current study.

4. Conclusion
We have carried out potential calculations by using the DFT method in order to investigate muon positions in Ce(Ru$_{1-x}$Rh$_x$)$_2$Al$_{10}$. We have found that all positions suggested by Kambe et al. and Khalyavin et al. are located at local minimum positions which could be a good candidate for muon sites. This explained the experimental data of internal fields measured in magnetically ordered phase. Since at least two muon sites have been identified in CeRu$_2$Al$_{10}$, we proposed that the difference of internal fields at muon sites came from the difference of those suggested muon positions. On the basis of the dipole field calculation, we proposed that the Kambe’s suggested positions were corresponding to the sites which had the lower field and the Khalyavin’s suggested positions were corresponding to those which had the higher field. We also investigated the changes in the electronic potential in the case of the Rh-doped system. It was found that the Rh doping introduced a change in the electrostatic potential around the Rh site. However, there are no big changes in the potential around the suggested muon sites.

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