Magnetic properties of Na-K clusters in low-silica X zeolite doped by pressure loading

Nguyen Hoang Nam, Tatsuya Ohtsu, Takashi Araki, Shingo Araki and Yasuo Nozue
Department of Physics, Graduate School of Science, Osaka University, Osaka 560-0043, Japan
E-mail: nam@nano.phys.sci.osaka-u.ac.jp

Abstract. Low-silica X (LSX) zeolite has the FAU-type framework structure constructed of supercages and β-cages with effective inside diameters of 13 and 7 Å, respectively. Respective cages are arrayed in a diamond structure. Na-K clusters are formed by the loading of guest potassium atoms nK into LSX, where the unloaded LSX has 4Na and 8K zeolite-cations per supercage (or β-cage) as given by Na₄K₈Al₁₂Si₁₂O₄₈. N-type ferrimagnetism has been observed at ambient loading densities of K atoms, 6.5 < n < 8.5. Ferrimagnetism was not observed at the maximum loading density at ambient pressure, n ≈ 9. In the present study, we extended the loading density for 9 < n by the pressure-loading technique. Spontaneous magnetization is observed again below 10.5 and 9.1 K at the loading pressures ≈ 400 and ≈ 520 MPa, respectively. Respective Weiss temperatures are −23 and −32 K. These results indicate that the ferrimagnetism appears again at higher loading densities.

1. Introduction
Alkali-metal clusters are generated in zeolite cages by the loading of guest alkali metals. They have been reported to show novel magnetic properties depending on structure types of zeolite frameworks, kinds of alkali metals and their loading densities, such as spin-canted antiferromagnetism, antiferromagnetism, N-type ferrimagnetism etc., although these materials consist of non-magnetic elements [1-5]. The loading density of alkali metals is limited at ambient pressure. The pressure-loading technique has been developed to extend the loading density of alkali metal beyond the upper limit at ambient pressure [6,7].

Zeolite LSX has the FAU-type framework structure constructed of supercages and β-cages, as shown in Fig. 1. Supercages of FAU and β-cages have effective inside diameters of 13 and 7 Å, respectively. They are arrayed in a diamond structure, respectively, with a lattice constant of 25 Å. The chemical formula is given by M₁₂Al₁₂Si₁₂O₄₈ per β-cage, where M means alkali cations of zeolites, such as Na⁺ and K⁺. They are distributed in the space of framework for charge neutrality. When zeolite LSX with the chemical formula Na₄K₈Al₁₂Si₁₂O₄₈ is loaded with K metal at the density of n atoms per supercage (or β-cage), abbreviated hereafter as Kₙ/Na₄K₈-LSX, Na-K clusters are generated in these cages, and an N-type ferrimagnetism has been observed at the loading densities 6.5 < n < 8.5 [4,8]. This ferrimagnetism is explained by the antiferromagnetic interaction between nonequivalent magnetic sublattices of supercage clusters and β-cage ones. According to the reflection spectra at infra-red region, array of clusters are metallic at higher loading densities [9]. The sublattice of supercage clusters is assigned to the metallic network because the wave functions of adjacent clusters largely overlaps.
through the large windows of 12-membered rings. The wave functions of $\beta$-cage clusters are well separated from those in adjacent $\beta$-cages, because they have double 6-mebered rings between them. However, they can have an antiferromagnetic interaction with clusters in adjacent supercages through the windows of single 6-mebered rings. This interaction may stabilize the ferromagnetic ordering of $s$-electrons in the supercage clusters. Then, the magnetic sublattice in $\beta$-cages is formed by indirect interaction through the supercage clusters. The ferrimagnetism disappears at lower and higher loading densities. Paramagnetic properties have been found at the maximum K-loading densities $n \approx 9$. In zeolite LSX with the chemical formula $\text{K}_12\text{Al}_{12}\text{Si}_{48}\text{O}_{48}$ (abbreviated hereafter as $\text{K}_n/\text{K}_{12}$-LSX), ferrimagnetic properties of K clusters has been observed at the saturated loading density $n = 8.9$ [8]. They also show metallic properties. Under pressure loading, this ferrimagnetism disappears and new ferromagnetism with positive Weiss temperature has been found at 800 MPa [7]. This is an almost pure ferromagnetism assigned to an itinerant electron ferromagnetism of K clusters in supercages.

In the present study, we extended the loading density of K metal in $\text{K}_n/\text{Na}_4\text{K}_8$-LSX by the pressure-loading technique. We observed a ferrimagnetism again with negative Weiss temperature around 500 MPa.

![Figure 1. Schematic illustration of the FAU-type framework structure of low-silica X (LSX) zeolite and typical cation sites (I, I', II, III'). The closed circles, open circles with dot and open circles represent Si, Al and O atoms, respectively.](image1)

![Figure 2. Temperature dependence of the magnetization at 10 Oe for $\text{K}_n/\text{Na}_4\text{K}_8$-LSX at various loading pressures.](image2)

2. Experiment
Distilled K metal was fully loaded into dehydrated zeolite $\text{Na}_4\text{K}_8$-LSX. Saturated powder $\text{K}_9/\text{Na}_4\text{K}_8$-LSX was dispersed in distilled K metal and a drop of K metal containing $\text{K}_9/\text{Na}_4\text{K}_8$-LSX powder was made. It was put in Teflon capsule in a dry-box filled with pure helium gas. The sealed Teflon capsule was set into a BeCu pressure cell. Loading pressure was applied at 0, 400, 520 and 800 MPa at room temperature. A slight decrease in the loading density is expected at lower temperatures, but we indicate the loading condition by the loading pressure at room temperature. The magnetization was measured by using a SQUID magnetometer (Quantum Design, MPMS-XL). The loading density under pressure was estimated from the difference in volume of sample with only K metal and sample with K metal and zeolite powder.
3. Results and discussion

Figure 2 shows the temperature dependences of the magnetization of $K_n/Na_4K_8$-LSX at various loading pressures, where magnetic field is weakly applied at 10 Oe. The curves a-d are for loading pressures 0, 400, 520 and 800 MPa, respectively. The loading density $n$ is estimated to be $\approx 9$, $\approx 10.2$, $\approx 10.4$ and $\approx 11.6$ per supercage (or $\beta$-cage) at the loading pressures 0, 400, 520 and 800 MPa, respectively. No spontaneous magnetization is observed at 0 MPa (curve a). At 400 MPa (curve b), a small spontaneous magnetization is observed below 10.5 K. The magnetization increases at lower temperatures. At loading pressure 520 MPa (curve c), a larger spontaneous magnetization is observed below 8 K. The extrapolated Curie temperature is estimated to be 9.1 K. This spontaneous magnetization totally disappears when loading pressure is increased to 800 MPa (curve d). The temperature dependences of the reciprocal of magnetic susceptibility are shown in Fig. 3. The Curie-Weiss law is seen as shown by the straight line for each loading pressure. The Curie constant is estimated to be $2.59, 3.48, 3.59$ and $1.94 \times 10^{-4}$ K emu/cm$^3$ for 0, 400, 520 and 800 MPa, respectively. The Weiss temperature is estimated to be $-2.3, -32, -23$ and $-2.3$ K, respectively. Magnetization curves are shown in Fig. 4. Magnetization curves at 0 and 800 MPa (curves a and d) show nearly linear increase. The magnetization curve at 400 and 520 MPa (curves b and c) show a round shape after the quick rise at low fields and the relatively smaller values of the magnetization at 5 T.

The temperature dependences of the spontaneous magnetization shown for 400 and 520 MPa in Fig. 3 are ferrimagnetic with negative Weiss temperatures, but different from a typical N-type ferrimagnetism observed at ambient pressure, where the magnetization has a zero minimum at the compensation temperature. The effective magnetic moment per supercage (or $\beta$-cage) is estimated to be $\approx 1.77$ and $\approx 1.8\mu_B$ from Curie constant at 400 and 520 MPa, respectively. The spontaneous magnetizations at 400 and 520 MPa indicate magnetic moment per supercage (or $\beta$-cage) as $\approx 0.04$ and $\approx 0.1\mu_B$, respectively. The Curie constant and magnetization have the contributions from two magnetic sublattices; the supercage clusters and $\beta$-cage ones. It is impossible to separate observed values to the components of two cages, but magnetizations are much smaller than the values estimated from Curie constants. In the present ferrimagnetic model, the reduction of spontaneous magnetization can be explained by the cancellation by the
antiferromagnetic interaction between non-equivalent magnetic sub-lattices.

The ferrimagnetism observed in $K_n/Na_4K_8$-LSX is different from the pure ferromagnetism with positive Weiss temperature observed in $K_n/K_{12}$-LSX at 800 MPa [7]. The ferromagnetism in $K_n/K_{12}$-LSX at 800 MPa is assigned to the itinerant ferromagnetism of K clusters. In ferrimagnetism of $K_n/Na_4K_8$-LSX at high pressure with negative Weiss temperature, $\beta$-cage clusters may play an essential role in the ordering of supercage magnetic moments. If we assume that all of supercages have the localized moment with $s = 1/2$ and $g = 2$, the Curie constant is estimated to be $3.34 \times 10^{-4}$ K emu/cm$^3$. The Curie constants at 400 and 520 MPa are larger than this value, indicating that magnetic clusters are formed in both supercages and $\beta$-cages. According to the structural analysis of non-loaded LSX, Na$^+$ cations are distributed mainly in $\beta$-cages [10]. When K metal is loaded into Na$_4$K$_8$-LSX zeolite cages, Na-rich (Na-K alloy) clusters can be formed in $\beta$-cages. The electronic potential of the Na-rich cluster is deeper than that of K-cluster in $\beta$-cage of $K_n/K_{12}$-LSX, because the ionization energy of Na atom is larger than that of K atom. An electron can be trapped easily in Na-rich cluster and have antiferromagnetic interaction with adjacent supercage clusters.

Magnetization curves in Fig. 4 show almost linear increase with the external field at 0 and 800 MPa. They have very small Weiss temperature. These paramagnetic behaviors can be assigned to metals which are just before the ferromagnetic condition. At 400 and 520 MPa, the Fermi energy of supercage clusters may be located at the high density of states of a narrow energy band. The ferromagnetic ordering of supercage clusters can be assisted by the antiferromagnetic interaction with $\beta$-cage clusters. Differently, $K_n/K_{12}$-LSX shows almost pure ferromagnetism at 800 MPa. The electron energy of K-clusters in $\beta$-cages is higher than that of Na-rich clusters. This energy difference in $\beta$-cage clusters may change the contribution to the supercage clusters, and then the total magnetic properties may be changed depending on Na concentration.

4. Summary
Magnetic properties are reported for Na-K clusters in LSX zeolite doped by the pressure loading technique. The ferrimagnetic properties at ambient pressure once disappear with increasing the loading densities, and reappear around 500 MPa. The Weiss temperature is estimated to be $-23$ and $-32$ K at 400 and 520 MPa, respectively. Na-rich clusters in $\beta$-cages may play an important role in the stability of this ferrimagnetism.

Acknowledgments
Authors would like to deeply thank Prof. Takehito Nakano for the fruitful discussion. This work was partially supported by Grant-in-Aid for Creative Scientific Research (No. 15GS0213), that for Scientific Research on Priority Areas (No. 19051009) from MEXT Japan, and also by the 21st Century COE Program “Towards a New Basic Science: Depth and Synthesis” and Global COE Program “Core Research and Engineering of Advanced Materials-Interdisciplinary Education Center for Materials Science”, MEXT Japan.

References
[1] Nozue Y, Kodaira T and Goto T 1992 Phys. Rev. Lett. 48 3789
[2] Nakano T, Kiniwa D, Ikemoto Y and Nozue Y 2004 J. Mag. Mag. Mat. 272-276 114
[3] Srdanov V I, Stucky G D, Lippma E and Engelhardt G 1998 Phys. Rev. Lett. 80 2449
[4] Nakano T, Goto K, Watanabe I, Pratt F L, Ikemoto Y and Nozue Y 2006 Physica B. 374-375 21
[5] Duan T C, Nakano T and Nozue Y 2007 e-J. Surf. Sci. Nanotech. 5 6
[6] Nam N H, Araki S, Shiraga H, Kawasaki S and Nozue Y 2007 J. Mag. Mag. Mat. 310 1016
[7] Araki S, Nam N H and Nozue Y, to be submitted
[8] Hanh D T, Nakano T and Nozue Y, to be submitted
[9] Nakano T, Hanh D T and Nozue Y, to be submitted
[10] Lee Y, Carr S W and Parise J B 1998 Chem. Mater. 10 2561