Anomalous magnetization of potassium clusters incorporated into zeolite A
at high magnetic field

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I attended an international conference named ICM2006 (International Conference on Magnetism 2006) supported by 21st COE Program. Firstly, I’d like to thank the 21st COE program for giving me the opportunity to attend this conference. This conference is held every 3 years and is one of the biggest conference in the condensed-matter-science field. In this time, more than 2000 researchers participated from all over the world and very wide subjects on strongly correlated electrons, novel magnetism, magnetic electronics and so on were discussed. I reported my recent study on magnetic properties of potassium clusters in zeolite A under high magnetic field at the poster session of this conference. The contents of my presentation were as follows.

Alkali-metal nanoclusters can be created in the nanospace of zeolite crystals by the loading of guest alkali atoms. Potassium clusters arrayed in zeolite A are known to show ferromagnetic properties at low temperatures[1]. A spin-cant mechanism of antiferromagnet has been proposed as the origin of the spontaneous magnetization[2], where an orbital degeneracy of the 1p-like quantum electronic state of the cluster strongly enhances the Dzyaloshinsky-Moriya interaction[3]. Aluminosilicate zeolite A has an LTA-type framework structure. The α cages with an inside diameter of ~11 Å are arrayed in a simple cubic structure with the lattice constant of 12.3 Å. We use K-exchanged A having the chemical formula of K_{12}Al_{12}Si_{12}O_{48}. Hereafter, this zeolite is abbreviated as K-LTA. K clusters are generated by the adsorption of guest K atoms in fully dehydrated K-LTA. The 4s-electrons of guest K atoms are shared with several K cations and confined in the α cage. Cationic K cluster is formed there. The average number of the guest K atoms per α cage, \( n \), can be controlled from 0 to ~7.2, where the chemical formula is given by K_{12n}Al_{12}Si_{12}O_{48}. The value of \( n \) is equal to the average number of s-electrons per cluster. In these clusters, the primitive quantum states of s-electrons are given as 1s, 1p, etc[4]. With increasing \( n \), s-electrons occupy successively 1s- and 1p-states; first two for 1s- and next six for 1p-state. Ferromagnetic properties have been observed at \( n > 2 \)[2]. In a previous work, magnetization process was measured for the ferromagnetic sample with an external field up to 14 T[5]. The magnetization at higher fields increases linearly with the applied field up to 14 T. This result is well explained by the spin-cant model of antiferromagnet[5]. In the present work, magnetization process was measured up to 52 T by using a pulsed magnet at KYOKUGEN, Osaka University.

Figure 1 shows the magnetization (right hand side of scale) of the sample with \( n = 4.5 \) measured at 1.3 and 10 K. The Curie temperature of this sample is ~ 6 K. The magnetization \( M \) at 1.3 K rises at very low fields due to the very soft ferromagnetism. The value of \( M \) up to ~ 25 T increases linearly.
with field \( H \), as the previously observed for \( H < 14 \) T\(^5\). At \( H > 25 \) T, however, \( M \) suddenly changes in the increasing rate, and amounts to 6.7 G at 52 T. This value corresponds to the magnetic moment of \( \sim 1.3 \, \mu_B \) per \( \alpha \) cage (left hand side of the scale). On the other hand at 10 K, \( M \) keeps a constant increase rate up to 52 T.

The Curie constant of the present sample is \( \sim 3.19 \times 10^{-4} \) K emu/cm\(^3\). This value corresponds to the \( \sim 95\% \) occupancy of the clusters with \( s = 1/2 \) and \( g = 2 \). The horizontal dashed-line in Fig. 1 shows corresponding maximum value of magnetization 4.8 G (0.95 \( \mu_B \) per cluster). It is noticed that the observed magnetization 6.7 G at 52 T is much larger than this value, although the Curie constant contains contribution from all of magnetic moments at higher temperatures. Hence, \( M \) observed at high fields cannot be explained by the frequently observed change in magnetic structure, such as a spin-flop behavior. It is indicated that the magnetic moment of K cluster at low temperatures increases at high fields. There have been several reports on the field-induced increase in magnetic moment of clusters, such as Cr-dimer complexes\(^6\). The stepwise increase in the magnetization is well understood as a spin-crossover between lower-spin and higher-spin states\(^6\). In these materials, the temperature dependence of magnetic susceptibility deviates from a Curie-Weiss law, because of a thermal distribution of multiple spin states. In K clusters in K-LTA, however, a Curie-Weiss law is clearly observed above \( \sim 40 \) K up to the room temperature. Furthermore, the anomalous increase in the magnetization is observed only at low temperatures as seen in Fig. 2. Therefore, the mechanism of increase in \( M \) is different from an ordinary spin-crossover. Here, we propose a new mechanism based on a spin-orbit interaction in the degenerate 1p-state of K cluster at low temperature.

According to the ESR study\(^3\), the \( g \)-value obviously decreases at low temperature for the samples with \( 2 < n < 6 \). This result is interpreted in terms of a large spin-orbit interaction due to the degeneracy of the 1p-state of cluster\(^3\). The high-symmetry arrangement of K\(^+\) ions can be expected for clusters stabilized in a cage of zeolite from the analysis of average structure of K-loaded zeolite A\(^7\). The degenerate state is usually unstable against the Jahn-Teller distortion without strong spin-orbit interaction. The degenerate state of K clusters, however, can be stabilized at low temperatures due to the strong spin-orbit interaction. At finite temperatures, the thermal vibration along the adiabatic potential may invalidate the effect of degeneracy, because the deformed non-degenerate states may dominate in the configuration coordinates. Hence, the effect of orbital degeneracy of 1p-state is remarkable only at low temperatures. In an ideal case, 1p state is triply degenerate in orbital. In the actual structure, the doubly degenerate state may be possible, such as 1p\(_x\) and 1p\(_y\) states. The 1p\(_z\) state Fig. 1. Magnetization process up to 52 T for K clusters in zeolite A with \( n = 4.5 \) measured at 1.3 and 10 K. Horizontal dashed-line shows the maximum magnetization expected from the Curie constant (see text).
may have a different energy due to the crystal field. In degenerate states with an orbital and spin angular momentums $L = 1$ and $S = 1/2$, respectively, the levels split into two multiplets with the $z$-components of total angular momentum $J_z = \pm 3/2$ and $\pm 1/2$, because of the spin-orbit interaction. If the ground state of K cluster is the $J_z = \pm 1/2$ state at zero field, a crossover with $J_z = \pm 3/2$ state will occur at a certain magnetic field. Since $J_z = \pm 3/2$ state has a larger magnetic moment due to the contribution of the orbital magnetic moment, the magnetization may suddenly increase at a critical field. However, the $z$-axis of clusters is randomly oriented against the applied field. The increase in the magnetization results not in the stepwise but in the slopewise change. If the ground state of K cluster is the $J_z = \pm 3/2$ or $1p_z$ state, an anomalous increase in magnetization is not expected.

References