μSR study on ferromagnetic properties of Rb clusters incorporated into zeolite A

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Abstract

We performed μSR experiments on rubidium clusters arrayed in porous crystals of zeolite A. These clusters are known to show spontaneous magnetization of ferromagntism at higher loading densities of Rb atoms in a previous study. The development of the internal field is observed below $\simeq$4 K in the temperature dependence of zero-field μSR spectra in the sample $n = 5.8$, where n is the average loading density of Rb atoms per unit cage. The Curie temperature of this sample is estimated to be $\simeq$ 5 K from the Arrott plot analysis. The amplitude of the relaxation is large enough to indicate the magnetic ordering in the major volume of sample. The internal field is confirmed to be almost static in the longitudinal-field μSR spectra below $\simeq$ 4 K. Difference of the ferromagnetic properties between K and Rb clusters is also discussed from the viewpoint of μSR study.

Key words: alkali-metal cluster, zeolite, ferromagnetism, ferrimagnetism, μSR

1. Introduction

Alkali-metal nanoclusters can be periodically arrayed in zeolite crystals by the loading of guest alkali atoms into the cages of zeolite. They show novel electronic properties such as ferromagnetism in K clusters in zeolite A[1], antiferromagnetism in Na clusters in sodalite[2] and N-type ferrimagnetism in Na-K clusters in low silica zeolite X[3]. They are novel magnetic materials because the magnetically ordered states are realized by the mutual interaction of s-electrons confined in the clusters. Recently, we newly found ferromagnetic properties in Rb clusters incorporated into zeolite A[4,5]. In the present work, we carried out μSR measurements on ferromagnetic samples of Rb clusters in zeolite A.

Zeolite A has the LTA-type framework structure. As shown in Fig. 1, the α and β cages with the respective inside diameters of $\simeq$ 11 and $\simeq$ 7 Å are alternatively arrayed in a CsCl structure. The framework ($Al_{12}Si_{12}O_{48}$) is negatively charged and alkali cations are distributed in the space of the framework for the charge neutrality. Guest Rb atoms are adsorbed into dehydrated Rb-type zeolite A ($Rb_{12}Al_{12}Si_{12}O_{48}$ in the ideal case). The 5s-electrons of the guest Rb atoms are shared among guest and host Rb^+ cations, and confined in the cages to form cationic clusters. We can widely control the average loading density of guest alkali atoms. A mutual overlapping of s-electron wave functions in adjacent clusters can lead to the magnetic phase transition at low temperature and an insulator-to-metal transition as well, depending on the kind of alkali metals and the loading density.

In the case of K-loaded K-type zeolite A, K clusters are generated in α cage[6]. The average number of s-electrons per unit cage, n, can be controlled up to $\simeq$ 7.2. The guest electrons successively occupy the quantum electronic states of cluster, such as 1s- and 1p-like states[6]. The ferromagnetic properties have been observed at $2 < n < 6$[7]. The origin of the spontaneous magnetization is explained by spin-canting mechanism of antiferromagnetism[8], where the degeneracy of 1p-like orbital of K cluster enhances the Dzyaloshinsky-Moriya interaction[9]. The very fast decay component is observed in μSR spectra and decoupled by the very weak longitudinal-field[10,11]. The decoupling is explained by the Fermi-contact interaction with spin-canting

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electrons in clusters[12].

In the present study, μSR measurements were made for Rb clusters in Rb-type zeolite A. In the case of Rb, the value of n can be controlled up to $\simeq 6$[4,5]. Antiferromagnetic interaction is observed as K clusters, but following differences have been found[4,5]. Spontaneous magnetization in Rb clusters is observed at $n > 4$ (*cf.* K clusters at $n > 2$). Rb clusters are formed not only in the α cages but also in the β cages. Furthermore, strong mid-infrared absorption is observed at $n > 3$ in Rb clusters, which indicates a metallic state, while K clusters is in the insulating state at any K-loading densities. Magnetic properties in Rb clusters can be explained by the model based on the ferrimagnetism constructed by non-equivalent magnetic sublattices of clusters in α and β cages, where the α cage clusters are in a metallic state[4,5]. In the present μSR study, we investigate the ferromagnetic properties of samples with higher loading densities in detail and also clarify the difference in the mechanism of ferromagnetism in K and Rb clusters in zeolite A.

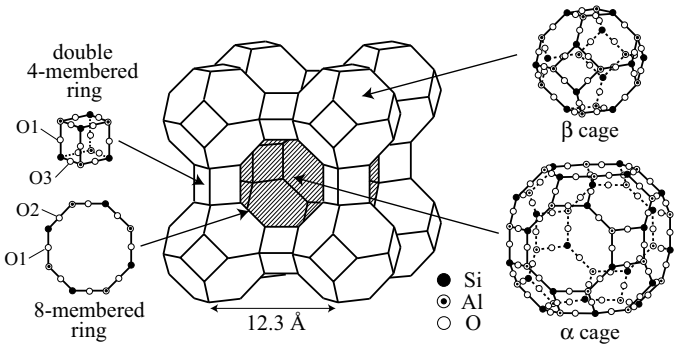

Fig. 1. Schematic illustration of the crystal structure of zeolite A. The framework has the LTA-type structure.

2. Experimental

Pure Rb metal was adsorbed into fully dehydrated powder of Rb-exchanged zeolite A ($Rb_{11}K_1Al_{12}Si_{12}O_{48}$). Zero-field (ZF-) and longitudinal-field (LF-) μSR measurements were carried out by using the ARGUS spectrometer at the RIKEN-RAL Muon Facility and also by using the GPS spectrometer at Paul Scherrer Institute (PSI). To avoid chemical reactions with the air, the sample powders were sealed in a Ti cell with mylar window and an Ag foil bag at RIKEN-RAL and PSI, respectively. Magnetic measurements were performed by using a SQUID magnetometer.

3. Results and discussions

Figure 2 shows temperature dependence of ZF-μSR spectra measured at RIKEN-RAL for Rb clusters in zeolite A loaded with Rb at $n = 5.8$. The loading density is just below the saturated value $\simeq 6$. The solid curves are fitting results shown later. The Curie temperature, T_C, is estimated to be $\simeq 5$ K for this sample from the Arrott plot analysis of the magnetization curves. The Gaussian-like slow relaxation is seen at 10 K. The exponential-like relaxation dominates the decay curve below $\simeq 6$ K, and the relaxation rate obviously increases at lower temperatures. At 1.4 K, the decay of asymmetry is very fast at early time. As the spectral shapes seem to be dependent on the temperature, the ZF-μSR spectra are analyzed in the following temperature dependent manner.

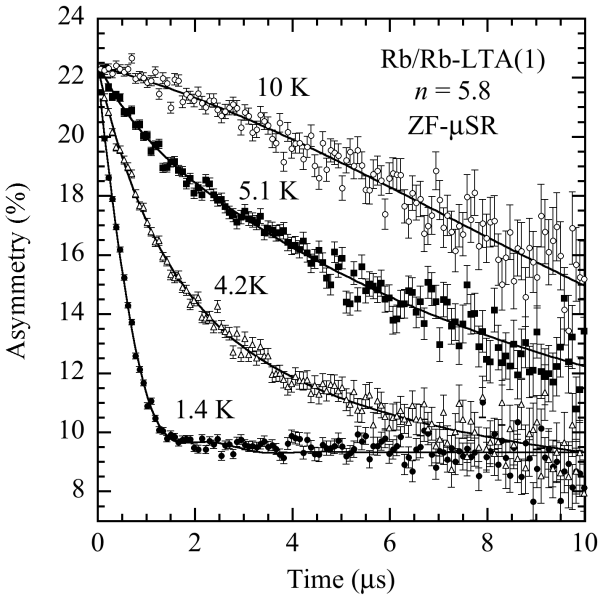

Fig. 2. ZF-μSR spectra of Rb clusters in zeolite A loaded with Rb at $n \simeq 5.8$ measured by using pulsed muon beam at RIKEN-RAL.

At higher temperature region $T > 6$ K, the spectra can be described by the product of Gaussian Kubo-Toyabe function $G_{\rm KT}(t)$ and an exponential relaxation function with the temperature- and time-independent background B;

$$P_1(t) = A_0 G_{\rm KT}(t) \exp(-\lambda_0 t) + B, \quad (1)$$

where $G_{\rm KT}(t) = 1/3 + (2/3)(1 - \Delta^2 t^2) \exp\left(1 - \Delta^2 t^2/2\right)$. As seen in the spectrum at 10 K in Fig. 2, the curve is well fitted to the experimental data. The relaxation rate of the Kubo-Toyabe function is estimated to be $\Delta \simeq 0.06$ μs^{-1}. This value corresponds to the width of the Gaussian field distribution, $\sigma \simeq 0.7$ Oe. The relaxation rate of the exponential decay λ_0 shows very small value as shown later. In this temperature region, the main part of muon spin relaxation is explained by the quasi static random field of nuclear dipole moments of ^{27}Al contained in the zeolite framework. Actually, the similar value of σ is commonly observed in another zeolite[3]. At $2 \leq T \leq 4$ K, the spectra can be fitted by the function with exponential components of slow and fast relaxation rates, λ_1 and λ_2, respectively;

$$P_2(t) = A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t) + B. \quad (2)$$

As seen in the spectra at 5.1 and 4.2 K in Fig. 2, the curves are well fitted to the experimental data. As shown later, however, the reliability of λ_2 is not good for $4 \leq T \leq 6$ K,

because of the temporal form of Eq. (2) as the trial function for $4 \leq T \leq 6$ K. Below 2 K, we could not obtain good fitting by Eq. (2). We used the third function given by

$$P_3(t) = A_3 \exp(-\lambda_3 t) + A_4 \exp(-\lambda_4 t) \cos \omega t + B. \quad (3)$$

As seen in the spectrum at 1.4 K in Fig. 2, the curve is well fitted by the following parameters; $\lambda_3 = 1.73\ \mu s^{-1}$ and $\omega = 0.45\ \mu s^{-1}$, the latter of which corresponds to the field of 33 Oe.

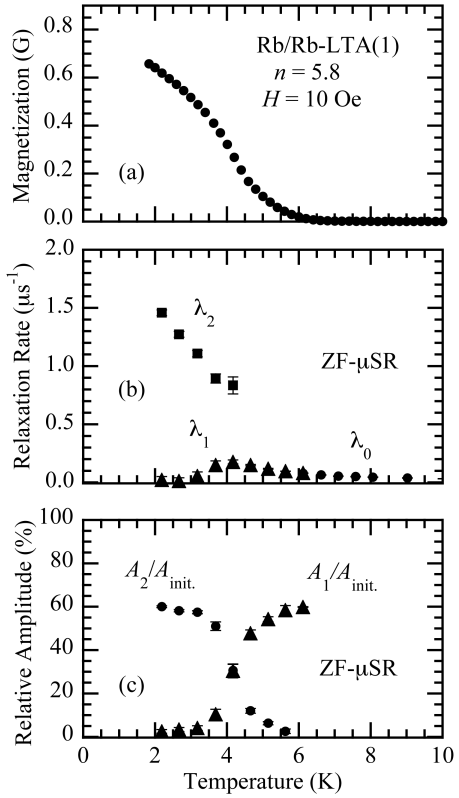

Fig. 3. Temperature dependence of of Rb clusters in zeolite A loaded with Rb at $n \simeq 5.8$, (a) magnetization under the external field of 10 Oe, (b) muon spin relaxation rates, λ_0, λ_1 and λ_2 in Eqs. (1) and (2), and (c) relative amplitude of relaxation terms in Eq. (2). The parameters shown in (b) and (c) are obtained by the fitting of ZF-μSR spectra.

In Fig. 3(b) and 3(c), the temperature dependences of some fitting parameters in Eqs. (1) and (2) are summarized for $2 \leq T \leq 10$ K together with the magnetization at 10 Oe in Fig. 3(a). The magnetization gradually increases below $\simeq 6$ K due to the spontaneous magnetization and has a large value below $\simeq 5$ K. Figures 3(b) and 3(c) show temperature dependences of λ_0, λ_1 and λ_2, and the amplitudes of slow and fast components A_1 and A_2 in Eq. (2) normalized by the initial asymmetry A_{init} $(= A_1 + A_2 + B)$.

At high temperature region, λ_0 shows very small value which can be explained by the quasi static field from nuclear spins ^{27}Al. The magnetic moments of Rb clusters are paramagnetic at this temperature region, and the internal field from the electron spins fluctuates very fast resulting in the very small contribution to λ_0. At 6 K, λ_0 increases and shows the value similar to λ_1.

Between 4 and 6 K, λ_1 gradually increases with lowering temperature, which indicates the fluctuation slow-down of magnetic moment. The relative amplitude of slow decay component A_1/A_{init} gradually decreases. At the same time, the relative amplitude of fast decay component, A_2/A_{init}, gradually increases and dominates the relaxation below $\simeq$ 4 K. As for λ_2, a reliable value was not obtained above 4 K, but the development of the fast component may correspond to the growth of the static internal field by the magnetic ordering of Rb clusters. The gradual changes between 4 and 6 K may indicate an inhomogeneity of the ferromagnetic properties as well as the dynamic behavior of local magnetic field near the Curie temperature $\simeq 5$ K. The slow and fast decay components in Eq. (2) may be an artifact given by the inhomogeneity and the dynamic behavior. The decay curve can not be simply expressed by two exponential functions between 4 and 6 K. An inhomogeneity of ferromagnetic properties may be caused by the disorder in the distribution of Rb cations.

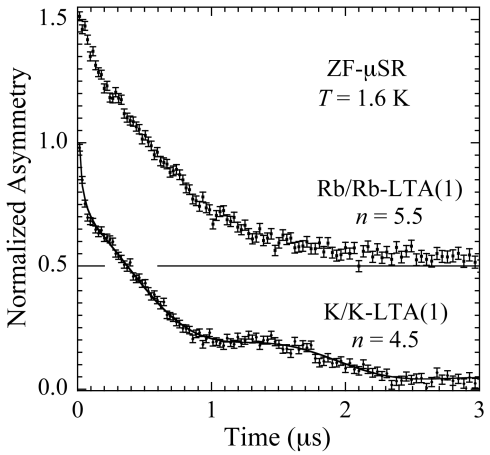

Fig. 4. ZF-μSR spectra of ferromagnetic samples of Rb and K clusters in zeolite A measured at 1.6 K by using dc muon beam at PSI.

Below $\simeq$ 4 K, the magnetically ordered phase have enough quality. Both λ_1 and A_1/A_{init} for the slow component decrease with lowering temperature below 4 K and have very small values. The value of λ_2 for the fast component increases roughly in proportion to the magnetization shown in Fig. 3(a). The relative amplitude of the fast relaxation component, A_2/A_{init}, amounts to $\simeq 60$ % as seen at the lowest temperature 2 K in Fig. 3(c). Usually, some amount of muons stop at the sample holder or another part of instrument, resulting in a finite background being independent of sample. This component is included in B. A typical value of such a background is about 10-30% of the total asymmetry. Therefore, it is rather good enough to conclude from the obtained value $A_2/A_{init} = 60\%$ that the static internal field arises from the major volume of sample. This means that the ferromagnetic ordering occurs in the major volume of sample.

Figure 4 shows ZF-μSR spectrum of Rb clusters in zeolite A loaded at $n = 5.5$ together with the that of K clusters at $n = 4.5$ for comparison[12]. The measurements were

made by using dc muon beam at PSI. The Curie temperatures of Rb and K clusters are $\simeq$ 4 and $\simeq$ 7 K, respectively. The spectrum of K clusters shows very fast relaxation within 0.1 μs together with the fast relaxation and precession components. The relaxation rate of the very fast decay is estimated to be $\simeq 20\ \mu s^{-1}$. This component is easily decoupled by a very weak longitudinal filed of $\simeq$ 10 Oe which is much smaller than the value expected from the relaxation rate, $\simeq$ 200 Oe. This decoupling property in the very fast relaxation component is quite unusual. The very fast relaxation is explained by the muons near O2 site at the inside of 8-membered ring (8R) shown in Fig. 1. The assignment to the O2 site is consistent with the spin-canting model[12]. In Rb clusters, however, such a very fast decay is not observed. Positive muons are generally expected to stop near the oxygen atoms of zeolite framework. The negative charges of framework are concentrated at the double 4-membered ring (D4R) shown in Fig. 1. The most stable stopping position for μ^+ is expected to be near the O1 and O3 sites at the inside of D4R. The second candidate is near the O2 site. Muons at the inside of D4R feel dipole field from the magnetic moment of clusters generated in the α and/or β cages, which give the fast relaxation and precession components in both K and Rb clusters. Muons near the O2 site can have the Fermi-contact interaction with the electrons of clusters in α cages, which leads to the very fast decay component only in K clusters.

The absence of very fast decay component in Rb clusters may have some reasons. The positive muon has an attractive potential for electrons. If materials are in the insulating phase, the states of positive muon can be defined as muonium ($Mu = \mu^+e^-$) or negative muonium ($Mu^- = \mu^+e^-e^-$) as well as bare muon ($Mu^+ = \mu^+$). Actually, Mu can be generated at high probability as well as Mu^+ in undoped zeolite X[13]. In doped zeolites, Mu is scarcely observed in muon spin relaxation and rotation experiment. Mu^- and Mu seem to become more stable by the doping of s-electrons, but their stability depends on the condition of Fermi energy[14]. Furthermore, Mu^- can not be clearly distinguished from Mu^+ in muon spin relaxation and rotation experiment. In metallic materials, however, we do not have a unique answer on the existence or clear definition of Mu^+, Mu and Mu^-. The local field at the muon site in ferromagnetic metal is formally given by the sum of the hyperfine coupling with itinerant electrons, dipole fields from magnetic moments, demagnetization field, *etc.* Unfortunately, we do not know these fields in the present materials. Anyway, some conditions in Rb clusters may be different from those in K clusters at O2 site, and then the very fast decay component in K clusters is changed to the ordinary fast decay component in Rb clusters. The most plausible reason for the absence of the very fast decay may be the metallic state in Rb clusters.

4. Summary

We measured μSR spectra for the ferromagnetic samples of Rb clusters in zeolite A. A gradual change of internal field is observed between 4 K and 6 K. Below $\simeq$ 4 K, a growth of static internal field is observed and magnetic phase transition is confirmed to arise in the major volume of the sample. A very fast decay observed in K clusters is not observed in Rb clusters. The origin of the difference is discussed in terms of the difference in the electronic state of materials.

Acknowledgments

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