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Ferromagnetism and paramagnetism in potassium clusters incorporated in zeolite LTA

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Abstract. Magnetic and optical properties are investigated for potassium clusters incorporated in zeolite LTA at loading densities of K atoms between 3.5 and 7.2 per cluster, the latter of which is saturated. The Curie–Weiss law with negative Weiss temperature −35 K is seen at 3.5 atoms per cluster, and gradually approaches the Curie law as the loading density increases up to 7.2 atoms per cluster. The Curie temperature, ~ 8 K at 3.5 atoms per cluster, approaches 0 K at 7.2 atoms per cluster. These results suggest that the antiferromagnetic coupling between localized magnetic moments of K clusters decreases with increasing K-loading density, and almost disappears at the K-loading density of 7.2 atoms per cluster. The insulator-like absorption tail is observed in the infrared region at any loading density, indicating that K clusters in LTA are in the Mott insulator phase. The average magnetic moment estimated from the saturation magnetization remarkably increases from 0.25 to 0.75 μ_B per cluster as loading density increases from 3.5 to 7.2 atoms per cluster. On the contrary, the average magnetic moment estimated from the Curie constant is $\sim 1.6\,\mu_B$ per cluster, and almost independent of the loading density. The explanation of these magnetic properties by the model of ferrimagnetism proposed in a previous paper proves difficult.

PACS. 36.40.Cg Electronic and magnetic properties of clusters – 71.24.+q Electronic structure of clusters and nanoparticles – 75.50.Dd Nonmetallic ferromagnetic materials

1 Introduction

Recently, new materials composed of nanoclusters have attracted much attention, because of their unique properties. Periodically arranged nanoclusters can be created by the loading of guest materials into the nanoscale space of zeolite crystals. A macroscopic phenomenon quite different from the original guest material is expected to be observed in the arrayed clusters, because of the intercluster interaction, as well as the new quantum electronic states of the cluster. In the present study, magnetic and optical properties are investigated for the K clusters incorporated in zeolite LTA at various loading densities of K atoms.

LTA is one of the framework structures of alminosilicate zeolites. The framework structure of LTA is schematically shown in Fig. 1. Closed circles show Si or Al atoms, and open circles show oxygen atoms, all of which are omitted in the left-hand-side figure. The α cages with inside diameter of ~ 11 Å are arrayed in a simple cubic structure with the lattice constant of 12.3 Å and are connected by shared windows of the eight-member rings. In the K-form LTA, K cations are distributed in the space of the framework to compensate the neutrality of zeolite, because the framework is negatively charged.

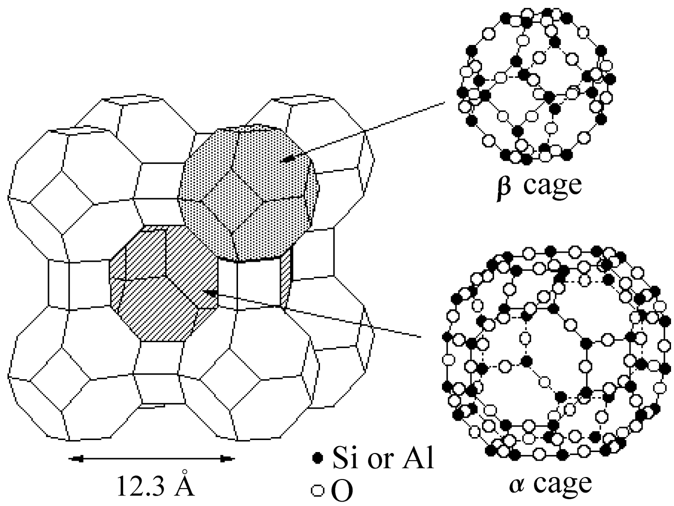

Fig. 1. Schematic illustration of the framework structure of zeolite LTA. The α cages are arrayed in a simple cubic structure by the sharing of the eight-member rings.

The chemical formula of the unloaded K-form LTA is given as $K_{12}Al_{12}Si_{12}O_{48}$.

According to the optical study, cationic K clusters are generated in α cages, when K is adsorbed into the dehydrated K-form LTA [1]. In these cationic clusters, 4*s* electrons of guest K atoms are shared with many

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K cations distributed in the α cage and repulsed by the negatively charged framework. K clusters in LTA show ferromagnetic properties, although no magnetic element is contained [2]. The most significant ferromagnetic properties have been observed at $n \sim 5$, where n is the average number of shared 4s electrons per cluster (or α cage). This number is equal to the loading number of K atom per cage. The origin of the ferromagnetism had been interpreted in terms of the itinerant electron model [3]. In a previous paper [4], however, the electric state is found to be an insulator at $n = 3.5$, and the magnetic properties are explained by the model of ferrimagnetism, where nonequivalent magnetic moments are coupled antiferromagnetically.

In the present paper, extensive studies are carried out on magnetic and optical properties of K clusters in LTA at the K-loading density between 3.5 and 7.2 atoms per α cage. With increase in the loading density, the systematic decrease in the intercluster interaction is found in the decrease in the Weiss and the Curie temperatures. K clusters in LTA are assigned to the Mott insulator at any loading density. It is found that the ferrimagnetic model is not suited to the present magnetic properties.

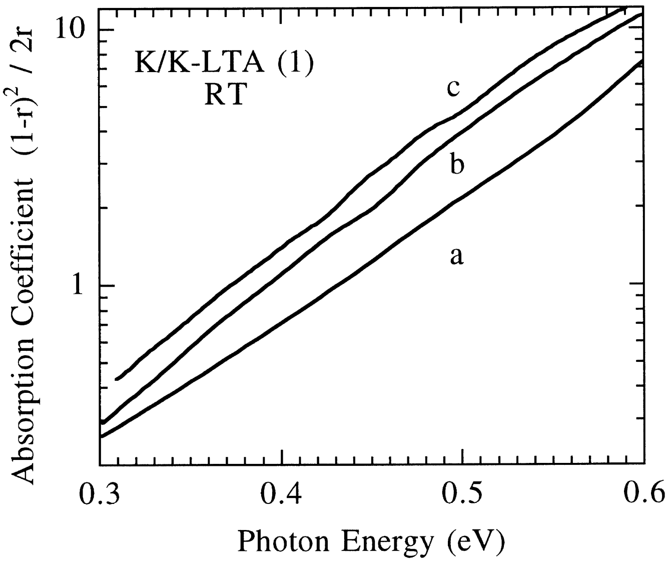

Fig. 2. Infrared absorption spectra of K clusters in K-form LTA at room temperature. The average loading number of K atoms is 3.5, 5.6, and 7.2 per α cage in curves a, b, and c, respectively.

2 Experimental procedure

Distilled potassium was adsorbed into fully dehydrated K-form LTA through the vapor phase. Samples with various average loading density of K atoms per α cage n, $3.5 \leq n \leq 7.2$, were prepared. K adsorption was saturated at $n \sim 7.2$. The average loading density of K atoms is estimated from the optical analysis normalized by the chemical analysis [1]. Samples were sealed in a quartz glass tube to be kept from the exposure to the air during all experiments. The absorption spectrum was obtained from the diffuse reflection spectrum by the Kubelka–Munk transformation. Magnetic measurements were performed by the use of a physical-property measurement system (Quantum Design, PPMS) and a magnetic-property measurement system (Quantum Design, MPMS-XL). The temperature-independent diamagnetic magnetization from both the quartz glass tube and zeolite framework is subtracted from the observed magnetization by the analysis of either the Curie–Weiss or the Curie law.

3 Results

Generally, it is very important to know whether the solid matter is metallic or insulating, when we try to understand the magnetic properties. The low-energy optical spectrum gives us important information about the existence of free carriers. Infrared absorption spectra of K clusters in LTA at room temperature are shown in Fig. 2 in the logarithmic scale. Curves a, b, and c are for samples #a, #b and #c, respectively. The values of n are 3.5, 5.6 and 7.2 atoms per α cage for samples #a, #b and #c, respectively. In all curves, the absorption coefficient decreases exponentially down to 0.3 eV. This is the typical spectral shape of an insulator, called the Urbach tail. There is no evidence of the Drude-like absorption tail, which indicates the metallic state, down to 0.3 eV. The lower-energy spectral data can confirm the insulating state, but the present spectral data indicate that the samples are basically in the insulating state. Therefore, these samples are assigned to the Mott insulators, because they are magnetic materials.

In Fig. 3, the external magnetic field dependence of magnetization M at 2 K is shown for samples #a–#c by curves a–c, respectively. Curie temperatures of samples #a and #b are estimated to be ~ 7.5 and ~ 3.5 K, respectively, from the Arrott plot analysis of the temperature dependence of the magnetization curve. Sample #c shows the Curie law, namely the Weiss temperature is 0 K, and does not show any magnetic phase transition down to 1.8 K, as shown later. In curves a and b, the magnetization quickly rises at low magnetic fields due to the spontaneous magnetization of ferromagnetism. In curve a, the magnetization is almost saturated around 0.2 T, and slightly increases up to 7 T. The saturation magnetization is estimated to be about 1.3 G by the extrapolation of the magnetization curve. In curve b, the magnetization is saturated gradually at higher magnetic fields. The saturation magnetization is estimated to be about 2.8 G. Curve c is paramagnetic, and fits the Brillouin function of the spin $s = 1/2$ at 75% of α cages. The saturation magnetization is estimated to be 3.75 G from the fitting of the Brillouin function. These magnetizations, 1.3, 2.8, and 3.75 G, in samples #a–#c, correspond to the average magnetic moments of 0.26, 0.56, and 0.75 μ_B per α cage. The above results show that the saturation magnetization increases remarkably with increasing K-loading density.

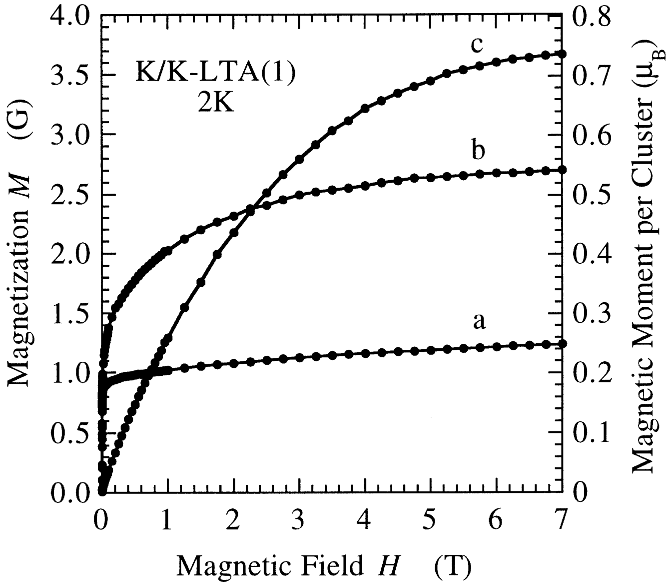

Fig. 3. External magnetic field dependence of the magnetization of K clusters in K-form LTA at 2 K. The average loading number of K atoms is 3.5, 5.6, and 7.2 per α cage in curves a, b, and c, respectively.

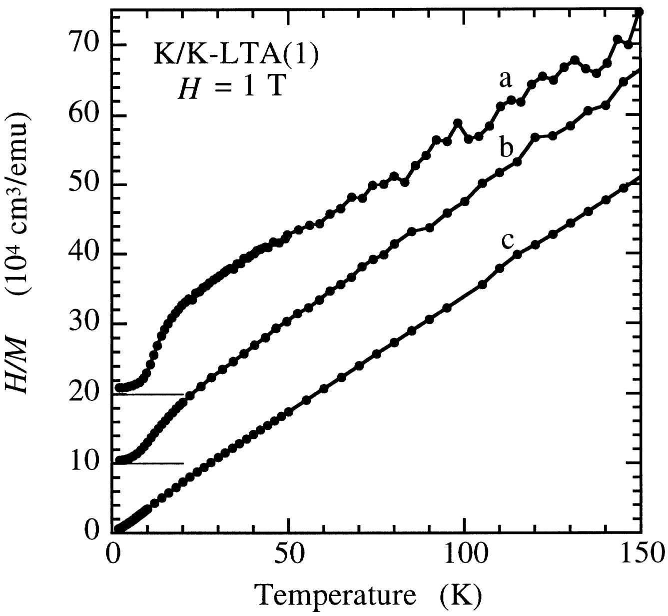

Fig. 4. Temperature dependence of the reciprocal of magnetic susceptibility of K clusters in K-form LTA. The external magnetic field H is applied at 1 T. The average loading number of K atoms is 3.5, 5.6, and 7.2 per α cage in curves a, b, and c, respectively.

In Fig. 4, the reciprocal of magnetic susceptibility, H/M, is plotted as a function of temperature for the samples #a–#c by curves a–c, respectively. The external magnetic field H is 1 T. The Curie–Weiss law is observed in curves a and b at higher temperatures, and the respective Weiss temperatures are estimated to be about -35 and -10 K. The Weiss temperature is estimated from the extrapolation of the Curie–Weiss behavior of magnetic susceptibility. The negative Weiss temperature indicates that an antiferromagnetic interaction exists between localized magnetic moments of clusters. In curve c, the Curie law is seen, and the Weiss temperature is estimated to be ~ 0 K. The effective magnetic moment is estimated from the Curie constant to be 1.76, 1.56, and 1.62 μ_B per α cage in samples #a–#c, respectively. The effective magnetic moment is almost independent of n, in contrast to the saturation magnetization, which remarkably increases with increasing K-loading density.

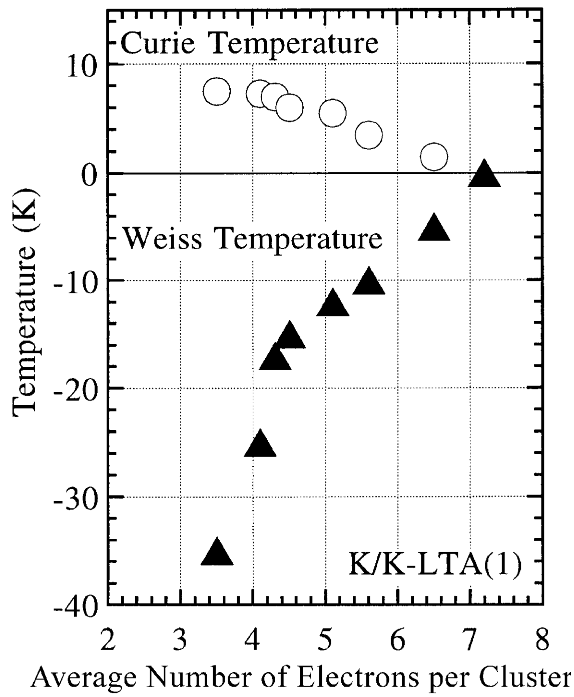

Fig. 5. The Curie temperature and the Weiss temperature of K clusters in K-form LTA as a function of the average loading number of K atoms (electrons) per cluster.

In Fig. 5, the Curie temperature and the Weiss temperature of all samples are shown as a function of n, in addition to the data of samples #a–#c. With increasing n from 3.5 to 7.2, both the Curie and the Weiss temperatures continuously approach 0 K. The paramagnetic phase is observed at the saturated K-loading density $n \sim 7.2$. These results indicate that the antiferromagnetic interaction between magnetic moments of clusters decreases with increasing K-loading density, and almost disappears at the saturated K-loading density.

4 Discussion

In ferrimagnetism, the antiferromagnetic ordering of two magnetic sub-lattices with different magnetic moments generates the spontaneous magnetization. In the previous paper, the magnetic properties of a sample with $n \sim 3.5$ per α cage, which is sample #a in the present paper, have been explained by assuming two sub-lattices with the magnetic moments of 2.02 and 1.50 μ_B [4]. If we assume a similar ferrimagnetic model, magnetic properties of sample #b can be explained by assuming the sub-lattices of 2.02 and 0.90 μ_B.

The one-electron quantum electronic states in the K cluster are expected as $1s$, $1p$, $1d$, etc. in the model of spherical-well potential with the inside diameter of a α cage. In the case of five electrons, for example, two of them occupy $1s$ state, and three of them $1p$ state. The $1p$ state electron can have an orbital angular momentum. Generally, the magnetic moment of the cluster is specified by the quantum numbers of spin and orbital angular momenta, s and l, respectively. The expectation value of magnetic moment μ is given by

$$\mu = g\sqrt{j(j+1)}\mu_B \,, \tag{1}$$

where j is the total angular quantum number. In the cluster, in a strong nonspherical potential, the orbital angular momentum disappears, and the expectation value is given by

$$\mu = g\sqrt{s(s+1)}\mu_B \,. \tag{2}$$

Actual value is given by the intermediate case of above two limits. The minimum magnetic moment μ with $s = 1/2$ is 1.73 μ_B when the g–value is 2. In order to explain a small value of the magnetic moment estimated in the two sub-lattice models, such as 0.90 μ_B in sample #b, we need to assume a small occupancy rate, such as 27% of α cages. For the intermediate value of the magnetic moment, such as 2.02 μ_B, we need to assume the mixture of different magnetic moments with $s = 1/2$, 1, 3/2, etc. These small occupancy rates remarkably violate the regular ordering of magnetic sub-lattice. A sharp ferromagnetic phase transition, however, is observed at the Curie temperature. The magnetic phase is not so disordered. Hence, the model of ferrimagnetism is not suitable to explain the magnetic properties of K clusters in LTA.

We can think another possibility of ferromagnetism: the weak ferromagnetism due to the canted spin structure of antiferromagnetism. Further investigations, however, are required for magnetic properties, as well as the structural analysis of K clusters in LTA for the determination of the origin of ferromagnetism.

It should be noted that the magnetic properties of the saturated sample #c are well explained by the paramagnetism with spin $s = 1/2$. If we assume that paramagnetic clusters with spin $s = 1/2$ are distributed among 75% of α cages, as estimated from the magnetization curve in Fig. 3, the average magnetic moment per α cage is calculated to be 1.50 μ_B by assuming the g−value of 2. This value is in good agreement with the average magnetic moment of 1.62 μ_B obtained from the Curie constant in Fig. 4. The clusters in the other 25% of α cages may form a closed shell containing 8 electrons with no magnetic moment.

According to the structure analysis of K-loaded K LTA by the neutron diffraction, a new periodic structure was proposed [5]. A ferrimagnetism seems to be supported. However, the sample in [5] did not show any ferromagnetism [6]. The neutron structural analysis is required for ferromagnetic samples.

A finite electron-transfer energy t between adjacent clusters is required for the intercluster exchange interaction of magnetic moments. Hence, the experimental results in Fig. 5 suggest that t decreases systematically with increasing n. In order to explain this behavior, we consider that the effective potential of cluster is deepened systematically with the increasing number of guest K atoms. When a guest K atom is added to a cluster in the zeolite cage, one K cation, as well as one $4s$ electron, is added. According to the spherical-well potential model, the first and second $4s$ electrons occupy the $1s$-like orbital of the cluster. The third to eighth $4s$ electrons occupy the $1p$-like orbital. In parallel, guest cations deepen the effective potential of the cluster. The ionization energy of the cluster increases with increasing n, similar to those in atoms, e.g., from Li to Ne. Therefore, the potential barrier between adjacent clusters is heightened, and t decreases. In conclusion, the gradual decrease observed in both the Weiss and Curie temperatures is explained by the increase in the potential depth of clusters.

5 Conclusion

Weiss and Curie temperatures of K clusters in LTA are found to decrease systematically with increasing the loading density of potassium. This behavior is explained by the increase in the potential depth of the cluster. The ferrimagnetism proposed in the previous paper is inadequate as a model of the observed magnetic properties.

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