Transactions of the Materials Research Society of Japan 26 [4] 1179-1182 (2001)

Magnetic Property of Potassium Clusters in Low-Silica Type Zeolite FAU

Yuka Ikemoto[*,**], Takehito Nakano[**], Momoko Kuno[**] and Yasuo Nozue[**]

[*] CREST, Japan Science and Technology Corporation (JST)

[**] Department of Physics, Graduate School of Science, Tohoku University, Sendai, Japan 980-8578

Fax: +81-22-217-6475, e-mail: ikemoto@msp.phsy.tohoku.ac.jp, nakano@msp.phys.tohoku.ac.jp, kuno@msp.phys.tohoku.ac.jp, nozue@msp.phys.tohoku.ac.jp

Potassium clusters with the mutual interaction are stabilized in supercage of aluminosilicate zeolite FAU with the Si-to-Al ratio of unity, so-called low-silica X. K metals are adsorbed at the average number n of 4.4 and 8.6 per supercage, and optical and magnetic properties are investigated. In the sample at n = 4.4, the temperature dependence of the spin susceptibility shows Curie-Weiss low with a negative Weiss temperature of – 10 ± 2 K. On the other hand, the sample at n = 8.6 has a temperature independent term. The Weiss temperature of the Curie-Weiss term is 5 ± 2 K. This value is positive, indicating that the ferromagnetic interaction is found for the first time in the alkali metal clusters in zeolites. The temperature independent term is assigned to the electrons distributed near the Fermi energy. A metallic phase is considered to be realized in the sample at n = 8.6.

Key words: zeolite, potassium clusters, spin susceptibility, Mott transition

1. INTOROCUCTION

More than one hundred types of structures are known as the framework type of zeolites, and some of them have periodic cages with the nanometer size. By using the periodic nano-cages, alkali metal clusters can be arrayed three dimensionally. One of the most important features of the alkali metal clusters in zeolite is the interaction between adjacent clusters. The electron wavefunctions of the clusters overlap with each other through the window of the cage. The interaction between the clusters causes the fascinating macroscopic phenomena, such as ferromagnetism[1] and antiferromagnetism[2].

FAU is one of the structure types of aluminosilicate zeolites. It has supercages with the inside diameter of about 13 Å. The supercages are arrayed in a diamond structure by sharing 12-ring window. In a previous paper[3], we used K-type FAU with the Si/Al ratio of 1.25, so-called KX. It is denoted by K-FAU(1.25), hereafter. When K atoms are adsorbed into K-FAU(1.25), K clusters are stabilized in the supercage. The average number of adsorbed K atoms per supercage equals to the average number of electrons per supercage, and denoted by n in the present paper. The K clusters in K-FAU(1.25) have been reported to show metallic properties with increasing n higher than about 0.4. At n ~ 0.5 ± 0.3, the sample has a large absorption coefficient at the infrared region due to the Drude term. The temperature independent term has been found in the spin susceptibility together with the Curie-Weiss term. The metallic phase in K-FAU(1.25) have been discussed from the viewpoint of the correlated electrons[4]. On the other hand, the insulating phase is found in K clusters in K-type FAU with Si/Al ratio of 1, so-called low silica X (abbreviated as K-LSX), even when n is similar to that in K-FAU(1.25), about 0.7 ± 0.3 [4]. K-type FAU with Si/Al ratio of 1 is denoted by K-FAU(1), hereafter. The infrared absorption coefficient is more than one order weaker than that in K clusters in K-FAU(1.25) with n of 0.5 ± 0.3. The temperature dependence of the spin susceptibility shows the Curie-Weiss law with the negative Weiss temperature of – 33 ± 3 K, and does not have temperature independent component. The K clusters in K-FAU(1) is considered to be in the Mott insulator phase[4]. The difference in the electronic state between K clusters in K-FAU(1.25) and K-FAU(1) was qualitatively explained by the competition between the intercluster electron transfer energy t and on-site Coulomb repulsion energy U. The value of U is roughly determined by the size of the cluster and is considered to be almost the same in K-FAU(1.25) and K-FAU(1). The value of t in K-FAU(1) is expected to be slightly smaller than that in K-FAU(1.25) from the difference in chemical composition[4]. Then U may overcome t and the Mott insulator phase is considered to be realized in K-FAU(1), differently from that in K-FAU(1.25). In the present paper, we increase n in K-FAU(1) up to 8.6. A temperature independent term of the spin susceptibility is found in the K clusters in K-FAU(1), when n is 8.6.

2. ZEOLITE AND EXPERIMENTAL PROCEDURE

Figure 1 shows the schematic illustration of the framework structure of aluminosilicate zeolite FAU. The chemical composition of K-type FAU is given by

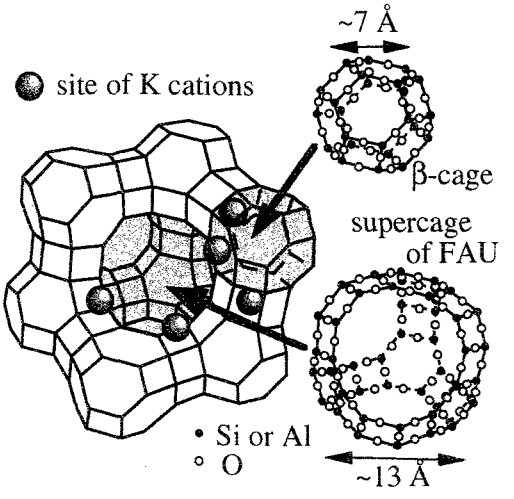

Fig. 1. Schematic illustration of the framework structure of aluminosilicate zeolite FAU. Typical sites of K cations are also shown.

$K_mAl_mSi_{24-m}O_{48}$, where the framework is given by $Al_mSi_{24-m}O_{48}$. K_m is potassium cations distributed in the space of cages, and can be exchanged for other cations. Typical sites of K cations are shown in Fig. 1. FAU has two types of cages, β-cage and supercage of FAU. Each of them is arrayed in a diamond structure. The Si/Al ratio, $(24-m)/m$, can be changed by the synthetic conditions in the range of $(24-m)/m \geq 1$.

Distilled K metal was adsorbed into fully dehydrated K-FAU(1) at n ~ 4.4 and 8.6, through the vapor phase in the quartz glass tube. The K-loaded K-FAU(1) is denoted by K/K-FAU(1), hereafter. The value of n is estimated from the optical analysis[5]. This analysis has an ambiguity of about 5 %. Optical, X-band EPR and magnetic measurements were performed. The optical absorption and reflection spectra were obtained from the analysis of diffuse reflection spectra.

3. EXPERIMENTAL RESULTS AND DISCUSSIONS

At n = 0.01, EPR spectrum has 10-line hyperfine structures with the full spectral width of 120 Oe. This is assigned to the isolated K_3^{2+} cluster in supercage with the C_{3v} symmetry. The absorption spectrum has several structures from 0.9 eV to 2.3 eV. The shape of the absorption spectrum is basically same as that of K clusters in K-FAU(1.25) at similar loading densities[3]. The electronic state in K clusters in K-FAU(1) is considered to be basically same as that of K clusters in K-FAU(1.25) when K clusters are isolated. A primitive model for electrons confined in the cluster has been given by the spherical well potential model with the inner size of the cage, i.e. 13 Å in case of supercage of FAU. The spherical well potential of isolated cluster has quantum state such as 1*s*, 1*p*, and so on. The observed absorption spectrum corresponds to the optical transition from 1*s*-like state to 1*p*-like one. The several structures indicate that the 1*p*-like excited state spreads over adjacent supercages as discussed in K clusters in K-FAU(1.25)[3].

In the reflection spectrum of K clusters in K-FAU(1.25) at n larger than ~2, a plasma edge appears at ~1 eV, and the samples are indicated to be metallic[6]. In the case of K clusters in K-FAU(1) at n = 4.4 and 8.6, we measured reflection spectra down to 0.3 eV, but the plasma edge was not observed in our spectral region. We, however, cannot determine definitely whether the sample is insulating or metallic, unless we measure much lower energy spectrum.

Figure 2 shows the temperature dependence of the reciprocal of spin susceptibility in K/K-FAU(1) at n = 4.4. The temperature dependence of the spin susceptibility was obtained from the temperature dependence of the integrated EPR intensity. The absolute value of spin susceptibility was determined by referring the total magnetic susceptibility measured by SQUID. The negative constant mainly due to the diamagnetic susceptibilities of quartz glass tube and zeolite framework was subtracted from the total magnetic susceptibility to fit the temperature dependence of the integrated EPR signal. In Fig. 2, open circles with error bars show integrated EPR intensity, and dots show spin susceptibility extracted by above procedure from the total magnetic susceptibility measured by SQUID under applied magnetic field of 1 T. The solid line is the guide for eyes. In Fig. 2, the Curie-Weiss low is observed at temperatures lower than ~150 K. The average value of the effective magnetic moment M_{eff} is estimated to be 0.99 μ_B from the Curie

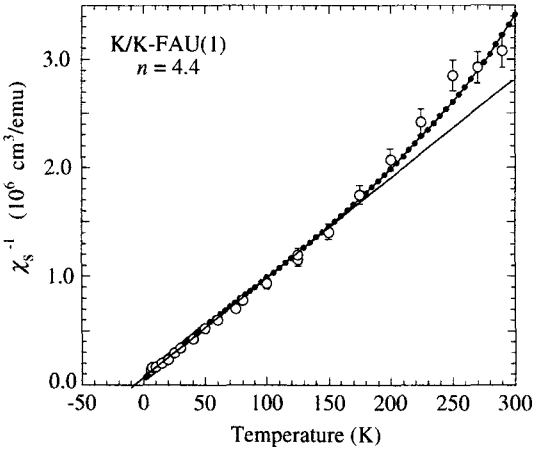

Fig. 2. Closed circles show the temperature dependence of the reciprocal of spin susceptibility χ_s in K/K-FAU(1) at K-loading density n of 4.4 per supercage. Open circles with error bars show χ_s obtained from the integrated EPR intensity. Solid line is the guide for eyes.

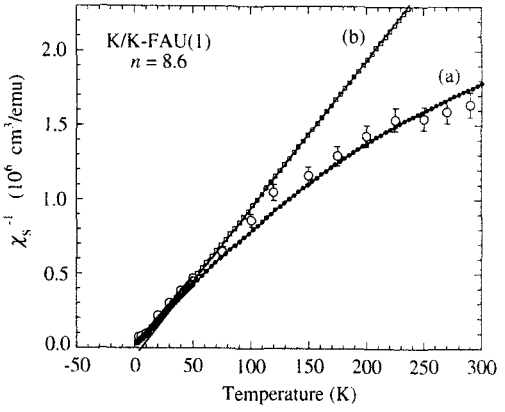

Fig. 3. (a) Closed circles show the temperature dependence of the reciprocal of spin susceptibility χ_s in K/K-FAU(1) with K loading density n of 8.6. Open circles with error bars show χ_s obtained from the integrated EPR intensity. (b) The temperature independent term 2.0 x 10^{-7} emu/cm^3 is subtracted from the curve (a). Solid line is the guide for eyes.

constant. The Weiss temperature T_w is estimated to be − 10 ± 2 K. Above ~150K, the reciprocal of the spin susceptibility deviates from the Curie-Weiss low, and the spin susceptibility rapidly decreases. The temperature independent component does not exist in Fig. 2. Figure 3 shows the temperature dependence of the reciprocal of spin susceptibility in K/K-FAU(1) at n = 8.6. The open circles with error bars in the curve (a) show integrated EPR intensity. The dots in the curve (a) show spin susceptibility extracted by the same procedure as in Fig. 2 from the total magnetic susceptibility measured by SQUID under applied magnetic field of 1 T. The curve (a) deviates from Curie-Weiss low. In the curve (b), temperature independent term of 2.0 x 10^{-7} emu/cm^3 is subtracted from the curve (a). The solid line is the guide for eyes. The curve (b) shows the Curie-Weiss low at M_{eff} = 0.97 μ_B per supercage and T_w = 5 ± 2 K.

The sample of K/K-FAU(1) at n = 4.4 does not have temperature independent susceptibility component, and the Curie-Weiss low is well explained by the properties of localized magnetic moment. If we assume spin quantum number s = 1/2 for each magnetic moment of clusters, the value of M_{eff} of 0.99 μ_B corresponds to 33 % occupation of supercages with magnetic moment of clusters. Most of the magnetic moments of the clusters are adjacent with each other. The negative Weiss temperature means that the magnetic moments interact with each other antiferromagnetically. The deviation from Curie Weiss low above ~150 K may be due to the existence of a small amount of magnetic moments with s = 1 at low temperatures. When temperature increases, the spin state may be thermally excited to s = 0 state, and the spin susceptibility becomes smaller than that expected from Curie-Weiss low. The sample is considered to be in the Mott insulating phase, because it has magnetic interaction and is considered to be the insulating material.

The temperature dependence of the spin susceptibility of K/K-FAU(1) at n = 8.6 has temperature independent component. The temperature independent spin susceptibility may be due to the finite density of states at the Fermi energy, and the sample is considered to be metallic. The metallic sample of K clusters in K-FAU(1.25) also has the temperature independent component in the spin susceptibility[4, 6]. In case of supercage of FAU, the unscreened Coulomb repulsion energy U of two 1s-electrons in the same cluster is estimated to be about 4 eV. When n is about 0.7 ± 0.3 in K/K-FAU(1), U is considered to overcome t, because Mott insulator phase was considered to be realized[4]. If n increases up to, for example, 4.4 and 8.6, the electrons occupy higher quantum energy level. Moreover, if the adsorbed K cations distribute at the window, they may lower the potential barrier between adjacent clusters. Both of them contribute to make t larger. The K clusters in K-FAU(1) at n = 4.4, however, is considered to be in the Mott insulator phase, and U may still overcome t. In the K clusters in K-FAU(1) at n = 8.6, t may slightly overcome U, and the metallic phase is considered to be found. The metallic phase is expected to be very close to the Mott transition. In Fig. 3, the temperature dependence of the spin susceptibility has the Curie-Weiss component as well as the temperature independent one, and the existence of the electrons with localized nature may be supposed. The Curie-Weiss low in the temperature dependence of the spin susceptibility cannot be explained by the simple metal model. We are now considering the strongly correlated electrons in the metallic phase.

It must be emphasized that the Weiss temperature in Fig. 3 is positive, 5 ± 2 K. It means that the magnetic moments of the cluster in K/K-FAU(1) at n = 8.6 interact with each other ferromagnetically. The Mott insulator phases in K clusters in K-FAU(1) with lower n have negative Weiss temperatures. The metallic sample of K clusters in K-FAU(1.25) also had the Curie-Weiss components but the Weiss temperature was negative, about − 4 K. Weiss temperatures observed in alkali metal clusters in zeolites are negative except for above case. In the Hubbard model, the Nagaoka's ferromagnetism is theoretically predicted when the number of electron is one less than the half-filling, and the Coulomb repulsion is infinitely large[7]. The insulating phase of K clusters in K-FAU(1) at n = 4.4 is considered to be in the Mott insulator phase. When the number of electrons is increased up to n = 8.6, the metallic phase are considered to be observed. The

metallic phase of K clusters in K-FAU(1) at n = 8.6 is considered to be very close to the Mott transition. If the situation in which a few carriers are injected into the Mott insulating material is considered to be realized in K clusters in K-FAU(1) at n = 8.6, the ferromagnetic interaction between the magnetic moments may be related to the Nagaoka's ferromagnetism. Further experiments, however, are necessary to discuss in detail.

4. SUMMARY

K atoms are densely adsorbed into K-FAU(1) at n = 4.4 and 8.6. The sample at n = 8.6 has a temperature independent term in the temperature dependence of spin susceptibility, and the metallic phase is considered to be realized. The sample at n = 8.6 has Curie Weiss term as well, and the Weiss temperature is positive. The ferromagnetic interaction is observed for the first time in the alkali metal clusters in zeolites.

Acknowledgement

Authors thank Dr. T. Ikeda, Dr. T. Kodaira and Prof. O. Terasak for the fruitful discussions. This research is supported by CREST-JST and CIR-Tohoku University.

References

[1] Y. Nozue, T. Kodaira and T. Goto, Phys. Rev. Lett. **68** (1992) 3789; T. Nakano, Y. Ikemoto and Y. Nozue, Eur. Phys. J. D **9** (1999) 505, Physica B **281/282** (2000) 688; Y. Maniwa, H. Kira, F. Shimizu and Y. Murakami, J. Phys. Soc. Jpn. **68** (1999) 2902.

[2] V. I. Srdanov, G. D. Stucky, E. Lippmaa and G. Engelhardt, Phys. Rev. Lett. **80** (1998) 2449.

[3] Y. Ikemoto, T. Nakano and Y. Nozue, Proc. 12th Int. Zeolite Conf. Vol. 3, p. 2103, Materials Research Society, 1999.

[4] Y. Ikemoto, M. Kuno, T. Nakano and Y. Nozue, to be published in Mag. Mag. Mater. 2001.

[5] T. Kodaira, Y. Nozue, S. Ohwashi, T. Goto and O. Terasaki, Phys. Rev. B **48** (1993) 12245.

[6] Y. Ikemoto, T. Nakano, M. Kuno and Y. Nozue, Physica B **281/282** (2000) 691.

[7] Y. Nagaoka, Phys. Rev. **147** (1966) 392.

(Received December 8, 2000; Accepted February 8, 2001)