Fast muon spin relaxation in ferromagnetism of potassium clusters in zeolite A

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Abstract

Potassium clusters arrayed in zeolite A are known to show ferromagnetic properties at low temperatures. A remarkable decrease in the initial asymmetry was observed previously below the Curie temperature in zero-field μSR by using pulsed muons. In the present work by using dc muons, we clearly observed the fast decay component which was assigned to the decrease in the initial asymmetry in the previous pulsed muon experiment. The relaxation rate amounts to $\simeq 20\ \mu s^{-1}$ which corresponds to $\simeq 200$ Oe in the random static field. This value cannot be explained by the ordinary dipole field, but by the Fermi-contact interaction with electrons in K clusters. The fast decay is easily quenched by applying a weak longitudinal field of $\simeq 10$ Oe. The low field decoupling of the fast decay component can be explained by the magnetization by the spin-canting mechanism of antiferromagnet under the assumption that some muons stop near the oxygen in 8-membered ring of zeolite framework.

Key words: alkali-metal cluster, zeolite, ferromagnetism, μSR, Fermi-cantact interaction

1. Introduction

Magnetically ordered states have been found in alkali-metal nanoclusters regularly arrayed in zeolite crystals [1–4]. They are fascinating magnetic materials because they contain no magnetic element and the magnetic orderings are realized by the mutual interaction between s-electrons confined in the clusters [5]. Muon spin relaxation (μSR) technique plays an important role in the investigation of the magnetically ordered states in these materials [3,6–8]. In the present work, we applied μSR technique to potassium clusters in zeolite A in order to investigate their ferromagnetic properties in detail.

Zeolite A has the LTA-type framework structure, and α and β cages with the respective inside diameters of $\simeq 11$ and 7 Å are arrayed in a simple cubic structure, as schematically shown in Fig. 1. The framework ($Al_{12}Si_{12}O_{48}$) is negatively charged and alkali cations are distributed in the space of the framework. When guest K atoms are loaded into K-type zeolite A ($K_{12}Al_{12}Si_{12}O_{48}$), the guest $4s$-electrons are shared among several K^+ ions, and K clusters are formed in the α cages [9]. We can control the average number of electrons per cluster, n, up to $\simeq 7.2$. Ferromagnetism is observed at $2 < n < 6$, which corresponds to the occupation of electrons to $1p$-like state of cluster. The origin of the spontaneous magnetization is explained by spin-canting of antiferromagnetism [10,11]. In a previous μSR study by using pulsed muons [7], the magnetic phase transition was clearly observed in the increase in the decay rate below the Curie temperature, T_C. We also observed a remarkable decrease in the initial asymmetry below T_C. The decreas is due to the very fast decay of asymmetry. The quantitative analysis of such fast decay is limited in the pulsed muons [8]. In the present study, we observe the fast decay component in the zero-field μSR (ZF-μSR) and low field decoupling in the longitudinal-field μSR (LF-μSR) with the enough time-resolusion by using dc muons. We discuss the origin of the fast decay and low field decoupling in relation to the spin-canting mechanism.

2. Experimental

Distilled potassium was adsorbed into fully dehydrated K-type zeolite A at $n = 4.5$. The magnetization was measured by using a SQUID magnetometer. For μSR measure-

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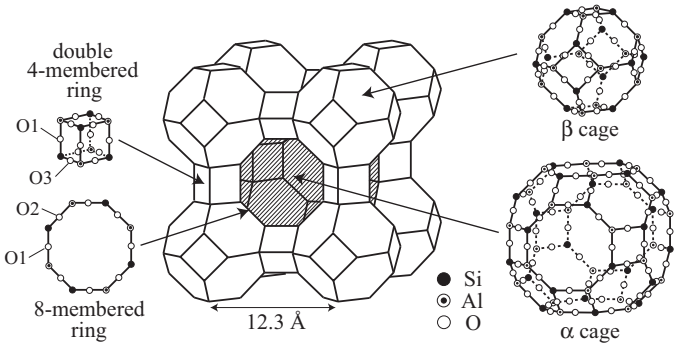

Fig. 1. Schematic illustration of crystal structure of zeolite A. The framework has the LTA-type structure. The α and β cages, the double 4-membered ring and the 8-membered ring are also shown. There are three oxygen sites, O1, O2 and O3. Cations are neglected here.

ments, the sample was sealed in a bag made of silver foils with pure He gas to avoid chemical reactions with the air. ZF- and LF-μSR measurements were performed using dc surface muon beams with the GPS spectrometer at the Paul Scherrer Institute (PSI), Switzerland.

3. Results and discussion

Figure 2 shows temperature dependence of ZF-μSR spectra of K clusters in zeolite A at $n = 4.5$. The Curie temperature, T_C, is estimated to be $\simeq 7$ K for this sample from the magnetization data. An exponential-like relaxation is observed at high temperature. With decreasing temperature, the relaxation rate increases. At lower temperature, the muon spin precession signal is clearly observed in addition to the slow exponential-like relaxation. Furthermore, very fast relaxation is seen within $\simeq 0.1$ μs. At low temperature region of $T \leq 6$ K, the spectra were well fitted by the following function:

$$A(t) = A_1 \exp(-\lambda_1 t) + A_2 \exp(-\lambda_2 t) + A_3 \exp(-\lambda_3 t) \cos \omega t + B, \quad (1)$$

where the first and second terms indicate the fast and slow relaxation components with the respective relaxation rates λ_1 and λ_2. The third term indicates the muon spin precession signal. The term B is for the time- and temperature-independent baseline. The ratio of each term to the total asymmetry, A_{tot} $(= A_1 + A_2 + A_3 + B)$, was $A_1/A_{tot} = 0.27$, $A_2/A_{tot} = 0.44$, $A_3/A_{tot} = 0.08$ and $B/A_{tot} = 0.21$. These values were fixed trough the whole temperature range. Above 6 K, the muon spin precession signal is not clearly seen and the fit by using Eq. 1 does not go well. The spectra were well fitted by using the following function at $T > 6$ K:

$$A(t) = A_1 \exp(-\lambda_1 t) + A_2' \exp(-\lambda_2 t) + B, \quad (2)$$

where we set $A_2' = A_2 + A_3$. The all fitting results are shown by solid curves in Fig. 2.

In Fig. 3, λ_1 and λ_2 are plotted in a logarithmic scale as a function of temperature. The magnetization M is also

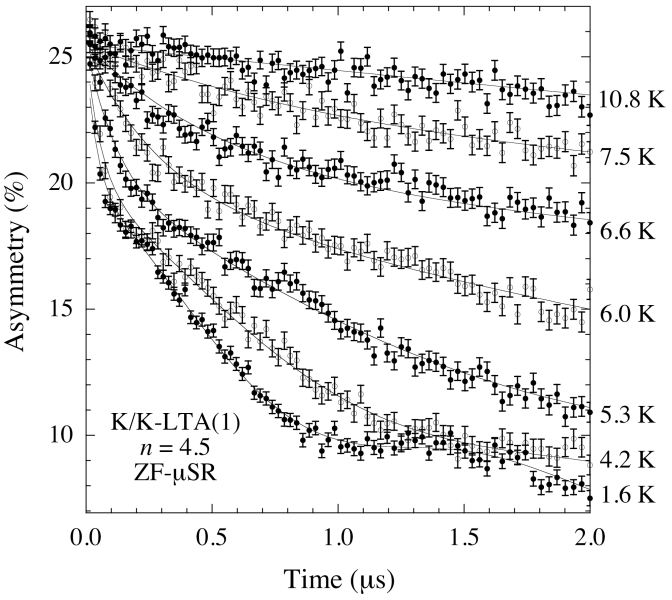

Fig. 2. Temperature dependence of ZF-μSR spectra of K clusters in zeolite A at $n = 4.5$.

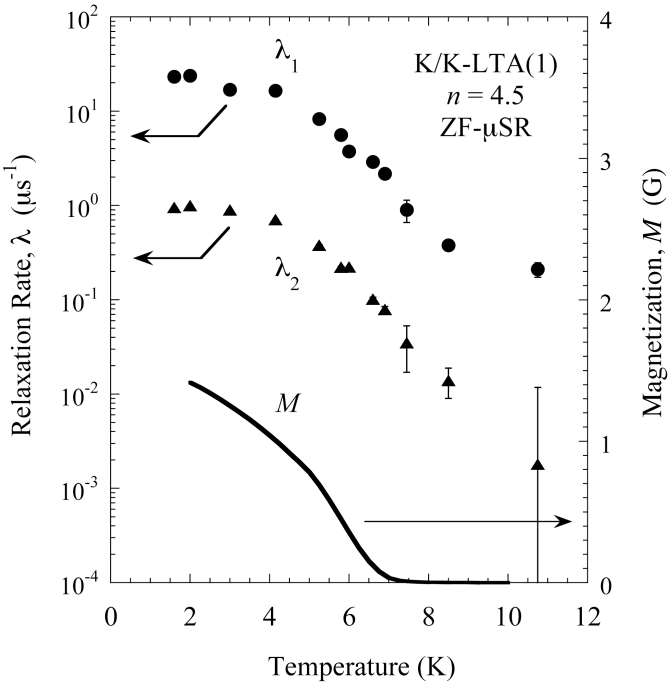

Fig. 3. Temperature dependence of the muon spin relaxation rates and magnetization of K clusters in zeolite A at $n = 4.5$.

shown in a linear scale. It is clearly seen that both λ_1 and λ_2 suddenly increase more than one order of magnitude below T_C. At low temperatures, λ_1 amounts to $\simeq 20$ μs^{-1}. This relaxation is decoupled by the very low field in LF-μSR, as shown later. The magnitude of the internal field is estimated to be $\simeq 200$ Oe in the static random field model. The temperature dependences of λ_2 and the precession frequency ω (not shown here) are consistent with that in the previous study by pulsed muons [7,8]. The muons contributing to the term B are not affected by the magnetic phase

transition. When we assume that all of the incident muons are stopped at the sample, the obtained results mean the volume of the magnetically ordered phase is estimated to be 79% of the sample because $B/A_{tot} = 0.21$. In the non-loaded zeolite, however, muoniums with strong hyperfine coupling are effectively generated [12], which do not contribute to the time-independent background, B, but to the decrease in the initial asymmetry. Furthermore, the paramagnetic samples of the alkali-metal loaded zeolite show muon spin relaxation due to the paramagnetic moments of electrons as well as the nuclear magnetic moments [12]. Hence, the paramagnetic regions in the sample also do not contribute to B. Therefore, the observed time-independent background may not from the sample. The plausible origin of B is the signal from the silver foil which is used to seal the powder sample as mentioned in the previous section, because silver is known to show no relaxation of the muon spins.

In order to investigate the property of the fast decay in detail, we measured LF-dependence of μSR spectra at 1.6 K as shown in Fig. 4. Note that only early time region up to 0.2 μs is shown. An exponential-like fast decay is observed at zero field and the baseline of this component is recovered by applying LF of several ten Oersteds. To analyzing the recovery of the baseline by LF, we fitted the spectra tentatively by using the single-exponential function, $A(t) = A_{LF}\exp(-\lambda_1 t) + B_{LF}$, at the time region of $t \leq 0.2$ μs. The term B_{LF} corresponds to the time-independent but LF-dependent baseline. Figure 5 shows LF-dependence of the baseline. The horizontal dashed line indicates the baseline at zero field. The solid curve shows the fitting result by using the function of decoupling [13]:

$$B_{LF} = A_{ZF}\left\{\frac{3}{4} - \frac{1}{4x^2} + \frac{\left(x^2-1\right)^2}{8x^3}\log\left|\frac{x+1}{x-1}\right|\right\} + B_{ZF}, \tag{3}$$

where x indicates the ratio of LF to internal field, H_L/H_{int}. From this fitting, the internal field H_{int} is estimated to be 5.5 Oe. This value is too small compared with that, $\simeq 200$ Oe, estimated from λ_1. Hence, this result can be explained not by the ordinary direct decoupling by the external LF but by the interaction with the magnetization made by LF, as shown later.

Positive muons are expected to stop beside negatively charged oxygen atoms of the zeolite framework. As discussed in the previous papers [7,8], the most stable position for μ^+ is expected to be inside the double 4-membered ring (D4R) near the O1 and O3 sites, because of the high concentration of negative charges (see Fig. 1). The second candidate is near the O2 site at the inside of the 8-membered ring (8R). The electron wave function of K cluster is expanded mainly inside the α cage, but may have no amplitude inside D4R [5]. Hence, the μ^+ inside D4R may feel only the dipole magnetic field from electron spin localized inside the α cage. The slow relaxation and muon spin precession signals (the second and third terms in Eq. 1) can be explained by the dipole field calculated by assuming a cubic antiferromagnetic spin structure [7,8].

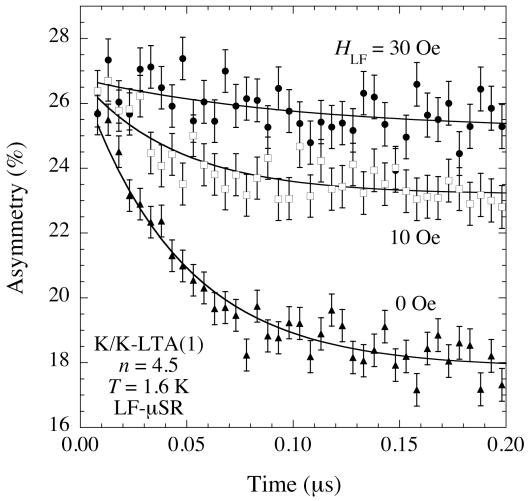

Fig. 4. LF-μSR spectra at 1.6 K for K clusters in zeolite A loaded at $n = 4.5$. The early time interval at $t \leq 0.2$ μs is shown. Solid curves are results of fitting by using single-exponential function.

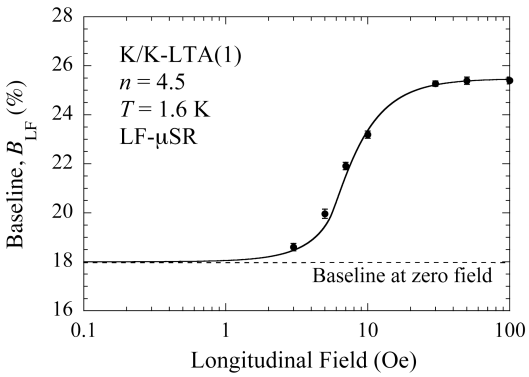

Fig. 5. LF-dependence of the baseline, B_{LF}, in Fig. 4. Solid curve shows the result of fitting using Eq. 3.

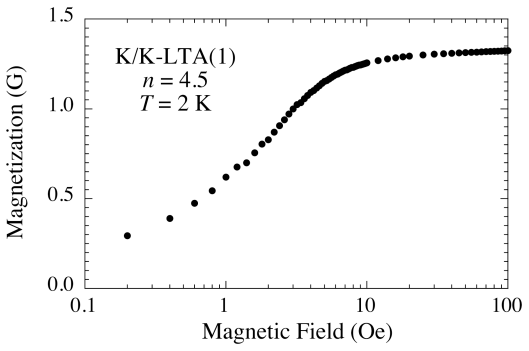

Fig. 6. Magnetic field dependence of magnetization of K clusters in zeolite A at $n = 4.5$ and $T = 2$ K.

According to the value of Curie constant, electronic spins with $s = 1/2$ are distributed in almost all α cages [10,11]. We estimate the dipole field near the O2 site (8R) for spin-canted antiferromagnet by assuming that a point dipole moment is located at the center of the α cage. The strength of the dipole field depends on the magnetic structure, but

the calculated value was ~ 80 Oe at maximum. This value is not enough for the estimated value $\simeq 200$ Oe from the fast decay component. The μ^+ at O2 site, however, is expected to have a finite Fermi-contact interaction with electrons in K clusters. This interaction may be much stronger than the dipole field. Hence, the Fermi-contact interaction is proposed for the origin of fast decay component. For the origin of the LF-sensitivity of the fast decay component, the basic idea has been already given by the Fermi-contact interaction in the previous work [7]. A detailed discussion is given in the present work as follows.

The O2 site has an equivalent distance to the clusters in both sides of 8R. This means that μ^+ at O2 site has the Fermi-contact interaction with the total magnetic moment of both sides of clusters. A basic interaction between adjacent clusters is antiferromagnetic with a spin canting interaction. The spontaneous magnetization has the orientation along the applied field, but each magnetic moment of cluster is not oriented to the applied field. Figure 6 shows the magnetization process. The magnetization increases linearly with the applied filed and is almost saturated at very low field of $\simeq 10$ Oe. Generally in the spin-canted antiferromagnet, such a quite soft magnetization process has been observed if we apply the external field along to the easy plain. In the α-hematite (α-Fe_2O_3), for example, the anisotropic field was estimated to be only $\simeq$ 1 Oe [14]. Unfortunately, in the present material, we have no direct information on the spin-canting direction with respect to the crystal structure. This may be decided by the three dimensional arrangement of the degenerated $1p$-orbital [11]. Anyway, the very soft ferromagnetic properties may be characteristic to the spin-canted antiferromagnet. For the powder sample, the canting direction (namely, the direction of spontaneous magnetization) is randomly oriented in each magnetic domain resulting in the fast decay of the muon-spin polarization at the zero field. By applying weak LF, the canting direction is gradually oriented to the LF direction. This gives the increase in the magnetization but the orientation of magnetization is not enough for the decoupling (less than ~ 3 Oe in Fig. 5). Higher fields (greater than ~ 5 Oe) gives nearly saturated magnetization in Fig. 6, and an orientation of each magnetization domain becomes enough for the remarkable decoupling. Hence, the observed LF-sensitivity for decoupling is well explained by the spin-canting mechanism.

As seen in Fig. 4, the fast decay component does not include clear precession signal. This result indicates that the Fermi-contact interaction is not completely homogeneous but has a rather wide distribution. According to the previous works, the ferromagnetic properties are attributed to the doubly degenerated $1p$-like orbital of K cluster [11]. The shape of the $1p$ orbital has an anisotropy. The anisotropy of $1p$ orbital may give different strengths of Fermi-contact interaction at O2 sites depending on the direction to the $1p$ orbital, even if O2 sites have the crystallographically equivalent sites.

4. Summary

We have successfully observed the fast muon spin relaxation of K clusters in zeolite A. The relaxation rate amounts to $\simeq 20\ \mu s^{-1}$, which corresponds to $\simeq 200$ Oe in the random static field. It is found that this value cannot be explained by the dipole field from the electron spins of K clusters but by the Fermi-contact interaction between muons at O2 sites and electrons confined in adjacent clusters. The LF-sensitivity for the decoupling of the fast decay component is well explained by the spin-canting mechanism of antiferromagnet.

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